Hydroformylation in Fluorous Biphasic Media

A Thesis presented by
Clare R Mathison
to the
University of St Andrews
in application for the degree of
DOCTOR OF PHILOSOPHY
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i) I, Clare Mathison hereby certify that this thesis, which is approximately 39 400 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

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ii) I was admitted as a research student in September 2002 and as a candidate for the degree of Doctor of Philosophy in September 2003; the higher study for which this is a record was carried out in the University of St Andrews between 2002 and 2005.

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iii) I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate for the degree of Doctor of Philosophy in the University of St Andrews and that the candidate is qualified to submit this thesis in application for that degree.

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Abstract

The hydroformylation of oct-1-ene is investigated under fluorous biphasic conditions, utilising the facile catalyst recovery that is provided by the temperature dependent miscibility of the perfluorinated solvent with normal organic solvents. High conversions and selectivities have been obtained in the batch process and the system is now described under continuous-flow conditions in a custom built reactor.

The continuous-flow reactor was successfully run for 46 hours, with conversions to nonanal of 60% and l:b ratios of approximately 10.

To understand the mechanism of this reaction more fully, a spectroscopic study of the catalyst formation and hydroformylation reaction was undertaken, using high-pressure infrared (HPIR) and nuclear magnetic resonance (HPNMR) techniques. The results of this study showed that although there is some effect of the strongly electron withdrawing nature of the perfluorinated ligand, the species formed under reaction conditions are very similar to those formed under the analogous triphenylphosphine system. It was found that under reaction conditions the perfluorinated ligand formed both the *bis*- and *tris*-phosphine complexes, compared to triphenylphosphine, which only formed the *bis*-phosphine complexes. The equatorial-equatorial and equatorial-axial isomers of \([\text{RhH(CO)}_2(\text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_3)]_2\) were identified by means of a deuterium study in the HPIR spectrometer.

The low levels of phosphorus and rhodium leaching to the organic phase were attributed to the predominant formation of \([\text{RhH(CO)}(\text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_3)]_3\) under ambient pressure and temperature (separator conditions) indicated by a well defined quartet in the metal hydride region of the \(^1\text{H}\) NMR spectrum.
Abbreviations

b/l branched / linear ratio
BTF benzotrifluoride
CFR continuous flow reactor
Co cobalt
CO₂ carbon dioxide
Cu copper
CuCl copper chloride
DCM dichloromethane
FB fluorous biphase
FBC fluorous biphasic catalysis
FBS fluorous biphasic system
FC70 perfluorous solvent containing primarily compounds with 15 carbons
FC72 perfluorous solvent containing primarily compounds with 6 carbons
FC77 perfluorous solvent containing primarily compounds with 8 carbons
HPIR high-pressure infrared
HP-NMR high-pressure nuclear magnetic resonance
ICPAAS Inductively Coupled Plasma Atomic Absorption Spectroscopy
ICPMS Inductively Coupled Plasma Mass Spectroscopy
l:b linear : branched ratio
Mn manganese
Pd palladium
pfd perfluorodecanoate
PFDMC perfluoro-1,3-dimethyl cyclohexane
PFMC perfluoro (methylcyclohexane)
pfo perfluorooctanoate
pft perfluorotetradecanoate
PFT perfluorotoluene
PPh₃ triphenyl phosphine
Rh rhodium
RT room temperature
S in the case of IR spectra = strong
scCO₂ super critical CO₂
TACN triazacyclononane
TBHP tert-butyl hydroperoxide
TEMPO
TOF turnover frequency
TON turnover number
TPPTS Triphenylphosphane trisulfonate
Contents

Declaration i
Acknowledgements ii
Abstract iii
Abbreviations iv

1 Literature Review 1
  1.1 Introduction 2
  1.2 Aqueous Biphasic Catalysis 3
  1.3 Fluorous Biphasic Catalysis 6
    1.3.1 Alkene Hydrogenation 10
    1.3.2 Alkene Hydrosilation 16
    1.3.3 Alkene Hydroboration 17
    1.3.4 Alkene Hydroformylation 18
    1.3.5 Alkene Epoxidation 28
    1.3.6 Other Oxidation Reactions 32
    1.3.7 Allylic alkylation 36
    1.3.8 Heck, Stille, Suzuki and Sonagashira and related coupling reactions 38
    1.3.9 Asymmetric alkylation of aldehydes 41
    1.3.10 Miscellaneous catalytic reaction 45
    1.3.11 Fluorous catalysis without fluorous solvents 46
    1.3.12 Continuous Processing 49
    1.3.13 Conclusions 51
  1.4 Reference List 52

2 Hydroformylation: A mechanistic Study 56
  2.1 Introduction 57
  2.2 Ligand Studies 61
  2.3 Initial NMR investigation in low pressure tube 64
  2.4 High Pressure Spectroscopic Study with Rhodium: Phosphorus ratio = 1:1 68
    2.4.1 Rh: P = 1:1 - HPIR 69
    2.4.2 HP-NMR results for Rh: P = 1:1 74
  2.5 Rhodium: P(C_6H_4-4-C_6F_{13})_3 Ratio = 1:5 Spectroscopic Investigation 78
    2.5.1 Infrared Spectroscopy Results 79
    2.5.2 HP-NMR data analysis 90
    2.5.3 HPIR investigation of hydroformylation 100
  2.6 Spectroscopic Study of Rh: Phosphine ratio = 1:10 112
    2.6.1 Spectroscopic study of Rh: P = 1:10 113
    2.6.2 Hydroformylation 121
  2.7 Conclusions 129
  2.8 Reference List 131
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Appendix 1</td>
<td>186</td>
</tr>
<tr>
<td>6.2</td>
<td>Appendix 2</td>
<td>214</td>
</tr>
</tbody>
</table>
Chapter 1

Literature Review
Literature Review

1.1 Introduction

Hydroformylation is an industrially important reaction as it provides precursors to detergents and plasticisers. 8M tonnes of aldehyde product are produced per annum\(^1\). Industry currently favours the use of cobalt-catalysed hydroformylation, rather than rhodium-catalysed systems, as rhodium is expensive and difficult to recover even though Rh-catalysed hydroformylation requires less harsh reaction conditions.

As with all homogeneous reactions the largest problem is the separation and recovery of the catalyst. Compared to similar heterogeneous reactions, which are used by industry due to the ease of catalyst recovery, homogeneous reactions prove too costly due to the losses of expensive metal complexes or the extra steps required after the reaction has occurred for product separation. This is preferably carried out by a distillation step, but the temperature sensitive nature of many homogeneous catalysts means that this is unfeasible, as it would lead to catalyst degradation.

These various hindrances provide a number of routes of investigation for the improvement of rhodium catalysed homogeneous hydroformylation, which on paper appears to be the most favourable method if certain issues can be overcome.

The last 25 years have seen prolific development of the standard hydroformylation system, some leading almost immediately to industrial processes whilst others are still being improved upon before industry will consider them over the reliable Co-catalysed route.

In his recent book\(^2\), van Leeuwen reports several methods of industrial processes which use rhodium catalysts for hydroformylation, all employing slightly
different catalytic species, conditions and more interestingly, separation techniques; distillations, extractions, heterogenizing and biphasic processes. A number of the processes differ only by their product retrieval methods and in the case of Union Carbide’s Stripping Reactor Process led to the development of distillative separation in a liquid recycle process.

Biphasic systems, in which the catalyst is designed to be dissolved in a liquid phase that is immiscible with the product (either with or without a separate solvent) potentially provide some of the most attractive solutions to the problem of product separation in homogeneous catalysis.

1.2 Aqueous Biphasic Catalysis

Aqueous biphasic systems are very elegant in that a water-soluble catalyst is kept completely separate from the lipophilic product except under conditions of fast stirring. Stopping stirring leads to rapid phase separation and the product can be collected by decanting. Such processes have been commercialised for short chain substrates, which have significant solubility in water. It has been observed that the rates of reaction when using longer chain, less hydrophilic substrates are too low to be of commercial interest, presumably because mass transport limitations dominate the reaction.

Ruhrchemie / Rhône-Poulenc (RR-P) developed aqueous biphasic catalysis (ABC) for the hydroformylation of short chain alkenes in 1982 and had applied it on an industrial scale within two years\(^2\). The concept of ABC uses the familiar rule that “like dissolves like” and therefore relies on a highly polar ligand to create a favourably water soluble catalyst. Separation relies upon the fact that the product is insoluble in the catalyst phase and the two phases can be easily separated without exposing the system to any unnecessary thermal stress, which may lead to catalyst
decomposition. The drive for this development arose from the wish to implement Rh
catalysed hydroformylation, which is well documented as having greater reactivity
under milder conditions than the commonly used cobalt catalysts. The success of this
plant and the further plants that have been built since, is shown in the volume of their
output, over 500 000 tons per year of C\textsubscript{4} products. The aqueous biphasic method
shows low ligand and rhodium leaching from the aqueous phase; this along with the
low cost of solvents makes it a very industrially attractive process.

The ligand used in the RR-P process is sodium triphenylphosphane
trisulfonate (TPPTS) and is highly water-soluble (1kg TPPTS in 1 kg water). The
optimised process uses a P: Rh ratio of at least 60/1 and by continuous addition of
fresh ligand, to replace any oxidised phosphane, the catalyst lifetime can be
prolonged. Further ligand design has been investigated and BINAS, a sulfonated
analogue of NAPHOS, see Figure 1.2.1, has so far proved to be the most selective
ligand. Rh-BINAS gives an l: b selectivity of 98: 2 with a P: Rh ratio of 7: 1
compared to the l: b of 94:6 at a P: Rh ratio of 80: 1 for the TPPTS system. TPPTS
continues to be used in industry as the higher manufacturing costs and lower stability
of BINAS would make the process too costly.

The only drawback to the aqueous biphasic process is the low solubility of
higher alkenes in water, resulting in lower activities for these substrates and limiting
the RR-P process to C\textsubscript{3} and C\textsubscript{4} substrates. The reaction is never homogeneous even
with C\textsubscript{3} and C\textsubscript{4} alkenes and it is unclear whether the reaction occurs on dissolved
alkene within the water droplets or only at the interface. Good mixing merely
increases the area of the liquid-liquid interface and may improve the transport of the
alkene into the aqueous phase. Good mixing is imperative to ensure high gas uptake
within the liquid phase(s).
The industrial process uses a similar method to that employed in our FBS as described in Chapter 3; the Rh-TPPTS catalyst is preformed under hydroformylation conditions before introducing the substrate. The reaction occurs in a stirred tank reactor; the crude product is transported to a phase separator where the gases are vented and the liquids separate by gravity, allowing the aqueous catalyst phase to be recycled to the reactor through a heat exchanger. The organic phase has to be processed to obtain pure product. This is done by stripping unreacted propene with synthesis gas, which is recycled to the reactor. The normal and branched aldehydes are separated by distillation.

In its present form, the RR-P process is unsuitable for the hydroformylation of alkenes greater than C_4, due to the limited solubility of such molecules in the aqueous catalyst phase. Some attempts have been made to adjust this process for the hydroformylation of higher alkenes, in order to overcome their low solubility. Additives can be included in the reaction, such as alcohols and glycols. However, these only add to the cost of the process, as an extra separation step is required to remove them from the product. Alternatively increasing the organic solubility of the catalyst may increase the hydroformylation rates, but it is also likely to increase the
loss of Rh and ligand to the organic phase. It seems more probable that a different solvent system or immobilisation (heterogenisation) of the catalyst will provide the desired results.

1.3 Fluorous Biphasic Catalysis

The unusual and interesting solubility properties of perfluorocarbons (organic solvents in which most or all of the hydrogen atoms have been replaced by fluorine atoms) have been known and investigated for over fifty years. Fluorous solvents are non-toxic, have low vapour pressure and very high gas solubilities. This leads to one of their interesting uses as blood substitutes and as “breathable liquids”. In 1966, Clark and Gollan reported the survival of mammals that were immersed in organic liquids that had been saturated with oxygen. Essentially the mammals were breathing in the liquid.

The advantages of fluorous blood substitutes are that they are non-toxic and have a longer shelf life than real blood. The other, more relevant, property of fluorous solvents is their temperature and pressure controllable miscibility with organic solvents.

Horváth and co-workers introduced an attractive biphasic system in 1994. They coined the term “catalysis in the fluorous biphas”. The process uses the temperature dependent miscibility of fluorinated solvents with normal organic solvents, to provide a possible answer to the biphasic hydroformylation of long-chain alkenes. At temperatures close to the operating temperature of many catalytic reactions (60-120 °C), the fluorous and organic solvents mix, but at temperatures near ambient they phase-separate cleanly. In the past twelve years, many other reactions have been demonstrated under fluorous biphasic conditions and these form the basis of this chapter. Fluorous biphasic systems operate on the premise that the catalyst
complex is preferentially soluble in the fluorous phase. This is achieved by synthesising fluorinated ligands that have a high weight-percentage of fluorine. It has been reported by Cavazzini et al, that for a complex to be preferentially soluble in fluorous solvents it must contain >60 wt % fluorine. However, work by Hope and co-workers, has shown that this is not necessarily so. In fact, ligands with identical analytical composition, such as para-, meta- and ortho- isomers, may have very different solvent preferences and it is more important that the organic core is enveloped to ensure preferential fluorocarbon solubility. They also report that the preferential solubility of a perfluorinated ligand does not immediately imply preferential solubility of the corresponding catalyst. Rábai and co workers report that increasing the length of a single fluorous ponytail will be detrimental to the solubilities in both solvents and an increase in the partition coefficients is observed when the number of fluorous ponytails attached to the ligand is increased. Provided that the partition properties of the solvent system are known (solubilities of one within the other), partition coefficients of solutes between fluorous and organic solvents can be calculated with remarkable accuracy using a model which relies only on estimating the molar volume ($V_b$) and the modified non-specific cohesion parameter ($\delta_b'$) of the solute, both of which can be estimated using group contribution incremental methods. The value of the partition coefficient (P) depends on the size and non-specific vaporisation energy ($E_v'$) of the organic core of the solute as well as the length and number of attached fluorous ponytails. Generally, log P increases with the chain length and number of chains unless $E_v'$ is very large, when either can lead to a decrease in partition into the fluorous phase. Some systems have been shown to give lower log P on increasing the chain length or number of fluorous chains, but these do not have very high values of $E_v'$ for the organic core. Therefore, some
modification of this aspect of the modelling is necessary. Clarke has recently published his findings with phosphino-amine fluorous soluble metal complexes.\textsuperscript{12} He demonstrates that the addition of one fluorous ponytail to a \((C_6F_5)_2P\) fragment is sufficient to ensure a high partition co-efficient in PFMC/toluene.

Initially the synthesis of fluorous soluble ligands focussed on fluorinating known ligands, for example; fluorous analogues of triphenylphosphine in Vaska’s complex\textsuperscript{13} and Wilkinson’s catalyst\textsuperscript{14} or other triaryl phosphines.\textsuperscript{15,16} Further work investigating the influence of the position of these perfluoroalkyl modifying “ponytails” on the aryl ring has been undertaken by Hope and co workers.\textsuperscript{17,18}

With the catalyst immobilised in the fluorous phase, the substrate can be introduced either in solution, e.g. with toluene, or neat.\textsuperscript{19} When heated the two phases form a single homogeneous phase, which allows the substrate to be in intimate contact with the catalyst at all times. With the addition of reacting gases, reaction will occur at this elevated temperature but the catalyst and product are easily separated by cooling the mixture and decanting the product allowing easy reuse of the catalyst phase. The concept is shown schematically in Figure 1.3.1 for the hydroformylation of alkenes, which was the test reaction first reported by Horváth and co-workers.

Although temperature dependent solubility is generally used to affect the required phase transitions (miscible – immiscible), an alternative involves the use of \(CO_2\) to affect the transition.\textsuperscript{20} Being soluble in both organic and fluorous solvents, the \(CO_2\) can render a biphasic system monophasic without raising the temperature. This concept has been demonstrated using hydrogenation and epoxidation of alkenes, and significant rate enhancements (50-70 \%) have been observed at room temperature. Similar enhancements can be achieved in the biphasic systems by using more efficient
The CO2 approach may have particular appeal in systems where one of the substrates or products is thermally sensitive.

![Fluorous biphase concept](image)

Figure 1.3.1 The Fluorous biphase concept illustrated for the hydroformylation of an alkene (substrate) to an aldehyde (product)

The influence of the fluorous ponytails on the metal complex is an important factor to understand as the strongly electron withdrawing effect of the fluorine atoms may affect the behaviour of the phosphorus atom. A spacer group between the phosphorus and the fluorine tail is usually included in the ligand design. Generally, this is an aryl or alkyl group that is effectively acting as a shield to the phosphorus and metal centre from the powerful electron withdrawing effect of the perfluoroalkyl tail. Horváth and co-workers studied the optimum length of an alkyl spacer group and found that the electronic properties of the ligand could be tuned by varying the length of the alkyl spacer group between the phosphorus atom and the perfluoroalkyl tail. The results they reported from theoretical calculations implied that two methylene groups would provide sufficient shielding of the phosphorus atom, but in practice, a C2H4 spacer does not entirely eliminate the electron withdrawing effect of the perfluoroalkyl tail. An alkyl spacer is expected to be a better insulator of electron effects than an aryl group, which may transmit electronic effects in particular to the o- and p- positions of the ring. Insulation of the effects of the fluorous substituents on
aryl groups can be achieved by using a C$_2$H$_4$ or O(CH$_2$)$_n$ (n = 1 or 5)$^{22}$ spacer between the aryl group and the fluorous tail, or by attaching the fluorous tail to a SiCH$_2$CH$_2$ spacer.$^{23,24}$ Ligands such as P(4-C$_6$H$_4$SiMe$_{3-n}$CH$_2$CH$_2$CF$_{13}$)$_n$ (n = 1-3) and \{CH$_2$P(4-C$_6$H$_4$SiMe$_{3-n}$CH$_2$CH$_2$CF$_{13}$)$_n$\}_2 have been shown to be electronically very similar to PPh$_3$ and Ph$_2$PCH$_2$CH$_2$PPh$_2$ and sterically only marginally larger. Only the ligands with n = 3 are preferentially soluble in fluorous solvents. The rhodium and nickel complexes tend to show much higher fluorophilicities because the coordination of multiple ligands better encapsulates the organic centre of the molecule. The percentage of fluorine in the complexes is in fact slightly lower than the individual ligands.

There has been great interest since Horváth’s original paper, in synthesising new and more fluorous soluble ligands for various reactions. From the wide ranging topics published it would appear that the general consensus is that if the reaction can be carried out under homogeneous conditions, then it should be possible to fluorinate the ligands and perform the reaction under fluorous biphasic conditions. The rest of this chapter will discuss the reactions that have been reported using fluorous biphasic systems.

1.3.1 Alkene Hydrogenation

Having successfully produced a fluorous analogue of Wilkinson’s catalyst for the hydroboration of alkenes, Horváth and co workers applied this complex \{ClRh[P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]\}_3 to the hydrogenation of a range of alkenes.$^{25}$ Using a PFMC / toluene biphasic system at 45$^\circ$C under a balloon pressure of H$_2$, the reaction of 2-cyclohexen-1-one showed clean conversion to cyclohexanone, 98 % yield. Throughout the study, conjugated alkenes, terminal alkenes and disubstituted alkenes were tested. Separation of the toluene layer and reuse of the PFMC layer for further
catalytic reaction of 2-cyclohexen-1-one showed a small drop in yield over 3 cycles (from 96 to 92 %). However, for the reaction of 1-dodecene, by the third cycle, a black solid had precipitated and any further hydrogenations suffered a substantial drop in rate. By recycling the catalyst solution into new vessels, the reaction proceeded normally. These results do not compare to those for the best homogeneous catalysts, but the ease of recycling the expensive catalyst, does make this a useful reaction system. Hope et al have also described a rhodium-catalysed hydrogenation of styrene in the fluorous biphase using a range of fluorinated ligands. The purpose of this study was to investigate the effects of the perfluorocarbon solvent and the fluorous ponytail substituents on the catalytic system. The best rates were achieved with the fluorous ligand P(4-C$_6$H$_4$OCH$_2$C$_7$F$_{15}$)$_3$, 201 mmol dm$^{-3}$ h$^{-1}$, in a toluene / hexane / PP3 solvent system. No free ligand was observed in the organic phase and recharging the reactor with further fractions of substrate resulted in no effect on the catalytic activity, which demonstrated high catalyst stability and recovery.

Hydrogenation of 1-octene was also carried out by van Koten and coworkers using analogues of Wilkinson’s catalyst containing P(4-C$_6$H$_4$SiMe$_2$(CH$_2$CH$_2$R$_f$)$_3$) (R$_f$ = C$_6$F$_{13}$ or C$_8$F$_{17}$). Comparison of this catalyst with [RhCl(PPh$_3$)] and with [RhCl(P(4-C$_6$H$_4$SiMe$_3$)$_3$)] under monophasic conditions in PhCF$_3$ showed that the SiMe$_3$ substituent slightly increased the reactivity compared with H, but that the fluorous tail reduced the activity back to the same as that using PPh$_3$ as the ligand. The ligands with the fluorous ponytails showed good activity under fluorous biphasic conditions (1-octene / PFMC) at 80 °C for the hydrogenation of 1-octene and the fluorous phase could easily be separated from the product by cooling below 25 °C. Over 8 cycles using the ligand with R$_f$ = C$_6$F$_{17}$ and carrying out the separation at 0 °C, the rate of reaction increased from 177 catalyst turnovers h$^{-1}$ to 600 h$^{-1}$, but this was
largely attributed to loss of significant amounts of the fluorous solvent into the organic phase. When the lost fluorous solvent was replaced for the 8th run the rate reduced to 155 h\(^{-1}\) (87.5 % of the initial rate). ICPAAS analysis showed that the overall leaching corresponded to 1 % of the Rh after 9 cycles (0.1 % after the first cycle, c.f. 0.3 % after the first cycle with R\(\text{f}=\text{C}_6\text{F}_{13}\)). The phosphine leaching to the organic phase was much more significant (1.3 % and 8 % per cycle for R\(\text{f}=\text{C}_8\text{F}_{17}\) and C\(\text{6F}_{13}\) respectively).

Rhodium complexes of triarylphosphines containing an OCH\(_2\) spacer, Figure 1.3.2, have been used for hydrogenation of methyl (E)-cinnamate in D100 (mainly perfluorooctane) or FC77 / ethanol.\(^{22}\) Generally speaking, the reactions were slow (<100 turnovers h\(^{-1}\)), they could be recycled twice but the reaction half-lives increased with time. Rhodium and phosphine leaching were of the order of 0.4 and 1-1.5 % respectively for ligands with only one ponytail, except where the ponytail was in the 2- position, where the leaching was much higher (2.8 and 5.6 %) because the steric congestion of this ligand inhibited coordination. Leaching was lowest (0.1 and 0.5 % in the second and third runs) for the ligand with two ponytails (as was the reaction rate). Higher leaching and lower rate in the first run were attributed to difficulties with coordinating the bulky ligand.
Fluorous solvents are of very low polarity so it would be expected that ionic compounds would not dissolve readily in them. Nevertheless, ionic rhodium catalysts have been used successfully in fluorous biphasic systems. \([\text{Rh(COD)}P(4-SiMe_2(CH_2)_2C_6F_{13})]\text{BF}_4\) is active for the hydrogenation of 1-octene and partial hydrogenation of 1-octyne.\(^{28}\) In the case of 1-octene in acetone, the lower rate of alkene isomerisation than for the unsubstituted analogue means that the fluorous compound is a better hydrogenation catalyst. This has been attributed to aggregation, which has also been observed for other analogues in which there is an Me_3Si- or Me_2Si(C_8H_{17})- substituent, but to a lesser extent. 1-octyne was hydrogenated (40°C, 1 bar H\(_2\)) under fluorous biphasic conditions with phase separation at 0°C. Better retention into the fluorous phase was observed when using a polar fluorous solvent and hexane (99.82%, insoluble catalyst emulsified in homogeneous reaction mixture) than when using a PFMC and acetone (97.5%), as expected for the ionic catalyst. Phosphine leaching was very similar to that of rhodium in this case suggesting that the diphosphine remains coordinated throughout the reaction. Turnover frequencies for these reactions were low (10-30 h\(^{-1}\)) and the selectivity to \textit{cis}-4-octene was 60-70 %. The other main product was 4-octyne (15-17 %).
Using similar cations, but heavily fluorinated anions (Figure 1.3.3) the catalyst was fully soluble in the fluorous biphasic mixture and could be recycled with only 1% losses after the hydrogenation of 1-octene. The complex containing more fluorous tails on the diphosphine and [B(4-C₆H₄CF₁₃)₄] was the more active hydrogenation catalyst.

![Fluorous soluble ionic catalysts for the hydrogenation of 1-octene](image)

\[
\text{Ar} = 4-C₆H₄SiMe₂(CH₂)₂C₆F₁₃
\]

\[
\text{Ar} = 4-C₆H₄SiMe((CH₂)₂C₆F₁₃)₂
\]

Figure 1.3.3 Fluorous soluble ionic catalysts for the hydrogenation of 1-octene.

\((R)\)-BINAP ligands bearing fluorinated substituents (Figure 1.3.4) have been prepared by Hope and co-workers. The ruthenium complexes of the two ligands were compared with Ru-(R)-BINAP for the asymmetric hydrogenation of dimethyl itaconate in methanol at room temperature and 20 bar H₂ with a substrate / catalyst ratio of 2000. The enantioselectivity of the compound, to the (S) enantiomer, was unaffected (>95% each) by the addition of the perfluoroalkyl groups, they did however, affect the conversions, only 42% with Ru-(B) and 83% with Rh-(A) compared to 88% conversion with the non-fluorous analogue; the more electron-
withdrawing ponytails lowering the activity of the catalyst. These reactions were not carried out under fluorous biphasic conditions.

\[
\begin{align*}
\text{F}_{13}\text{C}_6\text{C}_2\text{H}_4 \quad & \quad \text{A} \\
\text{F}_{13}\text{C}_6\text{C}_2\text{H}_4 \quad & \quad \text{B}
\end{align*}
\]

Figure 1.3.4 (R)-BINAP ligands used in ruthenium catalysed asymmetric hydrogenation of dimethylitaconate.\textsuperscript{10}

\[
\begin{align*}
\text{O} + \text{OH} \quad & \quad \text{Ir}(&\text{COD})\text{Cl}_2 \quad \rightarrow \quad \text{Me}_3\text{CO} + \text{OH} \\
\text{Y} \quad & \quad \text{X} \quad \text{N} \quad \text{N} \quad \text{Z} \\
\end{align*}
\]

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<td>Ph</td>
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<td>Bu\textsuperscript{t}</td>
<td>1b</td>
</tr>
<tr>
<td>X\textsubscript{2}</td>
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<td>H</td>
<td>2a</td>
</tr>
<tr>
<td>(CH\textsubscript{2})\textsubscript{4}</td>
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<td>Bu\textsuperscript{t}</td>
<td>2b</td>
</tr>
<tr>
<td>(CH\textsubscript{2})\textsubscript{4}</td>
<td>3,5-C\textsubscript{8}H\textsubscript{3}(C\textsubscript{8}H\textsubscript{17})\textsubscript{2}</td>
<td>Bu\textsuperscript{t}</td>
<td>3</td>
</tr>
<tr>
<td>(CH\textsubscript{2})\textsubscript{4}</td>
<td>C\textsubscript{8}H\textsubscript{17}</td>
<td>C\textsubscript{8}H\textsubscript{17}</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 1.3.5 Transfer hydrogenation of acetophenone in Galden D-100.\textsuperscript{31,32}

The asymmetric transfer hydrogenation of acetophenone by 2-propanol has been carried out in Galden D-100 (mainly perfluoro-octane) using iridium complexes of salicaldehyde diaminoethane Schiff bases as ligands (Figure 1.3.5).\textsuperscript{31,32} High yields (>90%) with enantiomeric excess up to 57% were observed when the reactions were carried out at 70 °C. These e.e’s are higher than observed with non-fluorous analogues (<22%), but the catalyst was destroyed during the reaction so that the
Chapter 1: Literature Review

recovered fluorous phase was much less active giving an e. e. of only 6%. The organic phase was also active, but not enantioselective. Other ketones and β-diketoesters were also reduced with e. e. between 18 and 60%.

1.3.2 Alkene hydrosilation

Complexes of the form \([\text{RhCl}(\text{P}(4-\text{C}_6\text{H}_4\text{SiMe}_3\text{C}_8\text{F}_{17})_n)]\) have been used for the fluorous biphasic hydrosilation of 1-hexene (Figure 1.3.6) in PFMC without an additional organic solvent (alkene: silane = 2:1). The reactions were monophasic at the reaction temperature (reflux), but the more fluorinated catalyst was not completely soluble in the monophasic mixture, although it was redissolved in the PFMC phase, which separated on cooling to room temperature. Reaction rates were similar to those obtained using \([\text{RhCl}(\text{PPh}_3)]\) in benzene.

Reactions were carried out for 15 minutes and the fluorous phase was recycled twice, with 100% conversion of the silane being observed in each case. ICPAAS analysis showed that for less fluorous catalyst, rhodium and ligand leaching were high (12 and 19% respectively), while the retention of the more fluorinated catalyst was better (1.7 and 2.2%).

In an interesting variant of the fluorous biphasic principle, fluorinated alkenes were hydrosilated with e. g. HSiMe_2Cl using \([\text{RhCl}(\text{PPh}_3)]\) in benzene or toluene. The fluorous product could be extracted using FC-72 (a mixture of perfluoro hexanes) and the organic phase containing the catalyst recycled. Rhodium and phosphorus were undetectable (<1 ppm) by ICPAAS in the fluorous phase.
Chapter 1: Literature Review

1.3.3 Alkene Hydroboration

FBC has been applied to the rhodium-catalysed hydroboration of alkenes and alkynes by Horváth and co-workers.\(^{14,34}\) This was achieved by synthesising a fluorous analogue of Wilkinson’s catalyst \([\text{RhCl}(\text{PPh})_3]\), using the perfluorinated phosphine \([\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{13})_3]\). The modified catalyst was highly soluble in PFMC and \(\text{CF}_3\text{C}_6\text{H}_5\), slightly soluble in THF and acetone, but insoluble in other organic solvents. The catalyst was effective at a loading of 0.01 – 0.25 mol%, affording turnover numbers (TON) as high as 8500. The reaction was carried out in PFMC without an added organic solvent as it was observed that the reactions occurred more rapidly in the absence of a non-fluorous solvent. A high degree of catalyst recovery was observed in repeat reactions of norbornene although some loss of catalyst was indicated by a drop in yield and TON, 90% yield with TON 854 in the first run compared to 83% yield and TON 785 in the second run.

In their later paper,\(^{34}\) this catalyst loss was studied further and quantitatively by atomic absorption analysis, the rhodium loss was found to be 0.4% per cycle, for the Rh complex bearing the above ligand. However, the Rh complex with \([\text{P}(\text{C}_2\text{H}_4\text{C}_6\text{F}_{17})_3]\) only showed a loss to the organic phase of 0.2% per cycle. It was also noted that after three cycles, the perfluorohexyl complex deposited a black solid and accordingly the activity dropped, suggesting decomposition of the catalyst. Low catalyst loading and Rh loss do make this a favourable method of hydroboration of...
alkenes and alkynes especially due to the ease of separation of the products from the fluorous phase.

### 1.3.4 Alkene hydroformylation

\[
\text{R} + \text{CO} + \text{H}_2 \xrightarrow{\text{[Rh(CO)\textsubscript{2}(acac)]}} \text{R} + \text{CHO} + \text{R} \text{CHO}
\]

**Figure 1.3.7 Hydroformylation of an alkene using a rhodium complex bearing a fluorous ponytail.**

In the original paper introducing FBC,\(^5\) the reaction Horváth chose to demonstrate the principle was the hydroformylation of dec-1-ene (Figure 1.3.7). Due to the lack of fluorous soluble ligands available, the synthesis of a new fluorinated phosphine was also necessary. \(\text{P}\{\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3\}_3\) was chosen. PFMC was used as the fluorous phase, toluene as the organic phase and the catalyst was prepared in situ from the Rh precursor \([\text{Rh(acac)(CO)}\text{2}]\) and the phosphine (P / Rh = 40) under CO / H\(_2\) (5 bar). The reaction was carried out under 10 bar CO / H\(_2\) (1:1) at 100°C. They report about 85% conversion to undecanals with an n / i ratio of 2.9 over 11 hours.

To demonstrate the low leaching of the catalyst into the product phase, they returned the product phase to the emptied and cleaned reactor, heated and pressurised to the required reaction conditions and injected a fresh solution of oct-1-ene in toluene. After 24 hours, they report that only trace amounts of conversion products were observed by GC analysis indicating that very little catalytic species has leached from the fluorous phase throughout the initial reaction.

In a later paper by the same authors,\(^{21}\) further investigation of the shielding of the phosphine from the electron-withdrawing fluorous tail indicated that although it
Chapter 1: Literature Review

does not completely shield the effects, a $-\mathrm{C}_2\mathrm{H}_4-\,$ group between the phosphine and fluorous tail provides sufficient shielding. A kinetic investigation carried out on this reaction showed it to be first order in both [Rh] and dec-1-ene. Increasing the $[\text{P(C}_2\mathrm{H}_4\text{C}_6\text{F}_{13})_3]$ increased the l:b ratio but decreases the activity of the hydroformylation, which is consistent with the known negative order in [phosphine] for hydroformylation reactions. This paper also reports the semi-continuous hydroformylation of dec-1-ene, recycling the catalyst phase in nine successive runs; a slight rise in activity, a slight decrease in l:b ratio (4.5 – 3.5) and a slight drop in selectivity to aldehydes (91.5 % to 88.3%), which corresponded to a rise in isomerisation (7.8% to 11.0%) was observed. These results are as expected if phosphine is being lost to the organic phase as the reaction has a negative order in [phosphine] and the linear selectivity is lower at lower [phosphine]. The Rh loss from the fluorous phase was measured as 4.2% over 9 runs. This is equivalent to 1.18 ppm Rh loss/mol aldehyde. Being a trialkyl phosphine and not very bulky, very high [phosphine] ratios (0.3 mol dm$^{-3}$) were required for high l:b ratios (7.8: 1) in the product aldehyde. The catalytic system was also tested for the hydroformylation of ethene using FC-70 (predominantly perfluoro compounds with 15 carbon atoms) as the fluorous solvent under continuous flow operation and gave a selectivity of 99.3% to propanal. This reaction was successfully carried out for two months with no loss in activity, but the product was removed in the gas phase.

Various groups have studied fluorous analogues of triphenylphosphine in attempts to increase the linear selectivity. Masdeu-Bultó and co workers have reported the successful fluorous biphasic hydroformylation of 1-octene using a Rh complex with the fluorinated phosphine $\text{P(C}_6\text{H}_4-4-\text{OCH}_2\text{C}_7\text{F}_{15})_3$. $^{35}$ $\text{Rh} / \text{P} = 5$, at 80°C and 40 atm. The biphasic solvent system used was PFMC / toluene (60/40, v/v) after
1 hour of reaction a conversion of 98% with an aldehyde selectivity of 97% was achieved. The l: b ratio was 2.6: 1%. However, when the catalyst solution was recycled, a drop in the aldehyde selectivity was observed without a drop in conversion, indicating a loss of ligand to the organic /product phase. Upon cooling, the toluene phase was observed to be slightly coloured symptomatic of catalyst leaching from the fluorous phase. By increasing the temperature of separation from 10°C to 50°C, the separation improved. Re-using this catalyst phase allowed three recycles with little reduction in aldehyde selectivity observed (99%, 97% and 91%). After the first recycle, analysis of the product phase showed Rh and P in the toluene and traces of aldehyde are reported as being observed by GC analysis in the fluorous phase. An increase of the substrate / Rh ratio from 500/1 to 2000/1 showed a lower conversion, 20% after 1 hour, as expected, but the selectivity to aldehydes remained high, 94%. By removing the toluene from the reaction an increase in activity (68% conversion in 1 hour) was observed. This effect has also been observed by others.¹⁹

Hope and co workers have synthesised a large number of perfluorinated ligands and carried out testing of these ligands in the hydroformylation of hex-1-ene using \([\text{Rh(acac})(\text{CO})_2]\) as the precursor and a P / Rh ratio of 3.

In a high pressure reactor using a 1:1 organic: fluorous solvent mixture, 70°C, 20 bar CO / H₂ (1:1), after 1 hour they found that their fluorous analogue of triphenylphosphine \([\text{P(4-C}_6\text{H}_4\text{C}_6\text{F}_{13})_3]\) had 89.2% selectivity to aldehydes, with an l: b ratio of 3.8 compared to triphenylphosphine 98.2% selectivity and l: b ratio of 3.1.

Further studies on this ligand with 1-octene as the substrate demonstrated that using \([\text{Rh(acac})(\text{CO})_2]\) (2 mmol dm⁻³) and \([\text{P(4-C}_6\text{H}_4\text{C}_6\text{F}_{13})_3]\) (20 mmol dm⁻³) at 60°C and 20 bar (CO/H₂, 1:1) in PFMC, an l:b ratio of 6.3: 1 (selectivity to linear aldehyde = 80.9%) could be obtained with a turnover frequency of 4400 h⁻¹ and with
99.95 and 96.7% retention of rhodium and phosphine into the fluorous phase. The rhodium retention is better than that of the free phosphine because at room temperature the catalyst is of the form [RhH(CO)(P(4-C₆H₄C₆F₁₃))₃], thus anchoring the rhodium into the fluorous phase with 9 fluorous ponytails. Higher rates and more Rh leaching were observed at higher reaction temperatures. By omitting the organic solvent, higher rates, linear selectivity and retention into the fluorous phase were observed. Even though the system becomes biphasic under the reaction conditions at 20% conversion, the kinetics are first order up to at least 80% conversion, showing that mass transport does not become rate determining provided that the mixture is stirred efficiently. The rate and selectivity are much better than those obtained using PPh₃ under the same conditions, because of the electron withdrawing effect of the fluorous tail, which is transmitted to the rhodium centre via the phenyl ring. The higher binding constant observed with the fluorinated ligand than with PPh₃ accounts for the better linear selectivity at low phosphine loadings. This conclusion was supported by the observation that the selectivity under comparable conditions but with less phosphine (80 °C, 30 bar, P: Rh = 3) for this system was higher (l: b = 3.5) than for the analogous ligand with an –OCH₂- spacer (80°C, 40 bar, P: Rh = 5, l: b = 2.6), although it should be noted that toluene, which may reduce the l: b ratio was present in the latter system. In the presence of toluene under slightly milder conditions and with the lower P: Rh (70°C, 20 bar Rh: P = 3) the selectivity of the complex without the spacer was still higher (l: b = 3.8). The high rates and selectivities and the omission of the organic solvent meant that this system was chosen for further detailed studies in a continuous flow system, which forms the basis of this thesis.
A comparison between \([P(4-C_6H_4C_6F_{13})_3]\), \([P(4-C_6H_4C_8F_{17})_3]\) and \([P(3,5-C_6H_4(CF_3)_{2}(4-C_6H_4C_6F_{13})_2]\) suggested that a catalyst bearing the ligand containing the \(C_8\) fluororous ponytail undergoes only 10% of the leaching of the other two ligands, whilst their activities (first order rate constant, \(k = 1.9 \times 10^{-3}, 1.3 \times 10^{-3}, 2.5 \times 10^{-3} \text{ s}^{-1}\)) and selectivities(l:b = 6.3, 6.7 and 4.7 respectively) were similar. Other studies have shown that the retention of the catalyst within the fluorous phase was very dependent upon the conversion, being much enhanced at high conversions (Figure 1.3.8).\(^{39}\)

The fluorinated analogue of triphenyl phosphite \(\{P(OC_6H_2C_6F_{13})_3\}\) also performed well in the hydroformylation of 1-hexene when compared with \(\{P(OPh_3)\}\) with a selectivity of 82.3% and l: b ratio of 6.4 compared to 92.0% and 2.9 respectively.\(^7\) This represented one of the first examples of phosphite ligands being used for hydroformylation in FBC.

Further optimisation\(^{19,37}\) of this system in perfluorodimethylcyclohexane (PFDMC) using 1-hexene and 1-octene showed that high rates and linear selectivities (l: b up to 9.9: 1) could be achieved, but alkene isomerisation was always ca. 13%, whilst leaching of Rh (>2.5%) and phosphine (>4%) were much higher than for the
phosphine analogue. This leaching, which was much worse when toluene was present, was attributable to degradation of the phosphite, either through direct reaction with the aldehyde, or through reaction with water formed by aldol condensation of the product. Either reaction would produce complexes in which one or more fluorous tails has been removed, so that the fluorous solubility would be reduced.

Mathivet et al have extended this work on phosphites in the hydroformylation of higher alkenes under fluorous biphasic conditions. By synthesising fluorous ligands with ponytails in different positions on the aryl group, they have studied the affects of the positioning of this group on the ligands, Figure 1.3.9. The two ligands with a single fluororous ponytail, A and B, partition in a solvent mixture of dec-1-ene and C\textsubscript{8}F\textsubscript{17}H in a 5 / 95 ratio and the ligand with two fluorous tails, C, partitions with a ratio of 1 / 99.

The three ligands were tested in the hydroformylation of 1-decene with no organic solvent using only C\textsubscript{8}F\textsubscript{17}H at 80°C under 40 bar CO / H\textsubscript{2} (1:1) and run to
100% conversion. A and C are both sterically hindered and gave similar results, 100% conversion was achieved quickly after 15 and 12 minutes respectively with an aldehyde selectivity of 85% in both cases, this results in TOFs of 10 000 and 11 000 h\(^{-1}\). The unhindered ligand B achieved 100% conversion in 30 minutes, but showed a higher aldehyde selectivity of 95%, TOF 3900 h\(^{-1}\). Results with B and various terminal alkenes demonstrate the high selectivity of this phosphite to aldehyde formation. Catalyst recycling was also considered. Using dec-1-ene as the substrate allowed direct comparison with Horváth’s work. Each reaction was run for just 10 minutes and the first three runs for each ligand showed a slight increase in conversion with the fourth run showing a marked drop for ligand A, however the selectivities for each ligand dropped slightly in each cycle. In the fourth recycle, the organic phase was noted as being yellow in colour, which indicated that leaching of Rh is occurring. The reason for the differences in results between the various ligands lies in the steric hindrance that exists with ligands A and C, which will results in only one phosphite coordinating to the Rh making the active species \([\text{HRhL(CO)}_3]\) and allowing facile binding to the alkene, causing the fast reaction. The single ligand makes the catalyst less selective, whereas B is more similar to the triphenyl phosphite modified catalyst, which forms the bis phosphite.

In an effort to overcome some stability issues with these ligands, further syntheses of ligands D-J were carried out and reported in a second paper.\(^{41}\) An investigation of the effect of the position of the fluorous group on the ring D-F show that the activity increases as the fluorous group gets closer to the phosphorus (TOF of 10 000 h\(^{-1}\), 6300 h\(^{-1}\) and 3500 h\(^{-1}\) for D, E and F). Conversely, aldehyde selectivity increases as the fluorous group moves away from the phosphorus atom; that is the \textit{para}-substituted phosphite shows the highest selectivity towards aldehyde (71, 80 and
85% for D, E and F). It is also noted from comparison of C and H that the removal of the ethyl spacer group has a marked effect on the aldehyde selectivity (85 and 46% respectively). This may be due to the electronic effect of the fluorous tail on the metal or may simply be due to the steric hindrance of the ligand about the metal centre. The hydroformylation of internal and different terminal alkenes was examined using E. It was found that decreasing the length of the substrate caused the activity, l: b ratio and aldehyde selectivity to increase Table 1.3.4.1

Recycling of the ligands was investigated for ligands D, E and J. Over four recycles the conversions dropped for all three phosphites. The most marked decrease was with E, which achieved less than 10% conversion in the fourth recycle. The selectivity of the catalysts to aldehyde products did not decrease as drastically but a decrease in the selectivity of E was most notable in the second recycle. This suggests that some leaching of the three phosphites to the organic phase does occur.

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<th>Alkene</th>
<th>TOF (h(^{-1}))</th>
<th>n/i</th>
<th>Selectivity to Aldehyde (%)</th>
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<tr>
<td>Oct-1-ene</td>
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<tr>
<td>Dec-1-ene</td>
<td>6300</td>
<td>5.8</td>
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Table 1.3.4.1 The results of hydroformylation reactions carried out using rhodium complexes of using ligand E Figure 1.3.9 \(^{40,41}\)

Another approach to the fluorous biphasic hydroformylation of alkenes has been investigated by Xiao and co workers using a fluorous soluble polymer catalyst.\(^{42}\) The poly(fluoroacrylate-\(co\)-styryldiphenyl phosphine) ligands are of the form shown in Figure 1.3.10. Neither ligand is soluble in normal organic solvents but both are soluble in fluorinated solvents.
The hydroformylation of dec-1-ene was performed in a batch reactor using a solvent mixture of hexane-toluene-PFMC (40:20:40) (the hexane proved necessary to form a homogeneous phase under the reaction conditions). The catalyst was formed in situ from [Rh(acac)(CO)$_2$] and the ligand (P / Rh = 6) under CO / H$_2$ (30 bar, 1:1). The results showed a turnover frequency of 136 mol aldehyde (mol Rh h)$^{-1}$ and a selectivity to aldehyde of 99%, the l: b ratios of 4.8 (polymer a in Figure 1.3.10) and 5.9 (polymer b in Figure 1.3.10) were also competitive with those obtained from homogeneous hydroformylation reactions in conventional solvents. The recycling of the catalyst phase was carried out in the hydroformylation of hex-1-ene. Three consecutive reactions were carried out and a 1 ppm loss of Rh was observed for each recycle, however by the end of the third run all PFMC had leached to the product phase which in turn caused loss of ligand and catalyst to the product phase.

![Fluorous polymers with bound PPh$_3$ used in the hydroformylation of 1-hexene.](image)

Ojima and co workers$^{43}$ have reported fluorinated analogues of BINAPHOS, an unsymmetrical bidentate ligand having one phosphine and one phosphite donor, for rhodium-catalysed asymmetric hydroformylation. Unlike the previous papers, this deals with the hydroformylation of styrene, which preferentially forms the branched
product. This is desirable because the linear product has no chiral centre and because the branched product is a possible intermediate in the formation of ibuprofen type anti-inflammatories. The ligands were found to be preferentially soluble in toluene over PFMC, possibly due to the aromatic nature of the naphthalene groups and the slightly low fluorine content. All ligands displayed good solubilities in perfluorotoluene (PFT).

![Figure 1.3.11](S,R)-[C₆F₁₃(CH₂)₃]₂-BINAPHOS and related ligands used in the rhodium catalysed asymmetric hydroformylation of styrene.

The hydroformylation reactions were carried out in a number of different solvent systems, Table 1.3.4.2, 50-60 °C and 40 atm CO/H₂ (1:1) using the (S,R)-[n-C₆F₁₃(CH₂)₃]₂-BINAPHOS ligand, Figure 17.

After 18 hours in the PFMC / toluene system, 100 % conversion was achieved with 100 % selectivity to aldehydes of which 92 % were branched, with an enantiomeric excess of 85 %. In the same time with only PFMC as solvent only 88 % conversion was observed, with a b:l ratio of 94:6 and an e.e. of 87 %. Changing the fluorous solvent to PFT showed 73 % conversion after 16 hours with 100 % selectivity to aldehydes of which 91 % were the branched form and an overall e.e. of 82 %.
Chapter 1: Literature Review

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<th>Conv. (%)</th>
<th>b/l</th>
<th>e.e. (%)</th>
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Table 1.3.4.2 The Rh / (S,R)-[n-C$_6$F$_{13}$(CH$_2$)$_3$]-BINAPHOS catalysed hydroformylation of styrene.$^{43}$

1.3.5 Alkene Epoxidation

The large amounts of molecular oxygen that can be dissolved in to fluorous solvents, together with their oxidation resistance makes them potentially very suitable solvents for oxidation reactions. Fish and co workers reported the synthesis of a novel perfluorinated triazacyclononane (TACN) ligand, shown in Figure 1.3.12, which is soluble in perfluoroalkanes.$^{44}$ Using this ligand along with a fluorinated carboxylate synthon, [M(O$_2$C(CH$_2$)$_2$C$_8$F$_{17}$)$_2$] (where M is Co or Mn), they have successfully carried out the epoxidation of a variety of alkenes, in a fluorous biphasic system. The suggested form of the catalyst produced in situ is [C$_8$F$_{17}$CH$_2$CH$_2$CO$_2$M{(C$_8$F$_{17}$(CH$_2$)$_3$)$_3$-TACN}]$^{2+}$. The reactions were carried out in perfluoroheptane with the substrate acting as the organic layer, in an O$_2$ atmosphere in the presence of tert-butyl hydroperoxide (TBHP). Alkenes bearing allylic hydrogens gave the highest yields under these conditions. Removal of the upper, organic layer and adding new cyclohexene and TBHP provided similar results to the first run, showing that leaching of the catalyst into the organic phase was negligible, however no quantitative data was provided. [CuCl{(C$_8$F$_{17}$(CH$_2$)$_3$)$_3$TACN}] is also active for alkene oxidation by Bu'OOH / O$_2$ in perfluoroheptane at room temperature (biphasic).$^{45}$ The best results were obtained with cyclohexene, which gave cyclohexanone and cyclohexanol (72: 28) in 435% conversion based on Bu'OOH. The catalyst as recycled twice with the yield dropping to 75% and 50% that obtained
in the first run, suggesting catalyst instability or leaching. Cyclohexane could be oxidised to cyclohexanone and cyclohexanol and toluene to benzaldehyde using the same system, but the yields were very low 97.5 and 17% based on Bu'OOH respectively. These values do represent catalyst turnover numbers of 5 and 13 respectively. A copper complex of bipyridine bearing fluorous ponytails, which also contained fluorinated carboxylate groups, was not successful in these oxidation reactions. The organic phase was blue at the end of the reaction and conversions were very low.

![Fluorinated TACN ligand](image)

**Figure 1.3.12 Fluorinated TACN ligand used in epoxidation reactions.**

Pozzi and co-workers have also reported a fluorous soluble cobalt complex, which is active in the aerobic epoxidation of alkenes in an FBS. The ligand used in this complex was a fluorinated tetraarylporphyrin, with eight perfluorooctyl chains shown in Figure 1.3.13. The cobalt complex was dissolved in perfluorohexane and added to a solution of the alkene with 2-methylpropanal (aldehyde: substrate = 2:1) at room temperature.
The yields for reaction of unsubstituted terminal alkenes were lower than for substituted alkenes but they were still reasonable and could be increased further by increasing the aldehyde / alkene ratio. Total conversions of substrate were reported with epoxide selectivity as high as 95% in some cases. The FBC system allows for a much higher substrate / catalyst ratio (1000:1) than the non-fluorous epoxidation reported (20:1) previously. Recycling the fluorous layer once showed no reduction in conversion or selectivity.
Further efficient ligands for the epoxidation of alkenes but using PhIO as the oxidant and pyridine $N$-oxide as an additive in FBS have been reported by Pozzi.\textsuperscript{6,47–49} Chiral (salen) Mn complexes have been synthesised, which are soluble in fluorous solvents and active in the epoxidation of a variety of alkenes. The catalysts were of the form shown in Figure 1.3.14. 1 and 2 were initially reported in 1998 although the free ligands were soluble in Et$_2$O and ethanol the Mn-complexes were insoluble in organic solvents. The FBS allowed a much smaller catalyst / substrate ratio (0.005 / 0.33 mol dm$^{-3}$) compared to other homogeneous systems and provided good yields of epoxides (up to 85%); no significant decrease in activity was observed when the fluorous phase was recycled a second time. However, only the epoxidation of indene showed a high enantioselectivity (92%). The low enantioselectivity (<15%) of the
ligands 1 and 2 was attributed to the low steric hindrance of the perfluoroalkyl groups, as well as possible inefficient shielding of the strong electron-withdrawing effect of these fluorinated groups. Further work and synthesis produced 3 and 4 as “second generation” (salen) Mn$^{III}$ complexes. They were, indeed, more enantioselective than the original complexes. In the case of 1,2-dihydronaphthalene, the e. e. increased to 50% from 10% with the second-generation complexes. Further investigation of the catalyst was carried out and it was found that the fluorous layer could be recycled up to three times after the first reaction, but the catalytic activity dropped significantly in the fourth run. This was attributed to oxidative decomposition of the catalyst as indicated by the gradual disappearance of the characteristic UV-Vis-absorption bands of the (salen)Mn$^{III}$ from the fluorous layer and their non-appearance in the organic layer.

The same catalysts have been investigated for the asymmetric oxidation of dialkyl sulphides using PhIO as the oxidant in CH$_3$CN / perfluorooctane.$^{50}$ Although the conversions (>80%) and selectivities to sulfoxides (>90%) were generally good, and the more heavily fluorinated catalysts could be recycled 4 times with only small drops in activity, attributed to oxidation rather than leaching: the e. e.’s in these reactions were poor (<20%).

### 1.3.6 Other Oxidation Reactions

Knochel and co-workers have reported biphasic aerobic oxidation of aldehydes, sulphides and alkenes, using nickel and ruthenium catalysts with a perfluorinated 1,3-diketone ligand, Figure 1.3.15.$^{51}$

The nickel complex when reacted with aldehydes in a toluene / perfluorodecalin reaction mixture at 64°C, provided yields of the expected carboxylic
acids of 71-87%. The same catalytic system was active for the oxidation of sulphides, but required the presence of isobutyraldehyde and the nickel catalyst did not oxidise alkenes. The ruthenium form of the catalyst in C\textsubscript{8}F\textsubscript{17}Br was active in the epoxidation of disubstituted alkenes.

After “several” recycles, the ruthenium complex was recovered in 95% yield. The catalytic leaching was negligible as yields of 70% were still obtained after 6 runs, but this corresponds to a drop in yield from 87% - 70% over the six recycles. Quantitative data of the metal loss to the organic phase would be much more accurate for comparison to other systems. Using the same fluorinated diketonate ligand, Knochel and co workers have also reported a fluorous biphasic system for the Wacker oxidation of alkenes to aldehydes, suitable for a variety of alkenes. \textsuperscript{52} The catalyst system was a palladium (II) complex of the same fluorinated β-diketonate complex as shown in Figure 1.3.15 in C\textsubscript{8}F\textsubscript{17}Br with the substrate in benzene and tert-butylhydroperoxide as the oxidant. Although a wide variety of alkenes was tolerated in this system, aliphatic alkenes required longer reaction times than styrene derivatised substrates (8-20 h compared with 2-5 h). The catalyst for the reaction of 4-methoxystyrene was reused 8 times, initially providing yields of 4-methoxyacetophenone of 78% but dropping to 72% yield in the 8\textsuperscript{th} recycle, which indicates low catalyst leaching to the organic solvent. The catalyst was also active for the epoxidation of some activated disubstituted alkenes.

![Figure 1.3.15](image_url)

**Figure 1.3.15** Perfluorinated β-diketonate complex used for a variety of oxidation reactions (M = Ni)\textsuperscript{51,52} or Wacker oxidation (M = Pd).
Uemura and co workers have reported the aerobic oxidation of alcohols to aldehydes and ketones with palladium complexes containing pyridines with fluorous tails in a toluene-perfluorodecalin biphasic system at 80°C, using molecular sieves to remove the generated water. Some catalyst decomposition occurred, but this could be minimised by using excess pyridine ligand. Generally, the organic phase contained palladium, but using the ligand shown in Figure 1.3.16, the organic phase was colourless. ICPOES analysis showed that only 0.8% of the palladium leached to the organic phase during oxidation of 1-phenylethanol to acetophenone. Recycling could be carried out three times, but the yield dropped from 90 to 74% even though extra ligand was added before the third cycle. A wide range of primary and secondary alcohols was oxidised in yields usually >75%. 4-Nitrobenzyl alcohol is oxidised to the corresponding aldehyde using air and TEMPO in perfluoroheptane in the presence of [Cu(O2CCH2CH2C8F17){(RfCH2CH2)3TACN}] at 90°C, when the system is monophasic. Yields greater than 90% can be obtained and cooling to room temperature allows phase separation and reuse of the catalyst. Using 6 mol% TEMPO in each run, the catalyst could be recycled 7 times with yields >90% for the first 5 cycles. Thereafter the yield dropped to 51 and 8% in runs 6 and 7.
Copper complexes synthesised in situ from \([\text{CuBr} (\text{SiMe}_2)]\) and bipyridine bearing – (\(\text{CH}_2\))\(_4\)C\(_8\)F\(_{17}\) in the 5 and 5' positions is also active for the oxidation of a wide range of primary and secondary alcohols to aldehydes and ketones by air in the presence of TEMPO under fluorous biphasic conditions (C\(_8\)F\(_{17}\)Br / PhCl at 90\(^\circ\)C).\(^{54}\) Yields were generally very high (>80%). For 4-nitrobenzyl alcohol, the yield of aldehyde was 93% after 1.5 h. The fluorous phase was separated and reused 7 times. In the 8\(^{th}\) run, the yield of 4-nitro benzaldehyde was still 86%. Sterically hindered alcohols are rather unreactive in this system, but this allowed the selective oxidation of cis-4-methylcyclohexanol, which remained essentially unreacted.

Pozzi has also reported a fluoro-functionalised tetraazacyclotetradecane macrocycle, which is selectively soluble in fluorocarbons and active in the fluorous biphasic oxidation of hydrocarbons.\(^{55}\) This ligand (Figure 1.3.17) was produced whilst trying to generate a simple method of synthesising fluorous ligands. Both the cobalt and copper complex of this ligand, using CuCl and the cobalt salt of pentadecafluorooctanoic acid (Co(C\(_7\)F\(_{15}\)COO\(_2\)) as precursors, catalysed the oxidation of saturated and unsaturated hydrocarbons. The copper complex gave slightly higher yields and higher ketone selectivities in the oxidation of cyclooctane (80% yield, 80% cyclooctanone, 20% cyclooctanol). The Co complex only gave 30 % yield, (76% ketone selectivity), but both complexes performed similarly in the oxidation of cyclohexene to give cyclohex-2-en-1-one and cyclohex-2-en-1-ol. Recycling the fluorous layer, in the cyclooctane oxidation and the cobalt oxidation of cyclohexene, showed no drop in activity implying negligible catalyst leaching, but the activity of the Cu catalyst for the oxidation of cyclohexene dropped to 50% on the second cycle (c.f. 80% on the first cycle).
1.3.7 Allylic alkylation

Maillard et al have reported perfluorous analogues of MOP (methoxynaphthylidiphenyl phosphine), see Figure 1.3.18, and their application in palladium catalysed allylic alkylation.\textsuperscript{56,57} Due to the somewhat low fluorine content in these ligands, (R) 56.0 wt% fluorine, (S) 56.88 wt% fluorine, they were slightly soluble in THF and toluene, which would result in loss of the ligand during reaction and would involve further separation steps to recycle the ligand fully. The ligands were used in Pd-catalysed allylic alkylation however they gave low enantioselectivities (0-37%) for various solvent / base systems.
Figure 1.3.18 Palladium catalysed allylic alkylation using fluorinated ligands.$^{56,57}$

An attempt to recycle the catalyst was made. However, on the second run a conversion of only 24% was obtained as apposed to 100% in the initial run. This drop in activity was attributed to significant leaching of the ligand to the organic phase and was unavoidable unless the fluorine content of the ligands was increased.

Bayardon and Sinou have reported the synthesis of chiral bisoxazolines, which also proved to be active ligands in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate, as well as cyclopropanation, allylic oxidations and Diels-Alder reactions.$^{58}$ The ligands do not have a fluorine content greater than 60% and so are not entirely preferentially soluble in fluorous solvent, which may results in a significant ligand loss in the reaction system and in fact: all recycling attempts were unsuccessful. The catalytic results achieved were comparable with those obtained with their non-fluorous ligands.
1.3.8 Heck, Stille, Suzuki and Sonogashira and related coupling reactions

Nakamura et al applied fluorous chiral BINAP ligands to the asymmetric Heck reaction. R-F$_{13}$BINAP see Figure 1.3.19, was easily air oxidised, but in a benzene / FC-72 biphasic system, the Heck coupling of 2,3-dihydrofuran with 4-chlorophenyl triflate occurred with high enantioselectivity (93%), but low yield (39%). Reuse of the fluorous phase gave a 2% yield, most likely because of deactivation of the catalyst by ligand oxidation. TLC monitoring of the reaction showed the ligand to be oxidised in the fluorous phase, but there may also be some catalyst leaching to the organic phase. Compared with the original reaction with non-fluorous BINAP in trifluoromethylbenzene, the e. e. was much higher (90% e. e. F$_{13}$-BINAP, 76% e. e. BINAP). Therefore, overcoming the air sensitivity of the fluorous BINAP would provide a highly competitive system for Heck couplings.

![Figure 1.3.19 Heck coupling catalysed by fluorinated (R)-F$_{13}$BINAP palladium complex.](image-url)
Heck coupling has also been used in tandem with ring closing metathesis to give bridged ring systems (Figure 1.3.20). In conventional solvents, the Heck catalyst poisoned the ruthenium catalyst used for the ring-closing metathesis. However, by carrying out the reaction in a fluorous biphasic system with a standard metathesis catalyst but a fluorinated palladium catalyst for the Heck reaction, the catalysts could be kept separate during the low temperature ring-closing metathesis. On heating, the system becomes monophasic, thus allowing the Heck reaction to proceed. Yields were significantly better (37-67%) than in a homogeneous system (0-37%) for reaction where the Heck reaction could be carried out under relatively mild conditions, but more forcing conditions led to decomposition of the fluorous tagged palladium complex. This method for keeping incompatible catalysts separate may have potential for a range of reactions.

Stille, Suzuki, and Sonigashira couplings (Figure 1.3.21) have been successfully carried out under fluorous biphasic conditions. Stille couplings of a variety of electron poor aryl bromides and electron rich aryl stannanes catalysed by $[\text{PdCl}_2(P(\text{C}_6\text{H}_4(CH_2)_n\text{C}_8\text{H}_{17}))_3]_2$ ($x = 3, n = 0; x = 4, n = 0$ or 2) were carried out in DMF / PFMC at 80°C in the presence of LiCl. The reaction shown in Figure 1.3.21a, gave 90% conversion with all three catalysts and could be repeated at least 6 times with minimal loss of activity. Reactions using 2-tributylstannylanisole were less
successful and could not be recycled, probably because the coordination of the ligand was inhibited by the ortho methoxy group.

(a) $\text{MeO} \cdot \text{C} \cdot \text{Br} + \text{Bu}_{2}\text{Sn} \xrightarrow{[\text{PdCl}_{2}L_{2}]} \text{DMF} / \text{PFMC} \text{MeO} \cdot \text{C} \cdot \text{Br}$

(b) $\text{R} \cdot \text{Br} + (\text{HO})_{2}\text{B} \xrightarrow{[\text{PdCl}_{2}L_{2}] / \text{Na}_{2}\text{CO}_{3}} \text{DME} / \text{PFMC} \text{R} \cdot \text{Br}$

(c) $\text{R} \cdot \text{Br} + \equiv \equiv \text{R'} \xrightarrow{2\text{CuI} / 5\text{L} / 2\text{BuNH}_{2}} \text{PFDMC} / \text{DMF} \text{R} \cdot \text{Br} \equiv \equiv \text{R'}$

$L = \text{P}(x\cdot \text{C}_{6}H_{4}(\text{CH}_{2})_{n} \text{C}_{8}H_{17})_{3} (x = 3 \text{ or } 4, n = 0 \text{ or } 2)$

Figure 1.3.21 (a) Stille,\textsuperscript{61} (b) Suzuki\textsuperscript{62} and (c) Sonigashira\textsuperscript{63} coupling catalysed by complexes of fluorous analogues of PPh\textsubscript{3} (R = NO\textsubscript{2}, COMe, CO\textsubscript{2}Et or OMe; R' = Pr\textsubscript{i}3, Ph or CME\textsubscript{2}OH.

The same palladium complexes have been successfully employed for the Suzuki coupling (Figure 1.3.21b) of a wide range of aromatic bromides (electron rich and electron poor) with phenylboronic acid.\textsuperscript{62} Using 1.5 mol% of catalyst in PFMCH / 1,2-dimethoxyethane at 75°C >90% conversion was achieved in 2 h. The catalysts were recycled 5 times, in most cases without appreciable loss of activity. At lower catalyst loadings (0.1 mol%) using an electron rich bromide and an electron rich aryl boronic acid, the conversions were high (100%) in the first run, but diminished substantially on recycling, generally to <10% by the third or fourth run.

The Sonigashira couplings (Figure 1.3.21c) were carried out using copper (I) iodide in perfluorodimethylcyclohexane (PFDMCH) / DMF in the presence of BuNH\textsubscript{2} at 100°C over 4 h.\textsuperscript{63} The best results (>98% conversion, recycled twice with little loss of activity) were obtained with electron poor substrates (R in Figure 1.3.21 = NO\textsubscript{2} or CO\textsubscript{2}Me) and Pr\textsubscript{i}3SiC≡CH. For less electron rich substrates and the other alkynes,
yields were between 10 ($R = OMe, R' = CMe_2OH$) and 80% and for the electron poor substrates fell off dramatically on recycling.

Knochel and Betzemeier have described palladium (0) – catalysed cross coupling between arylzinc bromides and aryl iodides as a facile method of forming carbon-carbon bonds and retaining the expensive catalyst for reuse. The perfluorinated phosphine used in this reaction was $P(C_8H_4-4-C_6F_{13})_3$ in a toluene / $C_8F_{17}Br$ solvent system. The Pd catalyst was preferentially soluble in fluorous solvents and reuse of this phase did not cause any significant change in the reaction yield. The presence of the electron-withdrawing perfluoroalkyl groups has a positive effect on the reaction. The activity of the catalyst was in fact higher than with the non-fluorous catalyst ($Pd(PPh_3)_4$]. This is explained by the electron-deficient phosphine favouring reductive elimination in the cross-coupling reaction. This is obviously an important effect, which is likely to be utilised further.

1.3.9 Asymmetric alkylation of aldehydes

$$\text{PhCHO} + \text{Et}_2\text{Zn} \xrightarrow{20 \text{ mol}\% \text{ S-isomer, } \text{Ti(O}^\text{iPr}_4} \text{, perfluoro(methyldecalin) / hexane} \xrightarrow{45 \, ^\circ\text{C}, 1 \text{ hr}} \text{OH}$$

Figure 1.3.22 Asymmetric alkylation of benzaldehyde catalysed by a titanium complex of (S)-$R_f$BINOL.65,66
Tian et al have synthesised perfluoroalkyl-BINOLS and shown them to be active ligands for titanium catalysed asymmetric carbon-carbon bond formation\(^{65,66}\) (the best one for fluorous biphasic reactions is shown in Figure 1.3.22). The reaction was carried out in perfluoro(methyldecalin) / hexane. PhCHO was dissolved in hexane along with the Ti(O\text{\textsuperscript{i}}Pr)\(_4\) and added to a solution of the ligand in perfluorodecalin. The catalyst complex was formed \textit{in situ} when the homogeneous phase was formed at 45\(^\circ\)C and Et\(_2\)Zn was then added. After the reaction, the mixture was cooled to 0\(^\circ\)C to induce phase separation. Although there was no apparent loss of the (S)-R\(_f\)BINOL to the organic phase in repeated cycles, addition of Ti(O\text{\textsuperscript{i}}Pr)\(_4\) was required every cycle. The catalyst containing four C\(_8\)F\(_{17}\) substituents was recycled nine times without substantial loss of yield or drop in e. e. but it should be noted that although the 2\textsuperscript{nd}-9\textsuperscript{th} cycles had yields of 80-70\%, the first cycle has a yield of only 69\%. This may indicate inadequate formation of the catalyst prior to the first cycle.

Generally, this system provided yields of 50-80\% with e. e.’s as high as 58\% and it was observed that the more electron deficient substrate, 4-chlorobenzaldehyde, reacted slightly faster than the electron neutral benzaldehyde. In turn the more electron rich substrate, 4-methoxybenzaldehyde reacted more slowly.

\[
\text{(R)}-{(\text{R}_f)}_3\text{Si} \quad \text{(R)}-{(\text{R}_f)}_3\text{Si} \\
\text{OH} \quad \text{OH} \\
\text{R}_f = -\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13} \\
\text{(R)}-{(\text{R}_f)}_3\text{Si} \quad \text{(R)}-{(\text{R}_f)}_3\text{Si}
\]

\text{Figure 1.3.23} (\text{R})-R\(_f\)BINOL used in the asymmetric alkylation of benzaldehyde.\(^{67}\)

Simultaneously, Takuechi and co workers reported another chiral fluororous BINOL (active in a similar reaction). Their isomer is the (R)-R\(_f\)BINOL\(^{67}\) as shown in
Figure 1.3.23. The ligand was dissolved in FC-72 (a perfluorous solvent containing primarily compounds with 6 carbons) along with Ti(O-iPr)_4. Diethyl zinc in hexane was added to this and the solution was cooled to 0°C before adding a benzaldehyde solution in toluene, thus creating an organic phase consisting of toluene and hexane. Under these conditions, the system is biphasic at all times. The organic phase was removed and quenched, before isolating the product. This system produced a higher enantioselectivity than Chan’s (>80% compared to 58% e. e. respectively) with comparable yields. Repeat cycles using the fluorous phase showed a slight drop in yield and e. e. over 5 recycles. Again the yield obtained in the first run was lower (81%) than those achieved in the subsequent runs (89-87%). Unusually, the ligand loss to the organic phase has also been reported, 0.2 mmol of the ligand was recovered from the organic layer per cycle. From this data, the authors conclude that the asymmetric catalyst is present in the organic phase and that the asymmetric reaction must occur in this phase.

Separating the organic and fluorous layers and performing the reaction in each, showed some catalytic activity in the organic phase, however a lower e. e. was achieved, than the fluorous phase or the biphasic system, suggesting a lower concentration of catalyst present in this phase than the fluorous phase.

Using AlEt₃ in place of Et₂Zn in the reaction shown in Figure 1.3.22, but carried out at 53°C afforded higher e. e. (63% rising to 82% at run 5) and high conversions (59% in the first run, rising to 88% in the third), but it was again confirmed that additional Ti(OPrⁱ)₄ was needed for each run. Higher enantioselectivities were obtained using zinc aminothiolates of the kind shown in Figure 1.3.24 (R₂ = (CH₂)₄, n = 10, e. e. = 94%) The reactions were carried out in
PFMC / hexane at room temperature and the catalysts could be recycled up to 4 times, although the e. e. dropped steadily after the second run to 29% in the fifth run.

\[
\begin{align*}
\text{R} &= \text{Me}, \text{R}_f = \text{C}_6\text{F}_{13} \\
\text{R} &= \text{Me}, \text{R}_f = \text{C}_{10}\text{F}_{21} \\
\text{R} &= \text{(CH}_2\text{)}_4, \text{R}_f = \text{C}_{10}\text{F}_{21}
\end{align*}
\]

**Figure 1.3.24** Alternative catalysts for the asymmetric alkylation of benzaldehyde.\(^{68}\)

High enantioselectivities could be obtained using \(\text{Ti(OPr}^i\text{)}_4\) and a BINOL ligand modified with \(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}\) only in the 6 and 6’ positions in the alkylation of benzaldehyde using 3-tributylstannylpropene (Figure 1.3.24).\(^{69}\) This system did not give good results in either the organic or the fluorous solvent alone, but in the biphasic system (hexane / FC-72, FC-72 mainly contains \(\text{C}_6\) fluorinated hydrocarbons), it gave 85% yield with 90.1% e. e. Very similar results are obtained using a \(\text{C}_8\text{F}_{17}\) chain (yield 83%, e. e. 89.9%), but in a much shorter time (5 h, c. f. 10 h for the ligand shown in Figure 1.3.25). Studies of different aldehyde substrates showed that good yields and e. e.’s are only obtained from electron withdrawing aromatic aldehydes.

\[
\begin{align*}
\text{PhCHO} + \text{SnBu}_3 &\xrightarrow{\text{Ti(OPr}^i\text{)}_4} \text{Ph} \text{OH} \\
\end{align*}
\]

**Figure 1.3.25** Asymmetric alkylation of benzaldehyde catalysed by a fluorinated Ti/BINOL complex under fluorous biphasic catalysis.\(^{69}\)
1.3.10 Miscellaneous catalytic reaction

Another fluorous biphasic system, which showed desirable results, was reported by Biffis and co-workers\textsuperscript{70} who described the preferential silylation of primary alcohols using [Rh\(_2\)(pft)\(_4\)], (pft = perfluorotetradecanoate). Ligands of the lower carbon number were found to leach to the organic (CH\(_2\)Cl\(_2\)) phase during the reaction. The best results were obtained with a DCM / FC-77 (mainly containing C\(_8\) fluorocarbons) solvent system, at room temperature, 1 mol\% catalyst and a 1:1 alcohol to silane ratio for 6 hours. This gave a yield of 68\%, which was not as good as the non-fluorous reaction (96\% yield in 3 h). Catalyst decomposition caused a decrease in yield by the second recycle of the fluorous layer. An interesting property of the system was observed when a range of alcohols was tested and the preference for primary alcohols over secondary and hydrophilic alcohols became apparent.

Endres and Maas have also described the use of rhodium (I) perfluorocarboxylates, see Figure 1.3.26, as active catalysts in the carbenoid reaction of diazoacetate with toluene in a toluene-PFMC solvent system.\textsuperscript{71} Both catalysts are insoluble in toluene. The complex containing the aryl carboxylic acid gave a total yield of 71\% and the other complex a total yield of 78\%. Decomposition of both catalysts was observed. This explains why only partial catalyst recovery could be made.

In a more recent paper,\textsuperscript{72} further perfluorinated chains have been attached to the dirhodium complex, introducing spacer groups. Only the ligand with R\(_f\) = CH\(_2\)C\(_6\)F\(_{13}\) was soluble in PFMC. The spacer group had been introduced to minimise the electronic effect of the electron withdrawing fluorous ponytail on the dirhodium complex, in order that it more resembled its non-fluorous analogue, [Rh\(_2\)(OAc)\(_4\)]. The polar carboxylate groups make these fluorinated catalysts different from others.
reported, which are generally non-polar. These complexes are also soluble in THF and diethyl ether at room temperature, which causes the catalyst to leach to the organic phase during a reaction.

Unfortunately, this study shows the limitations of the fluorous analogue of Rh-catalysed carbene transfer. As the electron-withdrawing effect has to be restricted, two or more methylene spacer groups are required but this in turn makes the catalyst insoluble in fluorous solvents. Clearly fluorous biphasic catalysis does have its limitations.

Figure 1.3.26 Carbene reaction catalysed by rhodium (II) complexes containing fluorinated carboxylates.\textsuperscript{71,72}

1.3.11 Fluorous catalysis without fluorous solvents

Wende and Gladysz have investigated the reaction of a perfluorinated catalyst system in the absence of any fluorous solvent.\textsuperscript{73} This system catalyses the conjugate addition of alcohols to methyl propiolate under homogeneous conditions in \textit{n}-octane at 65°C (Figure 1.3.27).
Chapter 1: Literature Review

The fluorinated phosphine, \{P(C_2H_4C_8F_{17})_3\}, without metal, shows temperature dependent solubility in \(n\)-octane such that it is essentially insoluble at \(-30^\circ\text{C}\) and it is reported that \(>97\%\) phosphine recovery is made every run. Through synthesis of a large number of fluorous ligands, it was observed that the solubilities of these compounds increased with increasing temperature. The process simply relies upon the same concept as ordinary FBS, whereby at room temperature there are two phases, in this case, solid and liquid, at reaction temperature a single homogeneous solution is formed and upon cooling the solid catalyst is again precipitated and can easily undergo a heterogeneous separation. If there is incomplete conversion, unreacted substrate and the organic solvent still have to be removed from the final product.

\[
\begin{align*}
\text{CO}_2\text{Me} + \text{PhCH}_2\text{OH} & \xrightarrow{P((\text{CH}_2)_2(\text{C}_8\text{F}_{17}))_3} \text{PhCH}_2\text{O} \\
& \xrightarrow{\text{CO}_2\text{Me}}
\end{align*}
\]

Figure 1.3.27 Conjugate addition of benzyl alcohol to methyl propiolate catalysed by a fluorous phosphine without a fluorous solvent.

The reaction was carried out by combining the phosphine ligand \{P(C_2H_4C_8F_{17})_3\}, the alcohol and methyl propiolate in \(n\)-octane at room temperature, the authors report no visual dissolution of the phosphine. On heating to \(65^\circ\text{C}\) a homogeneous phase was attained. After 8 hours the sample was cooled to \(-30^\circ\text{C}\) and the phosphine precipitated. The sample was kept at \(-30^\circ\text{C}\) whilst the supernatant liquid was removed. However, it was unclear why the phosphine underwent a colour change during the reaction. Before heating it was a white solid and the authors reported that most samples on cooling precipitated an orange solid, which upon recycling often darkened to red.
For benzylic alcohol (PhCH$_2$OH), a yield of 82% was achieved in the first cycle; this was maintained for three recycles but by the fifth recycle, had dropped to 75%.

Interestingly, by omitting the $n$-octane from the reaction and making this a totally solvent free system, the initial yield rose to 99% and was maintained for two further recycles before dropping to 95% in the fourth run.

By total omission of any solvent, not only is the cost reduced but also the process becomes much more environmentally friendly. There has been some work published by other groups working on a similar principle, these include catalysed condensation of carboxylic acids and amines to amides,$^{74}$ transesterifications$^{75}$ and benzylation of alcohols and esterifications of carboxylic acids.$^{76}$ This is an interesting approach from an economic point of view as there is no unnecessary expense on costly fluorinated solvents. It would appear that a phase change of the catalyst at or above the collection temperature, to provide a much less soluble form of the catalysts could provide even greater advantages. Such systems do not, to the author’s knowledge, appear to have been reported.

Clarke _et al_ $^{77}$ have published their findings for hydroformylation using perfluorinated ligands P(C$_6$H$_3$(CF$_3$)$_2$-3,5)$_3$ (5) and P(C$_6$F$_5$)$_3$ (6) under standard hydroformylation conditions (60 °C 20 bar CO/H$_2$ (1:1)), in an organic solvent (toluene), not fluorous biphasic conditions. It has previously been shown$^{78}$ that arylphosphines, which contain electron-withdrawing groups, show an increase in activity when used in rhodium hydroformylation catalysts. From the Tolman electronic parameters of these phosphines, Clarke _et al_ expected both ligands to demonstrate similar donor properties to phosphite ligands and the cone angle of (5) (184°) is comparable to other bulky phosphites, which may also suggest good
selectivity of this ligand to linear products. (6) showed similar activity and selectivity to PPh$_3$ (94 %, 3.0 n: i, compared to 95 % and 2.9 n: i respectively) for the hydroformylation of hex-1-ene. However, the bulkier (5) showed very poor activity, only 6% conversion and selectivity n: i 0.6.

A coordination study of the bulky phosphine showed that (5) coordinated poorly with late transition elements, and so the low activity may be explained by the incomplete coordination of the ligand to the metal, which causes the low activity. The conclusions made from this paper are that although the electronic and cone angle properties of these fluorinated ligands are very similar to those of phosphite ligands, this is merely a superficial similarity and does not continue to the catalysis using these ligands.

1.3.12 Continuous Processing

Yoshida et al recently reported the development of a continuous flow reaction system using a fluorous biphasic system. They report the acetylation of cyclohexanol and the Baeyer-Villiger reaction of 2-adamatanone using fluorous biphasic conditions (see Figure 1.3.28). The acetylation of cyclohexanol employed a fluorinated catalyst, ytterbium(III) bis(perfluorooctanesulfonyl)amide, PFMC at 40°C. The organic phase was made up of a solution of cyclohexanol in toluene to which was added acetic anhydride. This organic mixture was continuously added to the stirred tank reactor and once part filled with reaction mixture the mixture overflowed to a decanter (25°C) where separation occurred. Once this decanter had filled, the organic phase began to overflow to the product tank whilst the fluorous phase could be recycled to the reactor see Figure 1.3.30. The product was analysed by GC and the
results showed conversion was maintained at >90% over 500 hours (nearly 3 weeks) with less than 2 ppm ytterbium in the organic phase.

\[
\begin{align*}
\text{HO} & + \text{Ac}_2\text{O} \quad \text{[Yb(N(SO}_2\text{C}_8\text{F}_{17})_2]_3} \quad \text{toluene / PFMC} \\
& \rightarrow \text{OAc} \quad \text{HOAc}
\end{align*}
\]

Figure 1.3.28 Acetylation of cyclohexanol carried out continuously under fluorous biphasic conditions for 500 h.\textsuperscript{79}

\[
\begin{align*}
\text{H}_2\text{O}_2 & + \text{Sn(N(SO}_2\text{C}_8\text{F}_{17})_2)} \quad \text{1,2-C}_2\text{H}_4\text{Cl}_2 / \text{PFMC} \\
& \rightarrow \text{H}_2\text{O}
\end{align*}
\]

Figure 1.3.29 Baeyer-Villiger reaction carried out continuously over 200 h under fluorous biphasic conditions.\textsuperscript{79}

In order to see if the reaction system was suitable for water forming reactions the Baeyer-Villiger reaction of 2-adamantanone with 35% aqueous solution of H\textsubscript{2}O\textsubscript{2} was investigated. Using tin(IV) bis(perfluorooctanesulfonfonyl)amide in 1,2-dichloroethane / PFMC a conversion in the region of 50-60% was achieved with a high selectivity. The reaction was run for 200 hours. The success of these reactions indicated the possible future of continuous flow fluorous biphasic systems, however no high pressure or gas substrates were involved in these reactions.
Figure 1.3.30 Schematic diagram of a reactor used continuously for up to 500 h for fluorous biphasic reactions without gaseous reagents.\textsuperscript{79}Yoshida

1.4 Conclusions

Despite the expense of fluorinated ligands and solvents, the ease of catalyst recovery and the wide-ranging possibilities of application make the study of fluorous catalysis an interesting area of research at the current time. It would seem unlikely that any large-scale process involving large quantities of perfluorinated solvent would ever be commercialised until a cheaper source of solvent is discovered, however the use and effectiveness for small-scale synthesis of fine chemicals may benefit from the application of fluorinated processes and may still harbour areas of further development for this branch of chemistry.

In addition to this, it has been shown that a non-pressurised continuous flow reactor has been successfully operated for up to three weeks, with no noticeable loss in activity. This in turn may suggest that the application of FBC to the correct processes may yet yield commercially viable systems.

This literature review demonstrates the wide application of fluorinated catalysts and clearly indicates that despite the expense of these ligands and solvents, the improvement of catalyst recovery makes these processes an attractive alternative to conventional homogeneous processes.
Chapter 1: Literature Review

1.5 Reference List


Chapter 1: Literature Review


Chapter 1: Literature Review


Chapter 2
A Mechanistic Study
2 Hydroformylation: A Mechanistic Study

2.1 Introduction

In the mid-1960s, Wilkinson and co workers discovered that phosphine modified rhodium catalysts gave better selectivities to the desired linear aldehyde product and activities for alkene hydroformylation under lower temperatures and pressures than the common cobalt catalysts. They also produced fewer side-products such as isomerised alkenes, alcohols esters and acetals than are produced with a cobalt catalyst. Subsequently, these rhodium-based systems, usually employing triphenylphosphine as the ligand, have been commercialised for the hydroformylation of short chain alkenes, especially propene. Generally, the industrial process operates with a high concentration of triphenylphosphine, for instance, the Union Carbide process for hydroformylation of propene operates with a [P]: [Rh] ratio of 106: 1. This high loading of phosphine leads to increased selectivity to the linear aldehyde product as the increased amount of PPh₃ leads to more heavily substituted Rh complexes and increases the steric hindrance to the formation of branched products.

Wilkinson and co workers undertook a mechanistic study of the triphenylphosphine modified rhodium-catalysed hydroformylation and published the, now commonly accepted, dissociative mechanism, depicted below.
Figure 2.1.1 The dissociative mechanism for hydroformylation of an alkene by triphenylphosphine modified rhodium catalyst.³

The initial formation of the square-planar rhodium complex, if the starting materials are [Rh(acac)(CO)₂] and PPh₃ will involve a number of steps before the beginning point of this mechanism, as is postulated in this discussion.

The arguments for the dissociative pathway against the associative one include; that the square-planar 16-electron species are somewhat stabilised through solvation and are therefore more stable than the 20-electron species that would be expected to exist were the associative pathway correct.

It should be noted that many of the complexes in this mechanism have never been isolated and that there may be some variation in the configuration of the complexes. It has also been shown that five-coordinate species are likely to exist in fluxional exchange with the possible isomers. This fluxional exchange of five-
coordinate bis phosphine complexes has been explained using the Berry pseudorotation, in which two equatorial ligands exchange with two apical ligands as shown in Figure 2.1.2.

In a complex where all five ligands are equivalent, this exchange of positions between the ligands would show an averaging of the resonance frequencies and a $^{31}$PNMR signal would be observed between the two positions expected for the ea (two doublets of doublets and the ee (doublet) isomers). For these complexes, it is possible that the rapid exchange of positions of the ligands will result in a single broad peak, instead of the signals expected for the two separate isomers and any Rh coupling would be concealed. By cooling down the sample, the exchange should be slowed, allowing observation of the individual orientations of the two phosphine groups if in the ea arrangement, and the ratio of ea: ee, providing sufficiently low temperatures were obtained. The relatively high melting point of the fluorinated solvents and the temperature dependent miscibility of the solvent with deuteriated solvent restricted the lowest temperature to which we could take these samples without losing a lock or freezing the solution and therefore meant that observation of the individual isomers
might be difficult. However, any splitting or further broadening of the signal peaks would be indicative of a fluxional exchange within the solution. Even if the fluxionality cannot be frozen out, it is often possible to calculate the ee: ea ratio from $^2J_{HP}$ on the hydride signal. Assuming that the cis-$^2J_{HP}$ in the ee isomer is ca. $\pm 2\text{Hz}$ and trans-$^2J_{HP}$ is ca. $106\text{ Hz}$; under fast-exchange conditions the effective coupling constant ($J_{av}$) is an average of the 2 species and is dependent upon their concentration in the solution and thus can be expressed as:

$$J_{av} = x_{ee}J_{ee} + x_{ea}J_{ea} = x_{ea}J_{ea} + (1-x_{ea})J_{ee},$$

Where $x_{ea}$ is the mole fraction of the ea isomer. If we assume $J_{ee} = 0$ Hz and $J_{ea} = 106/2 = 53$ Hz, then $x_{ea}$ is calculated by;

$$J_{av} = 53x_{ea}$$

The previous work carried out in this group,\textsuperscript{13,14} had identified the improved rates of reaction achieved with the perfluorinated aryl phosphine when compared to similar reactions with a triphenylphosphine modified rhodium catalyst.

In the triphenylphosphine modified rhodium catalysed hydroformylation, low phosphine concentration results in a low linear to branched ratio (approximately 3:1)\textsuperscript{7}, similar to that of unmodified cobalt reaction and so industrial processes which utilise this catalytic system operate under a very high concentration of phosphine. However, with the perfluorinated triaryl phosphine ligand, high selectivity is achieved (6.3: 1) at relatively low ligand concentrations (Rh: P(C$_6$H$_4$C$_6$F$_{13}$)$_3$ = 1: 10).

In an effort to understand these differences between our ligand and triphenylphosphine, a study of the intermediate complexes present during formation of the catalyst and hydroformylation of octene was undertaken, utilising high-pressure NMR and IR spectroscopic techniques and is discussed here.
2.2 **Ligand Studies**

Attempts were initially made to isolate the \([\text{RhH(CO)}(\text{P} \left( \text{C}_6\text{H}_4\text{F}_{13}\right) \left( \text{C}_6\text{F}_{13}\right)\text{)}_3])\] complex by mixing \([\text{Rh(acac)(CO)}_2]\) with \{\text{P} \left( \text{C}_6\text{H}_4\text{F}_{13}\right) \left( \text{C}_6\text{F}_{13}\right)\text{)}_3\} \) in DCM under argon. However, after stirring together for 1 hour and removing the solvent *in vacuo*, we were left with a very viscous liquid which was clearly unsuitable for using as a catalyst and so catalytic solutions were prepared *in situ* and studied this way. The reason for the expected complex not forming a solid or crystals as might be expected for other ligands is due to the long perfluoroalkyl chains which are very flexible and tend not to favour crystallisation. This is also the reason for the difficulty in obtaining a crystal structure for the ligand itself. However, a small amount of crystallised ligand was formed during ligand synthesis and the resulting crystal structure is shown below, Figure 2.2.1.

![Figure 2.2.1 The \{\text{P} \left( \text{C}_6\text{H}_4\text{F}_{13}\right) \left( \text{C}_6\text{F}_{13}\right)\text{)}_3\} ligand single crystal structure](image)

As expected the three perfluoroalkyl tails are positioned such that they are as far from the other two tails as possible, however it is likely that there will be some movement of the \(-\text{C}_6\text{F}_{13}\) tails within the structure. Two slightly different structures of the ligand were observed in the crystal structure, with the change being a different
angle of the third aryl arm on the phosphine. The P-C bond lengths in both structures have an average of 1.83(6) Å. In the first structure, the average C-P-C bond angle is 102.1(3)° whilst the second structure displays an average C-P-C bond angle of 101.5(3)°. In comparison, the crystal structure of triphenylphosphine also shows a P-C bond length of 1.83(48) Å and an average C-P-C angle of 103.0(21)°. It is clear from this data that the structure of our ligand is very similar to that of triphenylphosphine and the effect of the electron withdrawing ponytails causes only a very small difference in the C-P-C bond angles, which in turn indicates that the lone pair on phosphorus is pulled slightly closer to the phosphorus atom in the fluorinated ligand.

\[ P((C_6H_4C_6F_{13})_3) \]

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>( C_{36}H_{12}F_{39}P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula Weight</td>
<td>1216.43</td>
</tr>
<tr>
<td>Unit cell Dimensions</td>
<td>( a = 10.887(5) ) Å, ( \alpha = 74.827 (15) )°</td>
</tr>
<tr>
<td></td>
<td>( b = 16.296(6) ) Å, ( \beta = 89.87 (2) )°</td>
</tr>
<tr>
<td></td>
<td>( c = 24.001(11) ) Å, ( \gamma = 80.41 (2) )°</td>
</tr>
</tbody>
</table>

Table 1.3.12.1 P((C_6H_4C_6F_{13})_3) crystal data

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>( PPh_3 )</th>
<th>( P((C_6H_4C_6F_{13})_3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C</td>
<td>1.83 (48)</td>
<td>1.83(6)</td>
</tr>
<tr>
<td>C-P-C</td>
<td>103.0(21)</td>
<td>101.5(3) and 102.1 (3)</td>
</tr>
</tbody>
</table>

Table 1.3.12.2 Comparison of triphenyl phosphine crystal structure with perfluorinated analogue.
The long-range order of the crystal structure is shown in Figure 2.2.2, the aryl arm that appears to be a “fourth” aryl arm on the central phosphine atom is in fact from the molecule stacked below the top molecule. Two arms appear to align lengthways and molecules stack above each other with these arms aligned, but the third arm which appears almost perpendicular to the length of the molecule is stacked on alternate sides and the perfluorinated alkyl group of this arm either sticks in or out of the plane of the rest of the molecule. Generally the long range ordering is quite good, with only the end of the arm C34, C35 and C36 showing some disorder.

The full crystal structural data can be seen in Appendix 1.
2.3 Initial NMR investigation in low pressure tube

Initial investigations of the species formed when a mixture of \([\text{Rh}(\text{acac})(\text{CO})_2]\) and \(\{\text{P}(\text{C}_6\text{H}_4\text{C}_6\text{F}_{13})_3\}\) was dissolved in perfluoro(methylcyclohexane) (PFMC) were carried out under atmospheric pressures of argon in a normal NMR tube. These initial studies looked at a 3:1 P: Rh ratio dissolved in PFMC. NMR spectra were recorded in the normal fashion using a benzene-\(d_6\) capillary within the NMR tube as a deuterium lock. \(^{31}\text{P}\ (\text{C}_6\text{D}_6)\) resonances were observed at \(\delta: 27.1, 22.8, 1.6 \text{ ppm, NMR} 1.3.12.1\), with the major peak being that at 1.6 ppm, which we know is not the expected position of the free ligand (-6 ppm). The proximity to the position of the free ligand coupled with the fact that this singlet was quite broad, suggested that we were seeing the fluxional exchange of the free ligand with a complexed ligand. The other two peaks were of a much smaller intensity, but one appeared to be the phosphine oxide (22.8 ppm). After bubbling CO / \(\text{H}_2\) through the solution for 5 minutes, and replacing the evaporated PFMC, the only discernable change to the \(^{31}\text{P}\) NMR spectrum was the slight shift upfield of the large broad singlet to 2.2 ppm along with the appearance of a very small peak at 40.5 ppm (s). In high-pressure NMR, discussed later, a doublet was observed around 40 ppm and was assigned to either the tris or bis-phosphine Rh complex.
Repeating this experiment under exactly the same conditions, but with improved mixing of the initial solution, gave the same results: a large, broad singlet at 1.6 ppm, with two much lower intensity signals observed at 22.8 (phosphine oxide) and 27.1 (unknown) ppm. However, after bubbling CO/H₂ through this solution, although the broad singlet was shifted to 4.8 ppm, there was no signal observed at 40 ppm and the oxide signal had increased in intensity.

The free ligand was dissolved in PFMC and using a benzene-d₆ capillary an NMR spectrum was recorded which showed a single peak at –5 ppm, NMR 1.3.12.2 and a small peak at 21 ppm from the phosphine oxide. After leaving the NMR tube open to air for 1 hour, the spectrum was recorded again and no change was observed. However, in later studies it was observed that solutions of [Rh(acac)(CO)₂] and the ligand would oxidise over time. The oxide was also observed during continuous flow reactions as a solid in the separator. It was therefore necessary to ensure complete
removal of oxygen from all solvents and substrates used in further reactions and studies.

Due to the apparent fluxional exchange occurring within the room temperature solutions containing rhodium complexes and excess \( \{P(C_6H_4C_6F_{13})_3\} \), we prepared a third solution and an acetone-\(d_6\) capillary (lower m.p.) and carried out a low temperature NMR spectrum of the solution, NMR 1.3.12.3. However, the relatively high m.p. of PFMC, -37°C, restricted us to only slightly below 0°C for this spectrum. At room temperature we observed a broad singlet at 5 ppm, and two smaller signals at 21.5 (oxide) and 25.8 ppm. When cooled to -21.5°C the large singlet had reduced in intensity and broadened, but was still at 5 ppm, the other two peaks had shifted slightly up field to 22.9 and 27.1 ppm.
In an attempt to prevent any fluxional exchange of ligand, the ratio of P: Rh was reduced from 3:1 to 1:1 and 2:1. The solutions were prepared in a similar way and the proton spectra were recorded, with particular care taken to observe any metal-hydride resonances.

Under argon and at room temperature, the 1:1 Rh: P solution showed a single peak in the $^{31}$P NMR at 30.4 ppm, this shifted slightly after bubbling CO / H$_2$ through the solution to 31.1 ppm, and again the phosphine oxide was observed at 22 ppm.

When the 1:2 Rh: P solution was examined under argon at room temperature, a broad fluxional signal was observed, this time at 7.8 ppm. Bubbling CO / H$_2$ through the solution caused this peak to shift to 8.6 ppm and no oxide was observed.

In each of the three cases discussed above, the same initial phosphine complex was being formed, and only the excess phosphine in solution was affecting the position of the fluxional signal that we observed in each case. From the shift of this peak in each spectrum after bubbling CO / H$_2$ through the solutions it was also
apparent that this species, $[\text{Rh(acac})(\text{CO})\text{P}]$, was reacting with $\text{CO} / \text{H}_2$ to give $[\text{RhH(\text{CO})}_n\text{P}_{4-n}]$. By changing the concentration of CO in solution, we were shifting the equilibrium of fluxional exchange slightly more towards the complex species and thus the average position of the fluxional signal shifted slightly up field.

By this argument, we might expect the 1:1 Rh: P ratio solution to show some Rh-P coupling as it was most likely to have all the phosphine react with the rhodium precursor. However, a broad signal was still observed suggesting that the Rh-P bond was labile.

It was apparent from the initial NMR studies that at low pressure and ambient temperature, the catalyst solution showed a fluxional exchange between the free ligand and a Rh complex. Further investigations were required by NMR and IR spectroscopy to understand this solution further.

### 2.4 High Pressure Spectroscopic Study with Rhodium: Phosphorus ratio = 1:1

The HPIR spectra were studied under the same concentrations as were used in the continuous hydroformylation reactions ($[\text{Rh}] = 2 \ \text{mmol dm}^{-3}$), however the nature of the HPNMR cell meant that this concentration was too low for conclusive results and so the HPNMR spectra were studied at five times the concentration of the continuous flow reactions ($[\text{Rh}] = 10 \ \text{mmol dm}^{-3}$).

The HPIR spectra were carried out in $n$-hexane solutions because PFMC showed a number of absorbances in the carbonyl region of the spectrum. The HPNMR spectra were collected in PFDMC with hexane-$d_{14}$ or in toluene-$d_8$. The PFDMC / hexane-$d_{14}$ spectra will be focussed on for the fluorinated ligand as a separate fluorous phase formed in the toluene solution after heating the solution. This
sank to the bottom of the cell and reduced the accuracy of the already poor results. Triphenylphosphine HPNMR studies were all carried out in toluene-d$_8$.

### 2.4.1 Rh: P = 1: 1 - HPIR

The spectra for the catalyst solution at room temperature under argon (1 bar) were the same for all ratios of Rh: P, HPIR 2.4.1.1(a), except that the intensity of the bands which corresponded to the [Rh(acac)(CO)$_2$] complex decreased in intensity as the [P] was increased. Three bands were observed at 2082.5 (m), 2014.7 (m) and 1994.9 (s) cm$^{-1}$. The peaks at 2082.5 and 2014.7 cm$^{-1}$ were the terminal carbonyl stretches from [Rh(acac)(CO)$_2$] and were also seen in the equivalent spectrum for triphenylphosphine, PPh$_3$, which also showed three peaks, the third was at 1986.5 cm$^{-1}$, HPIR 2.4.1.2(b). The third peak in both spectra is assigned to the carbonyl stretch of a square-planar monophosphine substituted Rh complex as shown below (Figure 2.4.1).
HPIR 2.4.1.1 Spectra of Rh: P(\text{C}_8\text{H}_8\text{C}_6\text{F}_{13})_3 (1: 1): a) RT 1 bar N\textsubscript{2}, b) RT 15 bar CO/ H\textsubscript{2}, c) 70°C 15 bar CO/ H\textsubscript{2} after 2 hours
Due to the large electron withdrawing effect of the fluorous ponytail on the fluorinated ligand, the carbonyl stretch of any complex when compared to that of triphenylphosphine was shifted to a higher frequency. This was explained by the reduced back-bonding of the metal to the carbonyl caused by the increased back-bonding from the metal to the ligand because of the high electronegativity of the fluorine atoms on the ligand.

When the cell was pressurised with CO / H\textsubscript{2} (15 bar), the room temperature spectrum showed a shift in equilibrium back towards [Rh(acac)(CO)\textsubscript{2}]; the three original peaks were observed but the intensity of the [Rh(acac)(CO)\textsubscript{2}] peaks had increased and the mono-phosphine complex reduced. There was also a small peak observed growing in the PRf\textsubscript{3} spectrum at 2066 (w) cm\textsuperscript{-1}, it was difficult to assign this peak, due to its very low absorbance, but it may possibly have been due to a mono-phosphine substituted trigonal bipyramidal complex. The triphenylphosphine spectrum at room temperature under CO / H\textsubscript{2} showed the same shift back towards the [Rh(acac)(CO)\textsubscript{2}] complex and four new signals were observed, also with very low intensity. These were at v: 2066 (w), 2055.3 (w), 2029.7 (w) and 1995.9 (m sh) cm\textsuperscript{-1}. 

Figure 2.4.1 Rhodium mono-phosphine square-planar complex
When the solutions were heated to 70°C a number of new signals were observed in both spectra and some of these new stretches appeared in the bridging carbonyl region of the spectrum 1750-1850 cm\(^{-1}\), for both ligands. This suggested the formation of bimetallic complexes, which would be expected with the low ligand concentration of these solutions. High concentrations of rhodium and low pressures
of hydrogen and CO are conducive to formation of dirhodium species. The spectrum of the perfluorous ligand with [Rh(acac)(CO)$_2$] under CO / H$_2$ at 70°C showed the formation of a number of new carbonyl stretches in both the terminal and bridging regions of the IR spectrum: 2100.9 (w), 2090.8 (m), 2074.4 (s), 2068.9 (w), 2061.1 (w), 2042.8 (sh), 2037.8 (m), 2026.4 (m), 2014.4 (w), 1910.4 (w), 1886.2 (m), 1877.5 (m), 1855.9 (m), 1820.6 (m) and 1718.2 (m) cm$^{-1}$. A number of these bands could be assigned to the Rh cluster complexes, [Rh$_4$(CO)$_{12}$] ($v$: 2075, 2070, 2062, 2044 and 1856 cm$^{-1}$, in petrol solution)$^9$ and [Rh$_6$(CO)$_{16}$] ($v$: 2070, 2060, 2044 and 1811 cm$^{-1}$, in CCl$_4$ solution)$^9$. A number of the bands appear to match with the literature values for [Rh$_4$(CO)$_{12}$], but nine bands remain unassigned. These are quite possibly due to another cluster or clusters, which remain unidentified.

Another band was observed in both spectra at 2338.3 (m) cm$^{-1}$, which was consistent with carbon dioxide, CO$_2$.

The HPIR spectrum of the equivalent triphenylphosphine solution was recorded at 70°C and showed a number of new peaks in both the terminal and bridging carbonyl regions; 2085 (m), 2073 (w), 2054 (s), 2030 (m), 2021 (m), 2010 (sh), 1905 (w), 1875 (m) and 1856 (m) cm$^{-1}$. These data were inconsistent with Wilkinson’s published data for [Rh(CO)$_2$(PPh$_3$)$_2$]$^{12}$. The band at 2073 cm$^{-1}$ was much weaker in this spectrum, HPIR 2.4.1.2(c), compared to the previous spectrum for the perfluorinated ligand, HPIR 2.4.1.1(c). This band may suggest that some [Rh$_4$(CO)$_{12}$] was present in the triphenylphosphine solution. The bands at 1875 and 1856 cm$^{-1}$ may be due to bridging carbonyls, but these are normally observed between 1750-1850 cm$^{-1}$. If this were the case they would further support the theory of rhodium complexes containing more than one metal centre. Unfortunately, no data were found to match with these bands. When the solution was cooled to room
temperature, the only change observed in the spectrum was a small change in the
intensity of absorbance of some of the signals, but we can conclude from this that the
species formed at high temperature have not disappeared once the solution was
cooled, and were not temperature dependent, HPIR 2.4.1.3. We assumed that the
perfluorinated triphenylphosphine complexes would also persist on cooling of the
system, and could therefore compare the HPNMR spectra, which had been heated and
cooled with the high temperature HPIR spectrum.

![Graph showing spectral data]

**HPIR 2.4.1.3 Rh: PPh₃ (1: 1) 15 bar CO / H₂ : RED = 70°C , GREEN = Cooled overnight to RT**

### 2.4.2 HP-NMR results for Rh: P = 1: 1

The high-pressure NMR results at the same Rh: P ratio also showed interesting
results when examined under the same conditions. The 1: 1 Rh: P solution was
examined in both toluene-d₈ and PFDMC / hexane-d₁₄ solvents. The $^{31}$P NMR of
PPh₃ and P(C₆H₄C₆F₁₃)₃ in solution showed singlets at –5 and –6.3 ppm respectively,
with O=PPh₃ and O=P(C₆H₄C₆F₁₃)₃ observed at 29 and 21 ppm respectively. The HP-
NMR for the solution under argon was only observed for the toluene-d₈ solution, see
NMR 2.4.2.1. However, both solutions were homogeneous at this stage so it was
appropriate to assume that similar species exist in both solvent systems. In the
toluene-d₈ spectrum recorded at room temperature under argon (1 bar), the $^{31}$P NMR
Chapter 2: A Mechanistic Study

The proton spectrum showed a doublet at 56 ppm with $^1J_{\text{Rh-P}} = 182.3$ Hz. No metal hydride was observed in the proton spectrum. The peak observed in the IR spectrum under these conditions at 1994.9 cm$^{-1}$ was assumed to come from this complex which we have already indicated to be the square planar complex [Rh(acac)(CO)(P(C$_6$H$_4$C$_6$F$_{13}$)$_3$)] as shown in Figure 2.4.1., similar species have been shown to exist in the literature with, for example, other phosphine ligands$^{18}$, phosphanes$^{19}$ and phosphites$^{15}$. The displacement of the single carbonyl group was not completely reversed by pressurising the cell with CO / H$_2$. In both solvent systems, a broad singlet was observed at 50 ppm, which suggested that there was some exchange occurring between the phosphine ligand and a carbonyl. The broadening of the peak and shift to lower frequency suggest some fluxional exchange between the free ligand and carbonyl as there was no excess phosphine in the solution.

NMR 2.4.2.1 Rh: P(C$_6$H$_4$C$_6$F$_{13}$)$_3$ (1: 1) (a) RT 1 bar Ar, (b) RT 20 bar CO / H$_2$

By heating the solutions to 70$^\circ$C, we observed formation of new species in the IR spectra and this was confirmed by the disappearance of the original peak and the appearance of new signals in the HP NMR spectrum see NMR 2.4.2.2. The results for
both solvents were similar. As these new complexes formed, it appears that they were insoluble in the toluene which caused the sensitivity of the spectra to become much poorer for the toluene solution, therefore only the PFDMC / hexane-d$_{14}$ solution is considered for the rest of this discussion.

The new signals were observed at 36 (d, $J=144.3$ Hz), 26.1, 22.1 and 19.3 ppm. These new species were also observed in the proton spectrum, with three metal hydride species observed at 70°C: -10.2, -11.1 and -16.8 ppm. When the solution was cooled to room temperature (22°C), the intensity of some of the signals in the $^{31}$P spectra increased, namely 23.3, 22.0 and 20.0 ppm. The doublet at 36 ppm was observed although its intensity had decreased significantly more than the other three signals and could have been mistaken for noise. The $^1$H spectrum showed four hydride signals. These four peaks do not necessarily indicate four species, but perhaps a rhodium dimer with different coordination around each metal. The solution was cooled to -20°C and the $^{31}$P NMR spectrum indicated peaks at 29.9 (triplet possibly), 23.5, 22.2 and a smaller shoulder at 21 ppm. The $^1$H spectrum was
unchanged, with the four metal-hydride signals observed with very little movement, which may have been expected with the change in temperature.

NMR 2.4.2.3 HP-NMR spectra Rh: \( P(C_6H_4(C_6F_{13}))_3 \) (1: 1) (i) cooled to RT, (ii) cooled to -20 °C, (iii) \(^1\)H NMR Cooled to RT
Chapter 2: A Mechanistic Study

The low Rh: P ratio used in this study, would not be used in a hydroformylation reaction. However, the study was useful in that it identified the square-planar complex [Rh(acac)(CO)(P(C₆H₄C₆F₁₃)₃)]. In the HPIR a broad carbonyl band was observed at 1994 cm⁻¹ and the HPNMR showed a doublet at 56 ppm (J_{RhP} = 182.3Hz) under the same conditions, which has also been assigned to this complex. In further studies discussed later in this chapter, the excess phosphine in solution make the identification of this species more difficult as it appears to exist in fluxional exchange with the free ligand.

Due to the low concentration of phosphine in this study, upon heating, it was not surprising to observe the formation of bimetallic complexes, indicated by the bridging carbonyl signals in the HPIR spectra.

2.5 Rhodium: P(C₆H₄-4-C₆F₁₃)₃ Ratio = 1: 5 Spectroscopic Investigation

The Rh: P ratio was reduced from 1: 10 in the original batch reactions to 1: 5 in the continuous flow reactions in an attempt to reduce the excess volume of the expensive perfluoro-phosphine ligand. This spectroscopic study investigated both ratios. Initially we shall discuss the complexation of Rh species with the phosphine ligand in 1: 5 ratio. A large amount of literature has already been published on spectroscopic studies of the rhodium - triphenylphosphine system, generally beginning with the isolated complexes, [RhH(CO)(PPh₃)₃] or [RhCl(PPh₃)₃].²⁻⁶,¹¹,¹²,¹⁷,²⁵ Below we use these studies as a comparison to our own data. Van Leeuwen and Moser have both published HPIR results for complexes formed in situ, the
conditions for the spectra that we report here, are not exactly the same as either group. However, comparison has been made in particular to these papers.\(^{10,16}\)

The triphenylphosphine solutions were made using standard Schlenk techniques, dissolving the two solids, triphenylphosphine and \([\text{Rh(acac})(\text{CO})_2]\), together in \(n\)-hexanes with slight heating if needed. However, it should be noted that Wilkinson and co-workers\(^{12}\) have reported \([\text{RhH(CO)}(\text{PPh}_3)_3]\) to be insoluble in hexane and only sparingly soluble in cyclohexane, but the carbonylation products, presumably \([\text{RhH(CO)}_2(\text{PPh}_3)_2]\) and possibly even \([\text{RhH(CO)}_3(\text{PPh}_3)]\), are soluble, but this insolubility must be taken into consideration as solid may be precipitating during the collection of spectra for these solutions.

### 2.5.1 Infrared Spectroscopy Results

In order to clearly understand the data that we obtained from the HPIR spectroscopy, we initially studied the equivalent spectra for triphenylphosphine. This allowed us to make a direct comparison to the literature data for the expected complexes of Rh-triphenylphosphine species and allowed us a better understanding of the spectra obtained with the perfluorinated ligand.

The reaction between \([\text{Rh(acac})(\text{CO})_2]\) and triphenylphosphine has been extensively studied and it is known that under hydroformylation conditions complexes of the form \([\text{RhH(CO)}_n(\text{PPh}_3)_{4-n}]\) (\(n = 0-3\)) are formed. Work by van Leeuwen and co-workers\(^{10}\) which studied the solution of \([\text{Rh(acac})(\text{CO})_2]\) and \(\text{PPh}_3\) (1: 5) in 2-methyltetrahydrofuran at 80\(^{\circ}\)C and 10 bar \(\text{CO}/\text{H}_2\) (1: 1) described a spectrum containing four bands at \(\nu:\) 2042 (m), 1992 (s), 1981 (s), 1947 (s) cm\(^{-1}\). Van Leeuwen assigned these bands to the two bis-phosphine isomers \([\text{RhH(CO)}_2(\text{PPh}_3)_2]\), which can exist either with the two phosphine groups in the equatorial-equatorial (ee) positions or the equatorial-axial (ea) positions. Two carbonyl stretches are expected
for each of the two isomers. Van Leeuwen paired the bands at 2042 and 1981 cm$^{-1}$ and assigned them to the isomer with both triphenylphosphine groups in the equatorial position (ee), leaving the two peaks at 1992 and 1947 cm$^{-1}$ to be assigned to the bis-phosphine complex which has one triphenylphosphine group *trans* to the hydride (ea). It is assumed that these identifications were made by means of a deuterium study and so the pairs of bands were assigned according to which bands “moved” when the synthesis gas was replaced with a mixture of CO / D$_2$. This occurs because of Fermi resonance between $v_{\text{RhH}}$ and $v_{\text{CO}}$ if the hydride ligand is trans to CO and because of the increased mass of a deuterium atom compared to a hydrogen atom, which in turn affects the vibrational frequency of this bond. Deuterium, the heavier atom vibrates at a lower frequency, and so by deuteriating a complex with a carbonyl group *trans* to a hydride the IR spectrum will show a new band at a lower frequency than the original carbonyl band. Carbonyl groups *cis* to the hydride will be unaffected by this change in atom, which allows a clear identification of complexes with carbonyls *cis* and *trans* to the hydride.

The HPIR spectra for [Rh(acac)(CO)$_2$] and PPh$_3$ (1: 5 ratio) in $n$-hexane under CO / H$_2$ (15 bar) at 70$^\circ$C were initially collected in a series format over 2 hours and are shown in HPIR 2.5.1.1. Several bands were observed forming at 2080 (w), 2044 (m), 2024 (m), 1997 (s), 1988 (s), 1974 (s), 1956 (s) cm$^{-1}$. The small band observed at 2080 cm$^{-1}$ was from some [Rh(acac)(CO)$_2$] in the solution, with the second band obscured by the other stronger peaks of the more abundant species.
The HPIR single spectrum of a solution of PPh₃ and [Rh(acac)(CO)]₂ (5: 1) in n-hexane, under a CO / H₂ atmosphere (15 bar) and room temperature showed a single band at 1986 cm⁻¹ which has been assigned to the square-planar, mono-phosphine complex [Rh(acac)(CO)(PPh₃)]. After the solution was heated to 70°C, the spectrum showed six bands in the terminal carbonyl region of the IR spectrum; \( \nu \): 2044.3 (m), 2024.2 (m), 1996.9 (s), 1987.4 (s), 1973.8 (sh), 1955.8 (s) cm⁻¹, HPIR 2.5.1.2 (red). The cell was purged and re-pressurised with CO / D₂ (20 bar) HPIR 2.5.1.2 (purple line), to allow identification of the separate bis-phosphine isomers. This data is summarised in Table 2.5.1.1.
Chapter 2: A Mechanistic Study

<table>
<thead>
<tr>
<th>Spectrum Conditions</th>
<th>IR data (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar N$_2$ RT</td>
<td>1986 (s)</td>
</tr>
<tr>
<td>15 bar CO / H$_2$ RT</td>
<td>2083 (vw), 2014 (vw), 1986 (s)</td>
</tr>
<tr>
<td>15 bar CO / H$_2$ 70$^\circ$C</td>
<td>2080 (w), 2044.5 (m), 2024 (m), 1996.8 (s), 1987.5 (s), 1974 (m), 1955.9 (s), 1714 (w)</td>
</tr>
<tr>
<td>20 bar CO / D$_2$ 70$^\circ$C</td>
<td>2071 (w), 2056.5 (w), 2024 (s), 1997 (s), 1972.4 (s), 1955.1 (m), 1714 (w)</td>
</tr>
</tbody>
</table>

Table 2.5.1.1 Rh: PPh$_3$ (1: 5) HPIR spectra results.

The bands at 2025 (m), 1997 (s), 1973 (s) and 1956 (m) were unchanged under the CO / D$_2$ atmosphere and, by comparison to van Leeuwen’s results, we assigned the bands at 1997 and 1956 cm$^{-1}$ to the ea isomer while the peaks at 2044 and 1987 cm$^{-1}$ did move and were assigned to the ee isomer. From the spectrum, HPIR 2.5.1.2, it was clear that these bands had moved but less obvious where their equivalent D$_2$ species’ bands occurred. However, a comparison to Wilkinson’s data$^{12}$ suggested that the deuteriated bis-phosphine species has bands at 2025 and 1970 cm$^{-1}$, and in our own case at 2024 and 1973 cm$^{-1}$. Unfortunately, these bands fell in the same place as two bands in the CO / H$_2$ spectrum, which gave the appearance of static peaks with the change in gas. It is possible that the band observed at 2056 cm$^{-1}$ in the CO / D$_2$ spectrum was hidden by the original band at 2044 cm$^{-1}$. The presence of six bands in the terminal carbonyl region of the 70$^\circ$C CO / H$_2$ spectrum, when the literature reported only four bands for the two bis-phosphine isomers, would possibly imply the formation of the tris-triphenylphosphine rhodium complex, resulting in the two apparently static bands at 2025 and 1973 cm$^{-1}$. However the published data for this species$^{2,12}$ in cyclohexane quotes two bands arising at 2005 ($v_{RhH}$) and 1935 ($v_{CO}$) cm$^{-1}$ and when deuteriated these bands shift, with the metal-hydride band moving to a much lower frequency so that only one band was observed in the terminal carbonyl region for [RhD(CO)(PPh$_3$)$_3$] at 1960 cm$^{-1}$ in DCM solution, which did not occur in our study and we therefore ruled-out the tris-triphenylphosphine complex.
Alternatively, these two bands were due to some other species that coincidentally match with the bands of the deuteriated bis-phosphine species and because these bands did not move upon the addition of deuterium, it is possible that they arose from complexes that did not contain hydrides or carbonyls trans- to any hydride.

From this study, the assignment of bands arising from the individual isomers of the [RhH(CO)$_2$(PPh$_3$)$_2$] can be made and is summarised in Table 2.5.1.2.

<table>
<thead>
<tr>
<th>Species</th>
<th>[Rh(acac)(CO)(PPh$_3$)]</th>
<th>[RhH(CO)$_2$(PPh$_3$)$_2$] (ee)</th>
<th>[RhH(CO)$_2$(PPh$_3$)$_2$] (ea)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPIR bands (cm$^{-1}$)$^a$</td>
<td>1986 (s)</td>
<td>2044 (m), 1987 (s)</td>
<td>1997 (s), 1956 (s)</td>
</tr>
</tbody>
</table>

* solvent was n-hexanes

Table 2.5.1.2 Summary of HPIR band assignments for Rh: PPh$_3$ (1: 5).

We next applied this strategy to examination of the perfluorinated ligand, under similar conditions in the HPIR cell.

As reported earlier, in section 2.4.1, the room temperature [Rh(acac)(CO)$_2$] / (P(C$_6$H$_4$C$_6$F$_{13}$)$_3$) hexane solution spectrum recorded under argon showed a single peak at 1994.5 cm$^{-1}$, the equivalent PPh$_3$ spectrum showed a band at 1986 cm$^{-1}$. In both cases, this was assigned to the square-planar Rh complex with one carbonyl substituted by a phosphine ligand as shown previously in Figure 2.4.1. On pressurising the cell with 15 bar CO / H$_2$, two new bands appeared at 2084 and 2014 cm$^{-1}$ and the original band decreased slightly in intensity. These new bands were the two carbonyl stretches of [Rh(acac)(CO)$_2$], confirmed by a spectrum of [Rh(acac)(CO)$_2$] in n-hexane. This indicated that the monophosphine complex and the Rh precursor existed in equilibrium and the HP-NMR confirmed this, showing a broad singlet (5.3 ppm) near the free phosphine position (-6.3 ppm) under similar conditions, which denoted fluxional behaviour of the phosphine. With the PPh$_3$ solution, the addition of CO / H$_2$ caused very weak signals of the [Rh(acac)(CO)$_2$]
carbonyls to appear. This was possibly due to the low solubility of the PPh$_3$ complexes in hexane.

When the temperature was increased to 70°C, a series of spectra was collected over 1.5 hours, recording a spectrum every 90 seconds, HPIR 2.5.1.3, to observe any new species as they were formed. The first spectrum in the series was very similar to that collected at RT under CO / H$_2$, but the [Rh(acac)(CO)$_2$] bands, 2084 and 2014 cm$^{-1}$, quickly disappeared and new bands were observed growing in over the first few minutes. After 2 hours, the spectrum collected showed none of the original bands. Six new bands were observed in the terminal carbonyl region of the [Rh(acac)(CO)$_2$] / P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$ spectrum at ν: 2073 (w), 2059 (m), 2037 (m), 2004 (s), 1993 (s) and 1972 (m) cm$^{-1}$. The series showed these bands growing in and most of the new bands were observed after only 6 minutes at temperature. Over time, the bands grew in intensity and the original band at 1996 cm$^{-1}$ decreased. A summary of this data can be seen in Table 2.5.1.3.
When this reaction was repeated and only single spectra were recorded, under a CO / H₂ atmosphere (20 bar) at 70°C the bands observed in the Rh: P(C₆H₄-C₆F₁₃)₃ (1: 5) solution were; v: 2056.4 (m), 2036.9 (m), 2004.0 (s), 1994.1 (sh), 1971.4 (m) and 1935.9 (w) cm⁻¹, as shown in HPIR 2.5.1.4.

This solution was cooled to room temperature and vented to atmospheric pressure and then re-pressurised with CO / D₂ (20 bar) and reheated to 70°C. The resulting HPIR spectrum, HPIR 2.5.1.5, showed bands in the terminal carbonyl region at the following positions; v: 2062.6 (w), 2038.7 (s), 2009.0 (m sh), 1992.3 (s), 1971.9 (m).
These bands corresponded to the bands observed in a second solution of [Rh(acac)(CO)]_2 / P(C_6H_4-4-C_6F_13)_3 (1: 5) which was only pressurised with CO / D_2 and heated to 70°C, although some of the intensities and resolutions of the bands differed slightly; \( \nu \): 2076 (w), 2062.9 (w), 2038.7 (s), 2011.2 (m), 1992.3 (s) and 1972.5 (w).

Interestingly, we found upon pressurising the cell with D_2 that only two bands shifted from 2060 cm\(^{-1}\) to presumably 2025 (sh) cm\(^{-1}\) and 2004 to 1985 (sh) cm\(^{-1}\). But the deuteriated spectrum contained eight bands in the terminal carbonyl region, \( \nu \): 2075 (s), 2062 (m), 2036 (s), 2025 (sh), 2010 (m), 1992 (s), 1985 (sh), 1969.3 cm\(^{-1}\) and a new band at lower frequency, 1869 (m) cm\(^{-1}\). From the comparison to the PPh_3 spectra we assigned the bands as follows; 2060 (m) and 2004 (s) cm\(^{-1}\) from the CO / H_2 spectrum shift to 2036 and 1992 (sh) cm\(^{-1}\) under a CO / D_2 atmosphere and were due to the ee-\textit{bis}-phosphine isomer. This meant that the ea isomer had bands at 2037 and 1992 cm\(^{-1}\) under a CO / H_2 or a CO / D_2 atmosphere. The band observed at 1972 cm\(^{-1}\) in the CO / H_2 spectrum and which decreased in intensity when the solution was deuteriated is possibly the \( \nu_{\text{RaaH}} \) signal which van Leeuwen also observed in his study.
Chapter 2: A Mechanistic Study

of the bulky phosphite ligand. Although this band would be expected to shift to a considerably lower frequency upon deuteriation, it is possible that some H₂ was left in the solution upon venting and resulted in a small amount of the hydride being observed when only the deuteride complex would be expected. We hoped that an HP-NMR investigation of similar solutions under the same conditions might yield further explanation of this data. The small band observed at 2084 cm⁻¹ under CO / H₂ atmosphere, appeared to be some residual [Rh(acac)(CO)₂], with the second band obscured by the stronger carbonyl bands. This band did not appear in the deuteriated spectrum, which suggested that all the [Rh(acac)(CO)₂] had reacted by this stage.

Under the deuteriated atmosphere, three bands appeared, which have not been accounted for, at 2075, 2010 and 1969 cm⁻¹. The band at 1969 cm⁻¹ may be a carbonyl band from [RhD(CO)(P(C₆H₄C₆F₁₃))₃], the tris-phosphine complex, this would also explain the observed band at 1936 cm⁻¹ in HPIR 2.5.1.4. Wilkinson and co-workers reported the IR spectrum of [RhD(CO)(PPh₃)₃] as 1960 cm⁻¹ compared to the spectrum for [RhH(CO)(PPh₃)₃], 2000 (s) and 1920 cm⁻¹. We were unable to assign the bands at 2075 and 2011 cm⁻¹.

<table>
<thead>
<tr>
<th>HPIR bands (cm⁻¹)</th>
<th>[Rh(acac)(CO)₂]</th>
<th>[RhH(CO)₂]</th>
<th>[RhH(CO)]</th>
<th>[RhD(CO)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2037, 1992 (ea)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5.1.4 Summary of HPIR band assignments for Rh: P(C₆H₄C₆F₁₃)₃ (1: 5). solvent was n-hexanes.

After analysis, the contents of the HPIR cell were collected and stored under air in glass vials. From a study of [Rh(acac)(CO)₂] and P(C₆H₄-4-C₆F₁₃)₃ (1: 5), after a few days, small orange, rectangular crystals were observed. These were sent for analysis and it was shown that the crystals were a rhodium dimer, which demonstrated some decomposition of the P(C₆H₄-4-C₆F₁₃)₃. Figure 2.5.1 shows that instead of two
bridging carbonyl groups, as might have been expected, we instead had one bridging hydrogen and a bridging \( \{P(C_6H_4-4-C_6F_{13})_2\} \) group, which indicated that a P-C bond has been broken and a \(-(C_6H_4C_6F_{13})\) group lost, presumably as \(C_6H_5C_6F_{13}\) as a hydride had also been lost. The crystal structure of this dimer is shown below, Figure 2.5.1.

![Figure 2.5.1 The Schematic of Decomposition Rh Dimer observed in HPIR solution](image-url)
The poor crystal structure was due to the large number of -CF$_2$- chains, which were quite disordered; there was also some stray solvent, which was rationalised as one water molecule in 2 locations. This made location of the bridging hydrogen impossible, however the core structure remained of interest. The full structural analysis of these crystals can be found in Appendix 2. With two terminal carbonyl
environments, this structure may have explained the unassigned peaks in the HPIR spectra. However, because these crystals grew in the HPIR solution once removed from the cell, we considered them to be a decomposition product and unlikely to be present in the high-pressure IR spectra collected for this solution. Due to the perfluoroalkyl chains these crystals were quite soft and difficult to isolate for any other form of analysis. Further study of this decomposition product would have been valuable had time allowed.

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>( C_{134}H_{47}F_{143}O_{3}P_{4}Rh_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula Weight</td>
<td>4751.42</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Triclinic</td>
</tr>
</tbody>
</table>
| Unit cell dimensions | \[\begin{align*}
          a &= 20.56(12) \text{ Å} & a &= 112.974(3)^o \\
          b &= 20.99(14) \text{ Å} & b &= 97.938(4)^o \\
          c &= 21.9013(15) \text{ Å} & c &= 102.251(4)^o
\end{align*}\] |

**Bond Lengths (Å)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(1)-Rh(2)</td>
<td>2.9346(9)</td>
</tr>
<tr>
<td>Rh(1)-P(1)</td>
<td>2.383(2)</td>
</tr>
<tr>
<td>Rh(1)-P(2)</td>
<td>2.354(2)</td>
</tr>
<tr>
<td>Rh(1)-P(4)</td>
<td>2.268(2)</td>
</tr>
<tr>
<td>Rh(2)-P(4)</td>
<td>2.2503(18)</td>
</tr>
<tr>
<td>Rh(2)-P(3)</td>
<td>2.3303(17)</td>
</tr>
</tbody>
</table>

**Bond Angles (°)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(2)-P(4)-Rh(1)</td>
<td>81.00(6)</td>
</tr>
</tbody>
</table>

Table 2.5.1.5 Crystal Data for the rhodium dimer structure

2.5.2 **HP NMR data analysis**

An investigation of the equivalent Rh: P = 1: 5 solutions with HP-NMR was carried out and provided some useful information in the identification of species present under the initial conditions.
Chapter 2: A Mechanistic Study

NMR 2.5.2.1 \(^{31}\text{P}\) HP-HPIR spectrum Rh: P(C\(_6\)H\(_4\)C\(_6\)F\(_{13}\))\(_3\) (1: 5) CO/H\(_2\) (15 bar) at (i) RT and (ii) 70°C after 40 minutes

NMR 2.5.2.2 \(^1\text{H}\)-HP-NMR of Rh(acac)(CO)\(_2\) and P(C\(_6\)H\(_4\)C\(_6\)F\(_{13}\))\(_3\) (1: 5) 70°C CO/H\(_2\)(15 bar) metal hydride region.

Once the HP-NMR cell was pressurised with CO / H\(_2\) the spectra at room temperature for both the fluorinated phosphine, see NMR 2.5.2.1(i) and PPh\(_3\) showed broad singlets at about 5 ppm in the \(^{31}\text{P}\) NMR spectrum, indicative of a fluxional species and in agreement with the HPIR data which on addition of CO / H\(_2\) only showed the reappearance of [Rh(acac)(CO)\(_2\)] and the initial square-planar complex, [Rh(acac)(CO)(PPh\(_3\))]. In order to obtain the actual shift for this initial species a low temperature spectrum would perhaps have frozen out the fluxional exchange between the two species. But from the previous Rh: P = 1: 1 ratio solution we have already observed a doublet (56 ppm, \(^1J_{RhP} = 182.3\) Hz) under similar conditions, the lack of
excess phosphine removed any fluxional exchange which obscured the spectra at these higher ratios.

Both solutions were heated directly to 70°C and left for 1 hour before their spectra were recorded. For both phosphine ligands, new species were observed in these spectra. The spectrum from the solution containing the fluorinated ligand, NMR 2.5.2.1(ii), showed $^{31}$P (hexane-d$_{14}$) δ: 38.1 (d, $^1$J$_{RhP}$ = 160 Hz), 36.0 (d, $^1$J$_{RhP}$ = 154 Hz), 19.6 (s, P=O), and -3.9 (broad s) whilst the $^1$H NMR spectrum showed a single peak in the metal-hydride region at δ: -10.1 ppm, NMR 2.5.2.2. When this solution was cooled to room temperature, the two doublets separated slightly and the spectrum appeared as δ$^{31}$P: 38.5(d, $^1$J$_{RhP}$ = 156 Hz), 36.6(d, $^1$J$_{RhP}$ = 148.5 Hz), 20.3(s, P=O), -5.4 (broad s). NMR 2.5.2.3(i).
NMR 2.5.2.3 Rh: P(C₆H₄C₆F₁₃)₃ (1: 5) cooled from 70°C to RT: (i) $^{31}$P NMR, (ii) $^1$H NMR, (iii) $^{31}$P cooled to -20°C.

Together with a broad singlet at $\delta$ -10.0 ppm in the $^1$H NMR spectrum, NMR 2.5.2.3(ii), showed a quartet at -10.1 ppm ($^2J_{HP} = 14.5$ Hz) in the metal-hydride region of the spectrum, which indicated a Rh atom surrounded by three equivalent phosphines and was assigned to the tris-phosphine complex [RhH(CO)(P(C₆H₄C₆F₁₃)₃)]₃. The overlapping metal-hydride signals made assignment of the second peak difficult; a schematic of the two peaks is shown in Figure 2.5.3.
Figure 2.5.3 Schematic of the metal hydride region of $^1$H NMR to describe the overlapping of two signals

By lowering the temperature further to $-20^\circ$C, NMR 2.5.2.3(iii), the $^{31}$P NMR spectrum showed that the fluxional peak shifted further downfield to $-6.2$ ppm the expected position for the free ligand, but remained broad. The positions of the two doublets were unchanged but the intensity of the smaller doublet (36 ppm) appeared to have decreased with respect to that of the other doublet, which indicated a change in the proportion of the two complexes present at this lower temperature. No further data was obtained from the proton spectrum at the lower temperature.

<table>
<thead>
<tr>
<th>Complex$^a$</th>
<th>T (°C)</th>
<th>$^{31}$P NMR</th>
<th>$^1$H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\delta$ (ppm)</td>
<td>$J_{P,Rh}$ (Hz)</td>
</tr>
<tr>
<td>Tris PPh$_3$ Rh</td>
<td>-28</td>
<td>42.5</td>
<td>155</td>
</tr>
<tr>
<td>Bis PPh$_3$ Rh</td>
<td>-28</td>
<td>39.9</td>
<td>138</td>
</tr>
</tbody>
</table>

Table 2.5.2.1 Brown's NMR Data for PPh$_3$ complexes$^4$. $^a$ where the solvent is Tol-d$_8$.

Brown and co-workers, have previously described the NMR spectra of the tris- and bis- triphenylphosphine hydrido-rhodium carbonyl species in toluene-d$_8$ and their results are tabulated above, Table 2.5.2.1. We therefore suggest that; under our reaction conditions and with the perfluorinated ligand, as shown in the above spectra, we have formed both the bis- and tris- phosphine complexes. Table 2.5.2.2. shows this data and correlates well with the literature data, Table 2.5.2.1. It was also
observed that at lower temperatures the equilibrium that exists between the two complexes, favours the *tris*-phosphine complex.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{31}$P NMR $\delta$ (ppm)</th>
<th>$^1J_{P-Rh}$ (Hz)</th>
<th>$^1$H NMR $\delta$ (ppm)</th>
<th>$J$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RhH(CO)$_2$(P(C$_6$H$_4$-4-C$_6$F$_13$)$_3$)$_2$]</td>
<td>38.5</td>
<td>156</td>
<td>-10.0</td>
<td>14.5</td>
</tr>
<tr>
<td>[RhH(CO) (P(C$_6$H$_4$-4-C$_6$F$_13$)$_3$)$_3$]</td>
<td>36.6</td>
<td>148.5</td>
<td>-10.05</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5.2.2 Observed data for Rh: (P(C$_6$H$_4$C$_6$F$_13$)$_3$) (1: 5) in PFDMC and hexane-d$_{14}$.

We conclude from this data that we have two Rh-phosphine complexes in our fluorinated system and we assume the fluxional exchange of the free ligand to be with one or both of these species as no other peaks appeared at lower temperatures.

To observe any discrepancies between the fluorinated ligand and PPh$_3$, a solution of the same ratio Rh: PPh$_3$ (1: 5) was prepared and examined by HP-NMR. The solution, similarly, was heated to reaction temperature and returned to room temperature to record a spectrum, NMR 2.5.2.4.(i) and (ii). The PPh$_3$ solution spectrum showed only one doublet at $^{31}$P $\delta$: 36.8 (d, $^1J_{P-Rh} = 139.5$ Hz) ppm which correlates well with Brown’s data for the *bis*-phosphine hydrido rhodium dicarbonyl ($\delta$ 39.9, $J = 138$ Hz)$^4$ and a broad singlet at –5 ppm, but the $^1$H spectrum showed two metal-hydride peaks $\delta$: -9.0 (s) and –9.7 (dt, $^2J_{P-H} = 11.8$ Hz and $^1J_{RhH} = 20.3$ Hz) ppm. The splitting of the hydride signal at $\delta$ –9.7 ppm, into a doublet of triplets is indicative of a rhodium-hydride complex with two equivalent phosphorus atoms attached, *i.e.* [RhH(CO)$_2$(PPh$_3$)$_2$], the rhodium causes the doublet coupling and the triplet arises from the two P atoms. According to Brown’s data the metal hydride signal for the *bis*-phosphine complex was observed at –8.9 and was not resolved at room temperature due to dissociative exchange of the phosphine. The doublet coupling would be considered very high for Rh coupling, Brown *et al* quoted Rh-H coupling as 3 and 6.5 Hz for the two *bis*-phosphine isomers (ea and ee respectively)$^4$, and only
after cooling the solution to \(-123^\circ\text{C}\). Furthermore the $^{31}\text{P}$ NMR spectrum showed only a single peak; the position and coupling of which, correlated well with the data for [RhH(CO)$_2$(PPh$_3$)$_2$] and would suggest the $^1\text{H}$ signal at $\delta -9.0$ ppm to correspond to it. This then leaves an unidentified species which may also have two equivalent phosphines around a rhodium centre, but we are unclear as to what this species is.

NMR 2.5.2.4 Rh: PPh$_3$ (1: 5) heated to 70°C and cooled to RT, CO/H$_2$ (15 bar) (i) $^{31}\text{P}$ NMR, (ii) $^1\text{H}$ NMR

The assignments for these spectra were made on the basis that the $^1\text{H}$ resonance at $\delta -9.0$ ppm arose from the two isomers of [RhH(CO)$_2$(PPh$_3$)$_2$] (literature $\delta -8.9$ ppm)$^4$ and the $^{31}\text{P}$ signal from this species was observed at 36.8 ppm (literature 39.9 ppm).$^4$ The doublet of triplets at $\delta -9.7$ ppm was not assigned to [RhH(CO)(PPh$_3$)$_3$] as the literature reported a peak at -9.3 ppm$^4$ and we would expect a quartet for the splitting of rhodium by three equivalent phosphines. Neither was a signal observed in the $^{31}\text{P}$ NMR (Brown reported a doublet at 42.5, $J_{\text{RhP}} = 155$ Hz), which implies that no [RhH(CO)(PPh$_3$)$_3$] was formed with triphenylphosphine under these hydroformylation conditions. The doublet at $\delta_P 37$ ppm was assigned to the interconverting isomers of [RhH(CO)$_2$(PPh$_3$)$_2$] and this was supported by literature
data (39.9 ppm). In an attempt to assign the hydride signal at –9.7 ppm the solution was cooled further to –60°C, and the following $^{31}$P-NMR spectrum was obtained.

At this much lower temperature, a number of phosphorus compounds were observed, the broad doublet at 38 ppm had already been assigned to [RhH(CO)$_2$(PPh$_3$)$_3$]. The signal observed at 33 ppm could be interpreted as two doublets, a doublet of doublets or a quartet, but with $J \sim 115$ Hz it is most likely a doublet of doublets and we assume that this phosphorus signal corresponds to the doublet of triplets in the proton spectrum, however, we remain unclear about the structure or form of this complex, although the resonance at 25 ppm also appears to be a doublet of doublets ($J \sim 171$ and 152 Hz) but poor shimming of this peak makes accurate coupling constants difficult to obtain. This suggests that the resonances at 33 and 25 ppm are from two inequivalent phosphines in the same complex, with the large value of $J_{pp}$ (Hz) suggesting aa or ee phosphines. This would mean that there is an impurity in the PPh$_3$ that coordinates or that reaction has occurred (perhaps to give PPh$_2$). Even if the PPh$_3$ was carefully recrystallised prior to use, the same doublet of doublet resonances were observed, perhaps diminishing the likelihood that an
impurity was responsible for one of the unknown resonances. The peak at 26 ppm was assigned to triphenylphosphine oxide, (literature 29 ppm).21

Both ligands were examined under the same conditions and the most obvious difference between the two, was that the perfluorinated phosphine ligand formed both the tris- and the bis- phosphine complexes under reaction conditions whilst PPh\(_3\) only appeared to form the bis- phosphine complex.

Brown and co-workers\(^4\) have shown that the bis-phosphine isomer with both phosphines in the equatorial position exists in the greater proportion for the PPh\(_3\) complex, the ee: ea isomer ratio is quoted as 85: 15 % when spectra were recorded at -125°C. For the fluorinated ligand we observed both, the bis and tris phosphine complexes of rhodium however, due to the overlap of the two signals a similar calculation of the proportion of the two bis-phosphine isomers was not possible.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(^{31}\text{P NMR} )</th>
<th>(^{1}\text{H NMR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta \text{ (ppm)})</td>
<td>(J_{P-Rh} \text{ (Hz)})</td>
</tr>
<tr>
<td>20</td>
<td>19.9 (s), 5.3 (br s)</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>38.1 160</td>
<td>36.7 154</td>
</tr>
<tr>
<td></td>
<td>19.6 (s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-3.9 (br s)</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>38.4 155.4</td>
<td>36.6 148.1</td>
</tr>
<tr>
<td></td>
<td>20.3(s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-5.4 (br s)</td>
<td>-</td>
</tr>
<tr>
<td>-20</td>
<td>38.7 156</td>
<td>37.0 147</td>
</tr>
<tr>
<td></td>
<td>21.6 (s)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-6.2 (s)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.5.2.3 HP-NMR data for Rh: \(\text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_3\) (1: 5) in PFDMC and hexane-d\(_{14}\) and 15 bar CO/\(\text{H}_2\).
The temperature range of this experiment was dependent upon the PFDMC, which has a melting point of \(-55^\circ\text{C}\), as well as the miscibility of the hexane-d\(_{14}\) in PFDMC. Although miscible at RT, it was possible that the two liquids would become immiscible at lower temperatures, which may have led to lower sensitivity in the spectra, as the lock signal for the spectrometer would have been lost.

From this investigation we can assign IR and NMR shifts to the species shown in Table 2.5.2.5.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(31^P) NMR (\delta) (ppm)</th>
<th>(J_{\text{P-Rh}}) (Hz)</th>
<th>(\text{H NMR} \delta) (ppm)</th>
<th>(J) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2 (br s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>36.8</td>
<td>139</td>
<td>-9.0 (br s)</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>36.7</td>
<td>137</td>
<td>-9.2 (s), -9.9 (m)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>36.8</td>
<td>139.5</td>
<td>-9.0 (s), -9.7 (dt) 11.8, 20.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5.2.4 HP-NMR data for Rh: PPh\(_3\) (1: 5) in Tol-d\(_8\)

Although only a single band was observed and assigned to the \(\text{tris}\)-phosphine complex, it is possible that the second band for this species was overlapped by others and therefore overlooked. Vaska cited the IR of [RhH(CO)(PPh\(_3\))] as 1923 and 2041 cm\(^{-1}\) for \(\nu_{\text{CO}}\) and \(\nu_{\text{RhH}}\) respectively\(^{24}\) and under a deuterium atmosphere \(\nu_{\text{CO}}\) was observed to have shifted to 1954 cm\(^{-1}\), with \(\nu_{\text{RhH}}\) not located. With the strong electron withdrawing nature of the perfluorinated triphenylphosphine ligand these signals are
expected to shift to higher frequency and would perhaps be lost within the other bands. We therefore, assigned the band at 1936 cm$^{-1}$ in the spectrum recorded under hydrogen to the carbonyl stretch of the *tris*-phosphine complex without assigning a band for the hydride.

### 2.5.3 HPIR investigation of hydroformylation

To observe any new species formed upon addition of octene to the HPIR cell, the catalyst solution containing [Rh(acac)(CO)$_2$] and P(C$_6$H$_4$C$_6$F$_{13}$)$_3$ was heated to 70$^\circ$C with CO / H$_2$ (15 bar) to pre-form the hydride complexes, but then vented and re-pressurised with CO (15 bar). The octene was introduced to the cell through the injection port by an over pressure of CO. The bands observed during this study are tabulated below, Table 2.5.3.1, with data for the equivalent PPh$_3$ solution shown in Table 2.5.3.2.

<table>
<thead>
<tr>
<th>Spectrum Conditions</th>
<th>IR data (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT 1 bar Ar</td>
<td>1995 (s) (saturated)</td>
</tr>
<tr>
<td>15 bar CO/H$_2$ RT</td>
<td></td>
</tr>
<tr>
<td>70$^\circ$C</td>
<td>2083 (m), 2014 (m), 1995 (s)</td>
</tr>
<tr>
<td>70$^\circ$C + 1.5 hr</td>
<td>2086 (w), 2073 (w), 2055 (m), 2039 (m), 2005 (s) (asymmetric), 1972 (m), 2073 (w), 2060 (br m), 2037 (m), 2025 (w), 2004 (s), 1988 (s), 1972 (sh)</td>
</tr>
<tr>
<td>Cooled to 30$^\circ$C</td>
<td>2056 (w), 2035 (m), 2015 (sh), 2004 (s), 1985 (s), 1970 (s)</td>
</tr>
<tr>
<td>Vented to 1 bar N$_2$</td>
<td>2080 (v w), 2055 (v br w), 2038 (m), 2016 (sh), 1993 (s), 1985 (sh), 1970 (sh)</td>
</tr>
<tr>
<td>10 bar CO 28$^\circ$C</td>
<td>2056 (w), 2035 (m), 2015 (sh), 2004 (s), 1985 (s), 1970 (s)</td>
</tr>
<tr>
<td>10 bar CO 70$^\circ$C</td>
<td>2073 (w), 2062 (w), 2038 (m), 2024 (m), 2006 (sh m), 1990 (sh), 1983 (m), 1720 (w)</td>
</tr>
<tr>
<td>Addition of Octene</td>
<td>2082 (w), 2073 (w), 2062 (w), 2038 (m), 2024 (m), 2008 (s), 1987 (s), 1822 (octene)1735 (w, nonanal), 1720 (w), 1695 (w), 1642 (saturated, octene)</td>
</tr>
<tr>
<td>t = 0 min</td>
<td>2073 (w), 2062 (w), 2038 (m), 2024 (m), 2008 (s), 1987 (s), 1822 (octene), 1735 (w, nonanal), 1720 (sh), 1695 (w), 1642 (saturated, octene)</td>
</tr>
<tr>
<td>t = 10 min</td>
<td>2082 (sh), 2073 (w), 2062 (w), 2038 (m), 2024 (m), 2018 (sh), 2008 (s), 1987 (s), 1822 (octene)1735 (w, nonanal), 1720 (sh), 1695 (sh), 1642 (saturated, octene)</td>
</tr>
<tr>
<td>T = 30 mins</td>
<td>2082 (w), 2073 (w), 2062 (w), 2038 (m), 2031(sh), 2024 (sh), 2017 (sh), 2008 (s), 1987 (s), 1822 (octene), 1735 (w, nonanal), 1720 (sh), 1695 (sh), 1642 (saturated, octene)</td>
</tr>
<tr>
<td>T = 60 mins</td>
<td>No change</td>
</tr>
<tr>
<td>T = 90 Mins</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5.3.1 Rh: P(C$_6$H$_4$C$_6$F$_{13}$)$_3$ (1: 5) Hydroformylation under CO (10 bar)
Table 2.5.3.2 Rh: PPh₃ (1: 5) Hydroformylation with CO/H₂ atmosphere.

<table>
<thead>
<tr>
<th>Spectrum Conditions</th>
<th>IR data (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar RT RT CO/H₂ 10 bar</td>
<td>1986 (s)</td>
</tr>
<tr>
<td>70°C CO/H₂</td>
<td>2081 (w), 2044 (m), 2029 (sh), 2014 (w), 1996 (s sh), 1987 (S), 1955 (m), 1940 (sh)</td>
</tr>
<tr>
<td>70°C</td>
<td>2081 (w), 2044 (m), 2029 (sh), 1996 (s), 1987 (S), 1955 (m), 1940 (sh)</td>
</tr>
<tr>
<td>+30 mins</td>
<td>2081 (w), 2044 (m), 2025 (w), 1996 (s), 1987 (S), 1972 (sh), 1955 (m), 1940 (sh)</td>
</tr>
<tr>
<td>70°C + octene t = 0 mins</td>
<td>2056 (w), 2044 (w), 2000 (s), 1982 (s), 1955 (m), 1822 (s, octene), 1735 (saturated, nonanal), 1640 (saturated, octene)</td>
</tr>
<tr>
<td>t = 10 mins</td>
<td>2080 (w), 2055 (w), 2043 (m), 2027 (w), 1997 (s), 1983 (s), 1954 (m), 1820 (sh), 1735 (br saturated, nonanal)</td>
</tr>
<tr>
<td>t = 60 mins</td>
<td>2080 (w), 2055 (w), 2043 (m), 2025 (w), 1997 (s), 1983 (s), 1954 (m), 1820 (sh), 1735 (br saturated, nonanal)</td>
</tr>
</tbody>
</table>

It is perhaps clearer from the HPIR spectra, the differences between the two ligand systems, see HPIR 2.5.3.1 and HPIR 2.5.3.2. The difference in the conditions of the two solutions should also be considered during this comparison: the triphenylphosphine solution was investigated under an atmosphere of CO / H₂, whereas the hydroformylation in the perfluorinated ligand was studied under a CO atmosphere, in an attempt to restrict the progress of the hydroformylation reaction. In the case of triphenylphosphine, upon the addition of octene to the solution, the seven peaks of the [Rh(η₅-C₅H₅)(CO)₂] / PPh₃, 70°C solution altered quite dramatically. Most obvious was the disappearance of bands at 2081 (perhaps only hidden in the broad CO band, 2143 cm⁻¹), 2025, 1996 and 1987 cm⁻¹, which were replaced by two strong bands at 2000 and 1982 cm⁻¹. We anticipated the formation of the acyl-rhodium species [Rh(C(O)C₈H₁₆)(CO)₂(PPh₃)₂], but it seems unlikely as Wilkinson et al have reported a similar acyl species with a benzoyl group [Rh(COPh)(CO)₂(PPh₃)₂]²⁵, which showed three bands in the IR spectra at 1985(s), 1955(s) and 1630(m) cm⁻¹ (cyclohexane solution) with the band at 1630 cm⁻¹ due to the acyl carbonyl group, which are very different from the bands we observed, 2000 and 1982 cm⁻¹ and no band
was observed in our spectrum around 1950 cm\(^{-1}\). Moser et al presented an alternative interpretation.\(^{16}\) During a study using \textit{para}-substituted triphenylphosphine ligands and observing the electronic effect of ligands upon the rate of hydroformylation of hex-1-ene, the following results were observed. With triphenylphosphine as the ligand and [Rh\(_4\)(CO)\(_{12}\)] as the rhodium source, the active catalyst, [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)], was pre-formed under a CO/H\(_2\) atmosphere (~11 bar), and this was reacted with hex-1-ene under a nitrogen atmosphere; the authors reported two metal carbonyl peaks at 1987 and 1939 cm\(^{-1}\), which they attributed to the alkyl complex [Rh(C\(_6\)H\(_{12}\))(CO)\(_2\)(PPh\(_3\))\(_2\)], having disregarded the possible acyl species due to it being stable only under a CO atmosphere and because they did not observe any acyl band in the IR spectrum. As our study was carried out under CO / H\(_2\) we can assume that the acyl species would have been formed. We could not confirm the presence of an acyl species as there was a broad band at 1640 cm\(^{-1}\), which arose from the octene, and obliterated any other bands that may have been present.

At 30\% conversion Moser et al, cite that for triphenylphosphine the predominant species present during the hydroformylation of hexene (70°C and CO/H\(_2\) ~11bar), was [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)]\(^{16}\), but by increasing the electron-withdrawing power of the ligand, by substitution at the \textit{para}- position of the phenyl ring with –Cl or CF\(_3\), the principal species observed was [Rh(C\(_6\)H\(_{13}\))(CO)\(_2\)(PR\(_3\))\(_2\)], determined from formation of this product by reacting [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)] and excess hexene under N\(_2\) atmosphere.
Similar results were observed with the fluorinated ligand, with two peaks appearing upon the addition of octene to the catalyst solution (70°C, CO 10 bar), at 2008 (s) and 1987 (s) cm\(^{-1}\) shown in HPIR 2.5.3.2. Upon the immediate addition of the octene to the catalytic solution two strong bands were also observed at 1822 and 1640 cm\(^{-1}\) from octene and a small band at 1735 cm\(^{-1}\) arose from nonanal, as some H\(_2\) will have remained in the solution. Another weak band at 1695 cm\(^{-1}\) was quite possibly the acyl carbonyl band. This band did increase in size over time however the nonanal band grew much faster and eventually obliterated it. This appears to be proof that the acyl complex formed upon the addition of octene to the catalytic solution and was indeed [\(\text{Rh(C(CO)}\text{C}_6\text{H}_{16})(\text{CO})_2\text{(P(C}_6\text{H}_{14}\text{C}_6\text{F}_{13})_3)_2\)] with bands at 2008(s), 1988 (s) and 1695 (w) cm\(^{-1}\).

However, after 90 minutes of hydroformylation, other peaks were observed in the carbonyl region; 2062 (m), 2037 (sh), 2017 (sh) cm\(^{-1}\). HPIR 2.5.3.3.
**Chapter 2: A Mechanistic Study**

**HPIR 2.5.3.2 Rh: \( P(C_6H_4C_6F_{13})_3 \) (1: 5) 70°C, CO (10 bar); Blue = solution prior to addition of octene; Red = solution with octene added (\( t = 0 \) minutes)**

**HPIR 2.5.3.3 Rh: \( P(C_6H_4C_6F_{13})_3 \) (1: 5) 70°C, CO (10 bar). Addition of octene, carbonyl region. Spectra recorded every 10 minutes. Red: \( t = 0 \) minutes.**

**HPIR 2.5.3.4 [Rh(acac)(CO)]_2 and \( P(C_6H_4C_6F_{13})_3 \) (1: 5) 70°C: PINK = 15 bar CO / \( \text{H}_2 \), Blue = 17 bar CO addition of oct-1-ene, \( t = 3 \) minutes, Red = 17 bar CO and addition of oct-1-ene, \( t = 90 \) minutes**
After 90 minutes it would appear that the species in solution were once again the bis and tris- phosphine complexes, observed in the original spectra. Not all the octene had reacted, as bands were still observed at 1822 and 1640 cm$^{-1}$, but perhaps all hydrogen left in the system had been consumed.

Hydroformylation was also studied in the HP-NMR cell see section 4.1.2.1. The procedure for these reactions was different from that of the HPIR reactions, as the catalyst solution was pre-formed under reaction conditions, see chapter 2.5.2, and the solution was cooled before addition of octene, the cell was re-pressurised with CO and then reheated to reaction temperature in the spectrometer. Poor mixing of the substrate, catalyst solution and gas may have caused problems and low conversions.

In the case of the PPh$_3$ solution, two metal hydride signals were observed in the $^1$H NMR prior to addition of octene, but these disappeared in the room temperature spectrum of the catalyst solution and octene. The $^{31}$P NMR signals also changed; previously a doublet at 36.9 ppm ($J = 138.4$ Hz) had been observed but upon the addition of octene a broad multiplet was observed at 25 ppm, NMR 2.5.3.1(i). This resonance coalesces with that from free PPh$_3$ at –6.2 ppm at 70$^\circ$C, NMR 2.5.3.1(ii). The singlet observed at 23 ppm was from the phosphine oxide. When the solution was cooled back to room temperature, a broad doublet appeared at 40.5 ppm, $J = 153$ Hz, and a small broad signal was observed at approximately 30 ppm, along with the oxide (24 ppm) and broad peak (-5 ppm) due to the free ligand, NMR 2.5.3.1(iii). The $^1$H NMR spectrum recorded once the hydroformylation reaction had been returned to RT is shown below, NMR 2.5.3.2. At higher temperature, no signal was observed. A single peak was observed at room temperature, but when the solution was cooled to –30$^\circ$C this signal, became two; a broad peak at –9.0 and a well-defined quartet at –9.4 ppm ($^2J_{PH} = 28$ Hz), a tris-triphenylphosphine complex.
By lowering the temperature to −30°C, $^{31}$P NMR spectrum NMR 2.5.3.1(iv), the broad doublet observed at room temperature was resolved into two doublets one at 41 ppm, ($^{1}J_{\text{Rh-P}} = 154$ Hz), which matched the literature values for [RhH(CO)(PPh$_3$)$_3$] and the smaller doublet at 37 ppm ($^{1}J_{\text{Rh-P}} = 138$ Hz), was assigned to [RhH(CO)$_2$(PPh$_3$)$_2$]. The broad doublet at 33 ppm, when cooled to −50°C showed a coupling constant of $J_{\text{Rh-P}}\approx137$ Hz and was possibly due to [Rh(C$_8$H$_{17}$)(CO)$_2$(PPh$_3$)$_2$] or perhaps more likely, [Rh(C(O)C$_8$H$_{17}$)(CO)(PPh$_3$)$_2$].

NMR 2.5.3.1 $^{31}$P NMR Rh: PPh$_3$ (1: 5) plus octene. CO (20 bar) (i) RT (ii) 70°C, (iii) Cooled to RT and (iv) Cooled to −30°C
NMR 2.5.3.2 $^1$H Rh: PPh$_3$ (1: 5) plus octene heated to 70°C and cooled to Room temperature and –30°C

The same experiment was carried out with the perfluorinated ligand; as described previously (NMR 2.5.2.3.), the RT $^{31}$P NMR spectrum obtained with the Rh: P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$ (1: 5) solution after being heated to 70°C for 1 hour, showed the bis- and tris-phosphine complexes, [RhH(CO)$_2$(P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$)$_2$] and [RhH(CO)(P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$)$_3$]. The corresponding $^1$H NMR spectrum showed a quartet at –10 ppm with a superimposed broad singlet. Upon addition of octene to the solution and pressurising with CO (20 bar) at room temperature, NMR 2.5.3.3, the metal-hydride region of the $^1$H NMR showed only a small broad peak at –9.6 ppm and the $^{31}$P NMR spectrum showed a large broad doublet at 26 ppm ($J$ ~ 123 Hz), a doublet at 39 ppm ($J_{RhP}$ = 155.4 Hz) indicated some [RhH(CO)(P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$)$_3$] was still in solution along with some phosphine oxide (singlet at 21 ppm) and free ligand at –5 ppm. At reaction temperature there was no metal-hydride observed and both doublets in the $^{31}$P NMR solution appeared to be in fluxional exchange with the free ligand as this peak at –3 ppm had broadened considerably and the two doublets disappeared, NMR 2.5.3.4.
Chapter 2: A Mechanistic Study

NMR 2.5.3.3 RT NMR of Rh: (P(C₆H₄-4-C₆F₁₃)₃) (1: 5) pre-formed with addition of octene; ³¹P and ¹H Metal-Hydride region

NMR 2.5.3.4 ³¹P NMR Rh: (P(C₆H₄C₆F₁₃)₃) (1: 5) 70°C CO (20 bar) with octene after 60 minutes.

By comparing the ³¹P NMR spectrum NMR 2.5.3.3, to the HPIR spectrum described earlier, HPIR 2.5.3.4, we assigned this new doublet at 26 ppm to the Rh-acyl species.

After the reaction had been at temperature for 1 hour, NMR 2.5.3.4, it was allowed to cool and spectra were recorded at RT. The ¹H NMR spectrum showed no signal in the metal hydride region of the spectrum, but the ³¹P NMR spectrum, NMR 2.5.3.5(i), showed a new doublet at 23 ppm, which was quite broad and a small broad peak at 19 ppm. By cooling the cell further, the broad doublet was resolved and two new doublets were observed, but no signals were observed in the ¹H spectrum. The
Chapter 2: A Mechanistic Study

low temperature spectrum is shown below, NMR 2.5.3.5(ii). We possibly have the formation of a number of new species, which have no metal-hydrides.

Bianchini and co-workers have reported a similar study with PPh$_3$. Under hydroformylation of hexene, Bianchini reported the appearance of three signals in the region 20-30 ppm and identified them as arising from dimeric rhodium compounds, Figure 2.5.5.

![NMR Spectrum](image)

NMR 2.5.3.5 Rh: P(C$_6$H$_4$-4-C$_6$F$_5$)$_3$ (1: 5) plus octene heated to 70°C for 1 hour and cooled (i) RT and (ii) -20°C

By generating the species directly from a known method, Bianchini assigned the peaks observed in the low temperature (-20°C) $^{31}$P NMR investigation of hydroformylation in the following manner; three different dimer complexes were assigned to the 5 peaks observed, see below. 8 showed a doublet ca. 23 ppm. 9 also showed a doublet at ca. 25 ppm and 10 was attributed to a doublet of multiplets centred at 28.5 ppm. It was surprising that complex 9 was not assigned a more complicated signal in the NMR because the single doublet assigned to it implies a single phosphorus environment, which is clearly not the case from the structure given.
However due to the close proximity of the signals of the three complexes it is possible that some overlap has occurred obscuring a clearer spectrum of 9.

![Diagram of three dimer species](image)

**Figure 2.5.5** The three dimer species Bianchini identifies in hydroformylation spectrum

Had we formed similar complexes, to those observed and assigned by Bianchini, we would have expected to see bridging carbonyl bands in the HPIR spectra collected under the same conditions but none were observed.

A similar HP-NMR study to our own, was carried out by Masdeu-Bultó and co-workers\(^1\) examining the hydroformylation of 1-octene using a rhodium / P(C\(_6\)H\(_4\)-4-OCH\(_2\)C\(_7\)F\(_{15}\))\(_3\) catalytic solution, with Rh/P = 1/5, 80\(^\circ\)C and 40 bar CO / H\(_2\). They detected two hydride species at –9.3 and –9.1 ppm and assigned them to [RhH(CO)(P(C\(_6\)H\(_4\)-4-OCH\(_2\)C\(_7\)F\(_{15}\))\(_3\))] and [RhH(CO)\(_2\)(P(C\(_6\)H\(_4\)-4-OCH\(_2\)C\(_7\)F\(_{15}\))\(_3\))]\(_2\)], the *tris*- and *bis*- phosphine complexes respectively. Unlike many other studies of a similar nature, Masdeu-Bultó prepared the catalyst *in situ* by dissolving [Rh(acac)(CO)\(_2\)] and P(C\(_6\)H\(_4\)-4-OCH\(_2\)C\(_7\)F\(_{15}\))\(_3\) in PFMC and then the solution was heated to 50\(^\circ\)C until all solid had dissolved. They also added an organic solvent, toluene, which gave a biphasic system of PFMC/toluene of 60/40 v/v. Spectra were recorded at room temperature, prior to the addition of octene the \(^{31}\)P NMR spectrum showed six signals \(\delta\) (ppm): 37.1 (d, \(^1\)J\(_{RhP}\) = 154.4 Hz), 32.1 (d, \(^1\)J\(_{Prh}\) = 136.4 Hz), 24.9 (s, oxide of P(C\(_6\)H\(_4\)-4-OCH\(_2\)C\(_7\)F\(_{15}\))), 19.9 (broad d, \(^1\)J\(_{Prh}\) = 159.0 Hz), 17.0 (broad d, \(^1\)J\(_{Prh}\) = 152.7 Hz) and 10.1 ppm (s, free ligand). These peaks were assigned by comparison to triphenylphosphine data, in the literature, and thus the following
species were identified; \([\text{RhH(CO)}(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)_3] \) (37.1 ppm), \([\text{RhH(CO)}_2(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)_2] \) (32.1 ppm) and two bimetallic species, \([(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)(\text{CO})_2\text{Rh(}\mu\text{-CO})_2\text{Rh(CO)}_2(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)] \) (19.9 ppm) and \([(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)_2(\text{CO})\text{Rh(}\mu\text{-CO})_2\text{Rh(CO)}_2(\text{P(C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3)] \) (17.0 ppm), which agrees with Bianchini’s observations of bimetallic species. These assignments would correspond to the similar doublets observed in our spectra NMR 2.5.3.5, at 23 and 19.5 ppm and would leave the third doublet at 15 ppm to be assigned to the acyl species. The formation of the rhodium dimers may be explained by the poor gas mixing in the HPNMR cell, as these complexes are known to form under high \([\text{Rh}]\) and \([\text{P}]\) and low \([\text{H}_2]\).

The \(-\text{C}_6\text{H}_4\text{-4-OCH}_2\text{-} \) spacer provided sufficient shielding of the \(\text{P}\) atom from the strongly electron withdrawing fluorous chain. However the TOF of this catalyst solution was much lower than that observed for our own ligand; 1040 h\(^{-1}\) compared to 13 500 h\(^{-1}\) respectively.

The high-pressure NMR spectra were recorded after the cell had been shaken for 12 hours at 50°C under CO/H\(_2\) (1:1, 40 bar), it was assumed that this method would remove any question of poor mixing in the NMR cell.

Under hydroformylation conditions no new peaks were observed in the \(^1\text{H}\) or \(^{31}\text{P}\) NMR spectra, the only difference observed in the \(^{31}\text{P}\) spectrum was the ratio between the \textit{tris-} and \textit{bis-} phosphine species (40 / 60 ratio). The spectra were recorded an hour after the addition of octene, having shaken the cell for that time, and from the data given in the paper this corresponded with nearly total conversion \(\sim 97\%\).
As we have previously described, under reaction conditions the perfluorinated ligand forms *bis*- and *tris*- phosphine complexes, and when octene is added to this solution an acyl complex is briefly observed under a CO atmosphere with little H₂ present. The speed of the reaction has also been demonstrated as formation of nonanal (product) was observed almost immediately upon the addition of octene to the catalytic solution in the HPIR.

### 2.6 Spectroscopic Study of Rh: Phosphine ratio = 1: 10

Although we halved the ratio of Rh: P in the continuous flow rig, the initial batch reactions were carried out with 1: 10 Rh: P ratio and by examining this higher ratio it was hypothesised that we would perhaps form the tris-phosphine-Rh complex with this larger excess of phosphine. For [RhH(CO)(PPh₃)₃],² the literature reports bands in the carbonyl region of the infrared at 2005 (s) and 1935 (m) cm⁻¹ in cyclohexane solution.¹² The $^{31}$P NMR data for this complex is quoted as δₚ: 42.5 ppm, a doublet with $J_{P-Rh} = 155$ Hz in toluene-d₈ and at −28 °C. The $^1$H NMR shows a hydride at −9.3 ppm (quartet) and $J_{H-P}$ is given as ±14 Hz.⁴

It was also necessary to investigate whether or not this change in ratio affected the complex formation of the catalytic species and as with the smaller ratio we compared our ligand to our own study of PPh₃ as well as the literature.
2.6.1 Spectroscopic study of Rh: P = 1:10

Very little difference in the room temperature HPIR spectra for the 1: 5 and 1: 10 solutions under CO / H\(_2\) was observed, see HPIR 2.6.1.1.

Once pressurised, both ratios show three peaks in their IR spectra, the large broad singlet and two smaller peaks from the carbonyls in [Rh(acac)(CO)\(_2\)]. The NMR results initially appeared different but this was explained simply as a matter of [P]. A large broad peak in both spectra, see NMR 2.6.1.1 arose from the fluxional exchange of the free ligand with the [Rh(acac)(CO)(PPh\(_3\))] square-planar complex and it was only the [P] in the two solutions which gave the different results for 1: 5 and 1: 10 Rh: P; 5.3 ppm and –0.1 ppm respectively. The evidence from the IR, which has a much faster timescale than NMR and is unaffected by fluxional exchange, showed the same species present in both solutions.
Chapter 2: A Mechanistic Study

NMR 2.6.1.1 HPNMR spectrum of (i) Rh: P(C₆H₄C₆F₁₃)₃ (1: 5) and (ii) Rh: P(C₆H₄C₆F₁₃)₃ (1: 10) at RT and CO/H₂ (20 bar)

After 2 hours of heating the solution (Rh: P = 1: 10) to 70°C whilst stirring in the HPIR cell, we observed the formation of five bands at ν: 2055 (m), 2036 (sh), 2004 (s), 1993 (sh), 1973 (w) cm⁻¹, as shown in HPIR 2.6.1.2, this spectrum was very similar to the corresponding spectrum at the lower phosphine ratio, suggesting very little difference between the two solutions. A small peak was also observed at 1720 (w) cm⁻¹, which was slightly low for a bridging carbonyl and was in fact into the triply-bridging carbonyl region (1620 – 1730 cm⁻¹), it was unclear if this was a triply-bridging carbonyl or an overtone of some aromatic or alkyl group.
Very similar results were observed with a triphenylphosphine solution under the same conditions; on initial heating to 70°C under pressure seven new peaks appeared, ν: 2080 (w), 2044 (s), 2025 (w), 1997 (s), 1988 (s), 1955 (s), 1941 (sh) cm⁻¹. See HPIR 2.6.1.3

We assigned the weak band observed at 2080 cm⁻¹ to [Rh(acac)(CO)₂] with the second expected peak for this species hidden under the other carbonyl bands in that region. Although there may seem to be more bands in the triphenylphosphine spectrum, the large broad peak at 2004 cm⁻¹ in the fluorinated ligand spectrum was not quite symmetrical, which suggested that there might have been more than one
vibration causing this band. This would correlate with the two bands observed very close together at 1997 and 1988 cm\(^{-1}\) in the PPh\(_3\) spectrum. Unfortunately due to the shift of bands, caused by the high electronegativity of the fluorinated ligand, these shifts may appear much closer together and more difficult to distinguish. In comparison, Wilkinson quoted 2038 (\(v_{\text{RhH}}\)) and 1980 and 1939 (\(v_{\text{CO}}\)) cm\(^{-1}\) for the hexane solution spectrum of [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)] and for the same complex isomers, van Leeuwen quoted the 2-methyl tetrahydrofuran solution spectrum as having four peaks at 2042, 1992, 1981 and 1947 cm\(^{-1}\), as reported earlier see section 2.5.1. In the 70°C solution of Rh: PPh\(_3\) (1: 10) under CO / H\(_2\) (15 bar) we again observed the two isomers of bis(triphenylphosphine) rhodium dicarbonyl hydride, [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)]. By venting the cell and pressurising with CO / D\(_2\) we confirmed this and distinguished between the bis-phosphine isomers with both the phosphine ligands in the equatorial plane of the complex and one with one phosphine \textit{trans} to the hydride, as shown in HPIR 2.6.1.4 at 70°C the intensities of the bands is the only difference between this spectrum and the corresponding Rh: PPh\(_3\) = 1:5 spectrum.

![HPIR 2.6.1.4 Rh: PPh\(_3\) (1: 10); Red = 70°C CO/H\(_2\); Blue = 70°C CO/D\(_2\) (20 bar)](image)

The four peaks for the two bis-phosphine isomers were much clearer under a deuterium atmosphere and confirmed that at 70°C, in a solution with a Rh: PPh\(_3\) ratio
Chapter 2: A Mechanistic Study

of 1: 10, the hydridodicarbonyl-bis(triphenylphosphine)rhodium \([\text{RhH(CO)(PPh}_3)_2]\) complex was formed. Interestingly, when these spectra were compared to those in HPIR 2.5.1.2, at a lower phosphine concentration, it was noted that the relative intensities of the bands was quite different. Although both spectra showed bands in the same positions their intensities differed quite noticeably; the spectra for the solution with lower phosphine concentration showed bands at 2044 and 2025 cm\(^{-1}\) to be approximately half the absorbance of the four other bands observed at 1996, 1988, 1974 and 1956 cm\(^{-1}\) under a CO / H\(_2\) atmosphere. But with a higher phosphine concentration, under the same conditions, the spectra showed the band at 2025 cm\(^{-1}\) to have a much lower absorbance and no band was observed at 1974 cm\(^{-1}\). When both solutions were placed under a CO / D\(_2\) atmosphere, they both showed four bands at 2024, 1997, 1972 and 1955 cm\(^{-1}\), but the intensities of the bands differed here too; at the lower Rh / P ratio the band at 1955 cm\(^{-1}\) had a much lower absorbance than the other three bands. The spectrum for the higher Rh / P ratio, showed the bands at 1997 and 1955 cm\(^{-1}\) to be almost half of the absorbance of the other two. This difference of intensities of bands suggested a difference in concentration of the species in the different solutions and was also observed to a lesser degree with the perfluorinated ligand solutions as described below.
Similarly, with the perfluorinated ligand under the same conditions a shift of bands was observed and correlated with that already seen and described for the P/Rh = 5 solution. In the deuteriated solution spectrum, the blue line in HPIR 2.6.1.5, six large bands were observed at \( \nu \): 2073 (m), 2038 (s), 2025 (w), 2011 (w), 1992 (s) and 1983 (s) cm\(^{-1}\). Upon the deuteriation of the cell the bands at 2058 and 2003 cm\(^{-1}\) disappeared and two peaks appeared in the deuteriated solution at 2025 and 1983 cm\(^{-1}\). These spectra were very similar to those for the solution with lower phosphine concentration, shown in HPIR 2.5.1.5. Like the triphenylphosphine solutions the intensities of the bands at the different Rh / P ratios differs, but not quite as markedly; under a deuteriated atmosphere the shoulder at 1984 cm\(^{-1}\) was not as pronounced in the Rh / P = 1/5 spectrum as it is in HPIR 2.6.1.5. These bands corresponded to the bis-phosphine complex with both phosphine ligands in equatorial positions, with a carbonyl \( \text{trans} \) to the hydride. The two bands that remained unmoved at 2038 and 1992 cm\(^{-1}\) were attributed to the bis-phosphine complex with one phosphine in the apical position and the other in the equatorial position. However, these band assignments only account for four of the six bands observed in the deuteriated spectrum, the other two being 2073 (m) and 2011 (w) cm\(^{-1}\). It was possible that the
small peak at 2011 cm\(^{-1}\) was hidden in the hydrogen spectrum by the larger peak at 2003 cm\(^{-1}\), but unclear if the “new” band at 2073 cm\(^{-1}\) was a different species or an overtone from some unidentified species. In the HP-NMR spectra for the Rh: \{P(C_{6}H_{4}C_{6}F_{13})_{3}\} = 1: 10 solution, a slightly broad doublet was observed after 1 hour at 70\(^{\circ}\)C pressurised with CO/H\(_{2}\) (20 bar), \(^{31}\)P NMR \(\delta\): 38.5 (d, \(J = 159\) Hz) and the \(^{1}\)H NMR spectrum showed a single metal hydride peak at -9.7 ppm. The high temperature of this NMR spectrum reduced the resolution of the spectrum. The HPIR spectra were recorded at 70\(^{\circ}\)C and after the solution had been cooled to RT. The only difference at the lower temperature was a slight shift of the peaks and an increase in the intensity of the peak at 1970 cm\(^{-1}\), but we can assume from this that the RT HP-NMR spectrum will be representative of the higher temperature solution. The species formed at reaction temperature are not temperature dependent and do not form other species at RT although any equilibrium between the species may be temperature dependent. Therefore the RT spectra of this catalytic solution provided much more useful information and are shown below in NMR 2.6.1.2. In the \(^{31}\)P NMR, two doublets were observed at 38.9 and 37 ppm with coupling constants of 156 and 148 Hz respectively. The large singlet at –5.6 ppm was assigned to the free ligand. The \(^{1}\)H spectrum showed a well-defined quartet in the metal-hydride region at –9.65 (\(J = 25, 11\) Hz) ppm which indicated the presence of the hydridocarbonyl tris(phosphine) complex together with a weaker resonance at –9.6 ppm.
The two sets of doublets matched with the literature values for 
[RhH(CO)(PPh\(_3\))] and [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)]\(^4\), \(^{31}\)P NMR 42.5 ppm, \(^1\)J\(\text{RhP} = 155\) Hz and 37.3 ppm, \(^1\)J\(\text{RhP} = 138.7\) Hz respectively. The large discrepancy in intensity of the two signals explained the weak hydride signal in the \(^1\)H spectrum and the fact that only one metal-hydride signal was observed. This data is not significantly different from that obtained with a [Rh]: [P] = 1:5 except that both the broad singlet at –9.6 and the doublet at 37 ppm are weaker in this sample.

The \(^{31}\)P NMR spectrum of the PPh\(_3\) solution, under similar conditions, showed only one doublet at 36.8 ppm with \(^1\)J\(\text{RhP} = 138\) Hz and this correlated nicely with the literature for the hydrido-dicarbonyl-bis(triphenylphosphine) rhodium complex. The
$^1$H NMR at RT shows a broad peak at $-8.8$ ppm. This also matched the data published by Brown and co-workers for the bis-phosphine complex.

By considering this data with the HPIR spectra for the fluorinated ligand we have suggested that the extra peak in the spectrum at $70^\circ$C under CO / D$_2$ arose from the presence of the tris-phosphine rhodium complex. The assignment of the peaks in the perfluorinated ligand system, so far, left the band at 2037 (m) cm$^{-1}$ in the CO / H$_2$ spectrum to have arisen from the tris-phosphine complex, however Vaska reported two peaks arising from the IR spectrum of the crystallised form of [RhH(CO)(PPh$_3$)$_3$]$^2$ v$_{\text{MH}}$ 2041 cm$^{-1}$ and v$_{\text{CO}}$ 1923 cm$^{-1}$ (nujol mull). Under a deuterium atmosphere the carbonyl band moved to 1954 cm$^{-1}$ and the metal-hydride band disappeared from the carbonyl region. Wilkinson reported similar values for the solid nujol mull spectrum but in cyclohexane solution he reported the two peaks to have appeared at 2005 cm$^{-1}$ ($\nu_{\text{RhH}}$) and 1935 cm$^{-1}$ with only a single peak appearing in the deuteriated spectrum at 1960 cm$^{-1}$. These data do not correlate well with the band assignment in the perfluorinated ligand system, however the HP-NMR data does seem to corroborate the presence of both the tris- and bis- phosphine complexes, with the tris phosphine complex being the more abundant. This was possibly the reverse in the HPIR spectra as the stirring and gas mix are better in the HPIR cell.

2.6.2 Hydroformylation

As described before, the initial investigations of hydroformylation in a fluorous biphasic system were carried out with a 1: 10 Rh: P ratio. To understand if reducing this ratio altered the reactivity at all, a spectroscopic study of this ratio was also carried out.
The catalyst was pre-formed under hydroformylation conditions, the cell was then cooled to room temperature and depressurised to allow for the addition of octene to the cell, which was re-pressurised with CO / H₂ (20 bar) and returned to the spectrometer. The resulting $^{31}$P NMR spectrum at room temperature showed a broad singlet at –4.5 ppm and a smaller broad signal at 26 ppm, along with the singlet of triphenylphosphine oxide, see NMR 2.6.2.1. No doublet was observed, which implied that the bis-phosphine complex had reacted with the octene and suggested that the peak observed at 26 ppm might have been due to an acyl-rhodium complex, this is similar to the Rh/P = 1/5 spectrum shown in NMR 2.5.3.1. A small hydride signal was observed at –9.5 ppm, but due to noise in the spectrum no coupling was observed.

The solution was heated to 70°C, to simulate reaction conditions and held there for 1 hour, NMR 2.6.2.2. The higher temperature spectra were less well resolved, but a small metal hydride signal was observed in the $^1$H NMR at –9.4 ppm. The $^{31}$P NMR at 70°C showed two signals, a sharp singlet at 22.6 ppm was assigned to the triphenylphosphine oxide and a broad singlet at –2 ppm was assigned to the free triphenylphosphine ligand, with the shift due to the change in temperature, although some fluxional exchange of free ligand with other complexes may also be involved. When this solution was cooled to room temperature the hydride signal was lost and...
the $^{31}$P NMR spectrum, again showed two peaks; the oxide and free ligand, with no clearer resolution at this lower temperature. Due to the absence of any other signals in the room temperature spectra, the solution was not investigated further.

A similar experiment was carried out in the HPIR cell, however the octene was injected into the pre-formed catalyst solution at reaction temperature and a series of spectra were recorded. As described previously, at 70°C, CO / H$_2$ (15 bar) five bands were observed in the carbonyl region of the spectrum for Rh: PPh$_3$ = 1: 10, as shown in HPIR 2.6.2.1. Upon the immediate addition of octene, very small changes to these five bands were observed; a slight separation of the two bands at 1995 and 1986 cm$^{-1}$. Two bands were observed arising from octene at 1822 and 1640 cm$^{-1}$ as well as a band at 1734 cm$^{-1}$ from nonanal and gave an indication of the speed and activity of this catalytic system.
After ten minutes of hydroformylation the band from nonanal had saturated and broadened and after 30 minutes the octene band observed at 1822 cm\(^{-1}\) had decreased in intensity and been obscured by the broad nonanal band. A small band at 1640 cm\(^{-1}\) indicated that some octene remained in solution, but after 35 minutes this was not observed, HPIR 2.6.2.2. In the terminal carbonyl region, four peaks were observed at 2043, 1996, 1985 and 1954 cm\(^{-1}\), the band at 2024 cm\(^{-1}\) had disappeared beneath the broadening band at 2043 cm\(^{-1}\). Therefore, even under hydroformylation conditions and in the presence of octene we continue to observe the [RhH(CO)\(_2\)(PPh\(_3\))\(_2\)] complexes.

HPIR 2.6.2.1 Rh: PPh\(_3\) (1: 10) CO / H\(_2\) (20 bar) at 70°C BLUE: without octene, RED: on addition of octene.
Any discrepancies observed between the NMR and HPIR results for hydroformylation of octene may be explained in part by the poor gas mixing of the HPNMR cell which may have led to gas starvation of the hydroformylation reaction and meant that some intermediate complexes were more prevalent in the solution, as the doublet arising from the bis-phosphine complex was not observed under hydroformylation conditions in the poorly stirred HPNMR cell, but the carbonyl bands arising from these complexes in the HPIR were almost completely unchanged upon the addition of octene. The efficient stirring of the HPIR cell allowed the reaction to proceed at a normal rate, which meant that the intermediate species were too short lived for observation. Had this reaction been repeated under a CO atmosphere, further species may have been observed.

When the hydroformylation of octene by [Rh(acac)(CO)$_2$] and P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$ (1:10) was carried out in the HP NMR cell under a CO atmosphere, a broad doublet was observed at 38 ppm ($^1J_{Rh-P}$ = 158.5 Hz), (tris-phosphine complex) along with a singlet at 21 ppm (phosphine oxide) and a broad singlet at –4 ppm in the $^{31}$P NMR, NMR 2.6.2.3. The $^1$H NMR showed a poorly resolved quartet signal at –10 ppm. Unlike the lower ratio solution no other signals were observed. This indicated
that the prevalent species observed during hydroformylation in the NMR was hydridocarbonyltris-(triphenylphosphine)rhodium(I) \([\text{RhH(CO)(PPh}_3]_3\)).

The solution was heated to 70°C and spectra were recorded after an hour and once the cell had cooled to room temperature, NMR 2.6.2.4. The \(^{31}\text{P}\) NMR spectrum at room temperature was very similar to the equivalent spectrum recorded for the \(\text{Rh: P} = 1:5\) ratio NMR 2.5.3.1, but less well resolved, this was possibly due to the higher concentration of free phosphine. Instead of a broad doublet at 23 ppm, a broad signal was observed in the same position along with a sharp singlet at 20 ppm (phosphine oxide). No hydride signal was observed at this temperature.
NMR 2.6.2.4 Rh: \( \text{P(C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_3 \) (1: 10) and octene, CO (20 bar) cooled to room temperature.

The solution was cooled further, to \(-20^\circ\text{C}\), at which temperature the \( ^{31}\text{P} \) NMR spectrum showed a number of separate signals, NMR 2.6.2.5, \( \delta \): 38.9 (d, \( J \approx 157 \text{ Hz} \)), 26 (broad multiplet), 23.4 (d, \( J \approx 76.2 \text{ Hz} \)), 22.2 (s, \( \text{C}_6\text{H}_4\text{C}_6\text{F}_{13})_3\text{P} = \text{O} \)), 19.8 (d, \( J = 145 \text{ Hz} \)), 15.1 (d, \( J = 154.9 \text{ Hz} \)) and \(-6 \) (s, free ligand) ppm. This spectrum also appeared to be very similar to the lower ratio solution (Rh: \( \text{P} = 1:5 \)), but at this higher Rh/P ratio a small amount of the bis-phosphine complex was observed at 38.9 ppm, the three doublets between 15 and 25 ppm were observed in both spectra and have been assigned in the previous section, section 2.5.3. Due to these spectra being recorded under a CO atmosphere the doublet at 15 ppm was assigned to the acyl complex \([\text{Rh(C(O)C}_8\text{H}_{16})(\text{CO})_2(\text{P(C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_3)]\) and the two smaller peaks were assigned to rhodium dimer complexes \([\text{Rh(CO)})_2(\text{P(C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_3)]_2\) and \([\text{Rh}_2(\text{CO})_3(\text{P(C}_6\text{H}_4\text{-4-C}_6\text{F}_{13})_3)]_3\).
Chapter 2: A Mechanistic Study

NMR 2.6.2.5 Rh: P(C₆H₄-4-C₆F₁₃)₃ (1: 10) with octene, CO (20 bar) cooled from 70°C to -20°C.

HPIR 2.6.2.3 Rh: P(C₆H₄C₆F₁₃)₃ (1: 5) 70°C GREEN: CO/H₂ (15 bar), RED: CO (10 bar)

The HPIR of the equivalent solution in n-hexane was recorded under similar conditions. As with all previous solutions, this was initially heated under CO / H₂ (15 bar) to 70°C for an hour, before being cooled to 30°C, vented, re-pressurised with CO (10 bar) and re-heated to 70°C. The difference in spectra under CO / H₂ and CO is illustrated in HPIR 2.6.2.3. In the absence of H₂, we observed a small amount of a bridging carbonyl appear at 1790 cm⁻¹, which suggested the formation of a bimetallic complex as previously discussed in the HPNMR spectra. Under CO (10 bar) and at 70°C, the terminal carbonyl region of the spectrum showed bands of similar frequency as those in the CO / H₂ spectrum, but with different intensities: ν: 2072.8 (w), 2062 (w), 2050 (sh), 2039.1 (m), 2020.2 (sh), 2004.9 (m), 1990 (sh) and 1981.7 (m). This was not an unexpected result, as the change in concentration of H₂ in the cell will have affected the equilibrium that exists between the Rh-phosphine complexes. This
in turn supported the assignment of the HP-NMR for this solution, when cooled to –
20°C. The three bands observed at 1925 (w), 1809 (w) and 1602 (s) cm\(^{-1}\) were all
assigned to the free ligand, by comparison to the spectrum of the ligand in hexane.

HPIR 2.6.2.4 Rh: \(\text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_3\) (1: 5) 70°C CO RED: 10 bar , AQUA: 15 bar and octene added.

Upon the addition of octene to the solution, HPIR 2.6.2.4, the terminal
carbonyl region of the HPIR spectrum showed an increase in intensity of the band at
1987 cm\(^{-1}\), octene and nonanal bands were observed at 1822 and 1640 cm\(^{-1}\) and 1735
\(\text{cm}^{-1}\) respectively. This indicated that upon venting the cell, a small amount of
hydrogen must have remained in solution to allow hydroformylation to occur. This
spectrum did not show any change after 90 minutes of reaction, except for a decrease
in the concentration of octene and an increase in nonanal. It is possible that the band
at 1987 cm\(^{-1}\) arose from the acyl complex \([\text{Rh(C(O)C}_8\text{H}_{16})(\text{CO})_2(\text{P(C}_6\text{H}_4-4-
\text{C}_6\text{F}_{13})_3)_2]\), as discussed earlier. According to the literature we should also have
observed a band around 1950 cm\(^{-1}\) and an acyl stretch around 1600-1640 cm\(^{-1}\), the
broad peak from the octene and free ligand, may have obscured this band.

### 2.7 Conclusions

The differences between the [Rh]: [P] = 1: 5 and 1: 10 HPIR and HPNMR
spectra for the perfluorinated triphenylphosphine and PPh\(_3\) ligands, were not great.
However, at the higher [P] the spectra were slightly better resolved, which we had hoped would allow further assignment especially in the HPIR of [RhH(CO)(P(C₆H₄C₆F₁₃)₃)₃]. However, the bands for this species were not observed or distinguished and so we can only rely upon the HPNMR data to indicate the presence of [RhH(CO)(P(C₆H₄C₆F₁₃)₃)₃] in the reaction mixture, under reaction conditions.

Interestingly, the perfluorinated triphenylphosphine ligand formed both [RhH(CO)₂(P(C₆H₄C₆F₁₃)₃)₂] and [RhH(CO)(P(C₆H₄C₆F₁₃)₃)₃], whereas the corresponding PPh₃ spectra only showed the formation of the [RhH(CO)₂(PPh₃)₂] along with another unidentified species. This discrepancy may help to explain the increased selectivity observed with the fluorinated ligand and also explains in part the low levels of [Rh] and [P] leaching recorded in the initial batch reaction as the wt% fluorine is greatly increased by the presence of a third ligand, which in turn will also aid in the increased enveloping of the metal centre, increasing its preferential solubility in the fluorinated solvent.

It appears from this spectral analysis that the change in concentration of [P] in the catalytic solution had very little influence, on this scale, on the complexes, which were formed.

By investigating the hydroformylation of octene in situ with the HPIR and HPNMR spectroscopy we were able to identify the acyl species, under a CO atmosphere and observed the speed of rhodium catalysed hydroformylation, by the almost instant formation of nonanal upon addition of octene.

Further analysis of the low temperature triphenylphosphine NMR may provide more information as to the species, which formed and resulted in the doublet of triplets in the ¹H NMR with the unusually high Rh coupling. This experiment was
repeated and yielded the same ambiguous data, of one P signal with two hydrides. Had time allowed, a deeper study would have been made to identify the other species, but it is highly probable that they were formed due to starvation of gases in the HPNMR cell and so may not be indicative of the actual reaction conditions.

2.8 Reference List


Chapter 3

Hydroformylation: Batch and Continuous Flow Reactions
3 Hydroformylation: batch and continuous flow reactions

3.1 Introduction

Hydroformylation was the first experiment used to demonstrate the method of fluorous biphasic catalysis by Horváth.\textsuperscript{1} The commercial importance of the aldehyde products as well as the considerable experience of this reaction in St Andrews made this an obvious choice for the continuous flow operation of the fluorous biphasic system. The required rig was designed and built in the Chemical Engineering Department of University College London (Perperi and Manos).

3.2 Batch Reactions

An initial investigation of suitable ligands was carried out in this group and has been fully described elsewhere.\textsuperscript{2} This investigation showed that the fluorinated phosphine $\text{P(4-C}_6\text{H}_4\text{C}_6\text{F}_{13})_3$ and phosphite $\text{P(O-4-C}_6\text{H}_4\text{C}_6\text{F}_{13})_3$ gave better results for the hydroformylation of 1-octene, in terms of rate and selectivity, compared with their non-fluorous analogues $\text{PPh}_3$ and $\text{P(OPh)}_3$, see Table 3.2.1. Due to the poor stability of the perfluoro-phosphite ligand under reaction conditions, the perfluoro-phosphine analogue was chosen for further study. This group has previously reported that the leaching of the catalyst (0.05 %) and the phosphine (0.3 %) into the organic phase was minimal, in individual batch reactions with a high conversion to nonanal (nearly 100 %). Partition studies have shown that at lower conversions the solubility of the ligand and catalyst complex was higher because of the higher concentration of the less polar 1-octene.\textsuperscript{3} These results were obtained in a small batch reactor that did not incur any mass transport problems. However, partition studies have shown that leaching is reduced by an increase in the conversion and as these reactions were carried out to
almost 100 % conversion, we would expect a very low loss of rhodium and phosphine to the organic phase. At low conversions, significant loss of phosphine is expected as the phosphine is much more soluble in octene than nonanal.

<table>
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<tr>
<th>Ligand</th>
<th>Solvent</th>
<th>[Rh] (mM)</th>
<th>[P] (mM)</th>
<th>T (°C)</th>
<th>Isom (^b) (%)</th>
<th>Conv. (^c) (%)</th>
<th>Linear selectivity (%)</th>
<th>L:B</th>
<th>TOF (h(^{-1}))</th>
<th>[Rh] (^d) (% loaded)</th>
<th>[P] (^d) (% loaded)</th>
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<td>6.0</td>
<td>70</td>
<td>3.9</td>
<td>97.6</td>
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<tr>
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<td>30.0</td>
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<td>13500</td>
<td>0.23</td>
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Table 3.2.1 Data from initial batch reaction studies of FBC system\(^2\): \(^a\) Reaction Solvent 4 cm\(^3\) of toluene (T), perfluoro (1,3-dimethylcyclohexane) (F1), perfluoromethylcyclohexane (F2) or a mixture of 2 cm\(^3\) each of toluene and perfluoro (1,3-dimethylcyclohexane) (T/F1), \(^b\) Percent of product by mole fraction. Isom = sum (2, 3- and 4-octene), \(^c\) Conversion (100 % residual 1-octene), \(^d\) Rhodium and phosphine lost to organic phase. Given as the % of rhodium or phosphine loaded initially in reactor.

3.3 Continuous Flow Hydroformylation

The continuous flow rig, Figure 3.3.1., was designed specifically for the hydroformylation of oct-1-ene in a fluorous biphasic system. The catalyst solution and substrate were pumped, through two HPLC pumps, into a continuous stirred tank reactor, heated and pressurised (70°C and 15 bar CO / H\(_2\)). The reaction mixture was removed from the reactor by a dip tube to a specially designed separator where the catalyst phase could be recycled through the HPLC pump into the reactor and the organic product phase was simply collected through an overflow. This system allowed the two pumps to work continuously at a slow feed rate eventually recycling the catalyst phase (once equilibrium had been reached) and introducing new substrate
to the reactor. Samples were collected by this overflow and analysed by GC to give the data shown in this chapter. For a detailed description of the operation of this equipment, see the experimental chapter, section 4.3.

3.3.1 First Continuous Flow Experiment

![Figure 3.3.1 Rig for Continuous Fluorous Biphasic Hydroformylation](image)

**Figure 3.3.1 Rig for Continuous Fluorous Biphasic Hydroformylation**

**Figure 3.3.1.1 GC data for Continuous Hydroformylation of Octene in fluorous biphasic system**

![Graph showing conversion over time](image)
This experiment was carried out under CO/H\textsubscript{2} (1:1, 15 bar), with [Rh] = 1 mmol dm\textsuperscript{-3} in the reaction mixture and P: Rh = 10:1 at 70 °C. It was recorded over 8.5 hours, when it was stopped overnight. Samples were collected every 15 minutes for the first two hours and every half hour thereafter. These samples were analysed by GC for their compositions and the results are shown in the graph above (Figure 3.3.1.1).

The experiment was continued the following morning and run for a further 8.25 hours, at which point a blockage caused the reaction to be stopped. The initial results recorded for this experiment demonstrate the expected initial drop in conversion to aldehyde due to the move from batch to continuous mode in the reactor. The marked increase in isomerised octenes around 9.5 hours can be attributed to the stoppage of the reaction overnight, leaving octene to react with the catalyst under the low pressure and temperature conditions of the separator.

ICPMS analysis of the collected organic phase, from the first 8.5 h, showed significant Rh loss from the fluorous phase and are shown in Figure 3.3.1.2. It is worth noting that the extremely high concentration of rhodium in the sample collected after 3 hours 40 min corresponds to the point of lowest conversion to nonanal, which explains this result when considered with the evidence that rhodium leaching increases at lower conversions. The extent of leaching is hundreds of times greater than the leaching recorded in the batch reactions carried out by Doug Foster previously\textsuperscript{2}.
3.3.2 The Second Experiment – Rh:P = 1:5

In an attempt to reduce the precipitation and blocking of the capillaries by excess phosphine or phosphine oxide, the phosphine concentration was halved from that in the previous reaction (5:1 instead of 10:1 P: Rh). Initially the experiment was run with the reactor closed to the continuous flow to allow a batch reaction to run for 1 hour. It was hoped that this would maximise the conversion and reduce the leaching of the catalyst. Once the reactor was opened to the continuous flow system the
conversion dropped from 27 % to 20 % selectivity to nonanal, as was observed from the data obtained from samples collected from the overflow port on the separator, which were analysed by GC-FID to give the graph above in Figure 3.3.2.1. The conversion to nonanal continued to drop until the composition of the reaction mixture in the reactor and separator was the same and a steady state was achieved after 3 hours. However, the steady state was only maintained for 2-3 hours and from 5 hours, an increase in the rate, as expressed by the conversion to nonanal, was observed. This was attributed to a loss of phosphine to the organic phase. The rate of the hydroformylation reaction is inversely proportional to the concentration of phosphine, [P]. The loss of phosphine to the organic phase was emphasised by the precipitation of phosphine oxide in the collection vessel, which was open to air. Eventually, the conversion began to drop again because there was insufficient phosphine ligand to maintain the rhodium as a preferentially fluorous-soluble complex. A decreasing [Rh] in the reactor, as well as the lower activity of [RhH(CO)$_n$P$_4$ -$a$], $n = 3, 4$, than of [RhH(CO)$_2$(PPh$_3$)$_2$] accounts for the drop in rate towards the end of the reaction. Although this reaction never attained the high conversions observed in the batch reactions, the continuous flow hydroformylation did run for 21 hours and achieved >15 000 catalyst turnovers, which averages to a rate of >750 h$^{-1}$. Although there remains room for improvement, this experiment was a good indication of the feasibility of the designed Continuous Flow Reactor (CFR) demonstrating a maximum conversion to nonanal of 40 %.

### 3.3.3 Miscellaneous Continuous Flow Reactions

Subsequently a number of continuous flow reactions were carried out with particularly low and disappointing conversions and high levels of phosphine oxidation. With stringent steps taken to degas the PFMC and reactor system before
each reaction, the only other possible source of oxidation was from peroxides in the octene feed. Until this time, the octene had been degassed by bubbling argon through the solvent for 1-2 hours. Better purification was required and so the octene was treated by shaking with a saturated solution of iron (II) ammonium sulfate, under anaerobic conditions and was then passed through an alumina column under argon.

Another possible cause of low conversion in the continuous flow operation was an insufficient residence time of substrate in the reactor. The residence time was controlled by the flow rate of the system, which was controlled by the length of the capillaries between the reactor and the separator and was dependent upon the pressure in the reactor to force the reaction mixture through the capillary. Therefore, to increase the residence time in the reactor the CO/H₂ pressure of the overall system was reduced from 20 bar in the initial batch reactions to 15 bar in the CFR.

With these changes made to a system we had previously considered optimised, we were no longer sure if the batch reaction at the start of each continuous flow experiment was running at optimal conversion. It was necessary to repeat some of the initial batch reactions with these new conditions to ensure that we were working to as close to 100% conversion as possible. In the initial batch reactions, the catalyst had been preformed for an hour under the reaction conditions before addition of the substrate. In the CFR, the fluorous and organic phases mixed at room temperature before reaching the reactor. It was necessary to investigate what difference this step made to the activity of the catalyst solution. By carrying out two batch reactions under the CFR, conditions but pre-forming the catalyst before the addition of the octene in one and not in the other it was possible to observe any differences that these small changes made to the overall activity of the reaction. It was found from analysis
of the gas uptake curve of each that by not pre-forming the catalyst the reaction took almost twice as long to reach completion.

With the preformed catalyst the reaction had reached completion within an hour of adding the substrate and the gas uptake plot was found to be fitted best by a double exponential, with two sequential reactions with rates of $1.36 \times 10^{-3}$ s$^{-1}$ and $5.88 \times 10^{-3}$ s$^{-1}$. This suggests that two simultaneous and competitive reactions are occurring; hydroformylation and isomerisation perhaps. However, the overall isomerisation in the reaction, from the GC data is shown to be low and so it is more likely that this double exponential arises as a function of the partition coefficients between the fluorous phase and the nonanal.

Without preforming the catalyst, the second batch reaction took twice as long to reach 100% conversion to aldehyde and again the gas uptake curve was best fitted by a double exponential, with two sequential reactions with rates of $0.86 \times 10^{-3}$ s$^{-1}$ and $2.47 \times 10^{-3}$ s$^{-1}$. This suggested that the initial batch reaction when running a CFR experiment would need to be run for 2 hours before setting the reactor to continuous flow, to ensure as high an initial conversion as possible and reduce the extent of leaching to the organic phase.

It may have been more advantageous to adapt the reactor to allow for two separate inlets of the two phases, but to avoid modifying the rig; a longer initial batch reaction was opted for. This, along with the more efficiently purified 1-octene was anticipated to improve the efficiency of the CFR and allow longer reactions at higher concentrations.
3.3.4 The Third Experiment – purification of octene

![Graph showing conversion to aldehyde and isomerised octenes over time]

The first experiment to include all these modifications to the running of the CFR was carried out over two days, running continuously for 30 hours and the results are shown above, Figure 3.3.4.1. The gas flow meter had been removed from the system due to a malfunction, so the pressure was maintained and monitored by the regulator on the CO/H₂ cylinder and the pressure gauge on the reactor during this experiment. The pressure did not drop below 16 bar CO/H₂ throughout the reaction, however after 24 hours the pressure rose slightly to 20 bar at 26 hours, from where it dropped to 16 bar again by the end of the reaction (30 hours).

After the first batch reaction the initial conversion to nonanal was 45 %. The second sample was not collected until the separator had begun to overflow, but showed a higher conversion to nonanal of 56 %, total conversion to aldehyde was 66 %. Over the course of the next 6 hours, under continuous flow mode, the conversion dropped to a steady state of ca.26 % nonanal, where it remained for 13 hours, only
rising slightly in this time. This was still not as high a conversion as we had hoped to obtain under the continuous flow operation.

After 23 hours, the familiar steep increase in rate, indicative of the loss of phosphine to the organic phase, was observed, reaching a peak of conversion at 45 % nonanal and rapidly dropping away over the final 7 hours until the conversion to nonanal was less than 15 %. Interestingly the conversion to isomerised octene was equal to the conversion to nonanal for much of the reaction (20 %).

Generally, such high isomerisation indicates poor mass transfer of the gas into the homogeneous liquid phase. This is easily explained by examining the reaction mechanism for the hydroformylation reaction. When the alkene reacts with the Rh – complex, if there is no CO to insert into the Rh-alkyl bond, the alkene is released in either its original form or the double bond moves away from the terminal carbon causing isomerised alkenes which are likely to undergo further isomerisation if no carbonyl groups are available. It is perhaps easier to see the formation of the isomerised octenes from the depiction in, Figure 3.3.4.2. Depending upon the addition of the alkene across the double bond, two possible products can be released if no further reaction occurs, as would be the case if the system were starved of CO/H₂.

![Figure 3.3.4.2 Formation of isomerised Alkenes during Hydroformylation](image-url)
The inefficient stirring is best understood by considering the position of the stirring mechanism within the biphasic system that exists inside the reactor. Not only will there be two liquid phases during the reaction, the nonanal is immiscible with PFMC even under reaction conditions, but there is the third, gas phase, also to be considered. The small-scale batch reactions carried out for kinetic studies do not pose any mass transfer problem due to the small total volume (5 cm$^3$).

Consider the diagrams in Figure 3.3.4.3, depicting the possible positions of the stirrer’s paddles. By altering the position of the paddles within the reaction mixture, we can affect the efficiency of the mixing or in order to improve the mass transport within the reactor a gas entrainment stirrer can be introduced. This stirring attachment has a hollow shaft with a hole at the top through which gas can enter and the suction created by stirring pulls the gas down and out into the liquid at the paddles of the stirrer.

Figure 3.3.4.3 Schematic of position of Stirrer and Sparge Stirrer affecting mixing
3.3.5 Experiment 4: The Gas Entrainment Stirrer.

In this final continuous flow experiment, the only difference made to the reactor and procedure was the introduction of a gas entrainment or sparge stirrer, to improve the mass transport of gas into the liquid phase during the reaction. This experiment was carried out over 46 hours, stopping after the conversion to nonanal had dropped below 30 %, Figure 3.3.5.1.

The heat exchanger had been removed from the system as it previously had been proved superfluous and merely dead volume of reaction mixture. In doing this, we reduced the time of flow from the reactor to the separator.

Catalyst leaching is known to be higher at lower conversions to nonanal, therefore to ensure minimal catalyst loss, the initial batch reaction was run for 2 hours, which gave an overall conversion of 89 % with a selectivity to nonanal of 70 %. A batch reaction carried out under the same conditions in a system where mass transport limitations do not occur gave nearly 100 % conversion in the same time. This suggests that the mixing in the continuous reactor may still not be completely

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Figure 3.3.5.1 Continuous flow hydroformylation with Gas Entrainment Stirrer
efficient. Once the initial batch reaction was complete and the system had been filled from the reactor to the separator with 1:1 fluorous: organic solvent mixture, the reactor was refilled to replace the removed liquid volume. A second batch reaction was carried out to increase the polarity of the organic phase and reduce the catalyst leaching before setting the system to continuous flow mode. For this reaction, the flow rate of both liquid phases was set to 0.3 cm$^3$ min$^{-1}$. A more efficient sampling method was used in this reaction. A syringe removed a sample from the separator immediately after the first batch reaction and we observed the conversion and selectivity to nonanal to match the results observed in the test batch reactions, when mass transport was not an issue due to the size and volume of reactor and reaction mixture.

The results over the first 7 hours show the expected drop in conversion corresponding to the switch from batch to continuous mode and the results then level off at ca. 30%, which is significantly lower than the expected drop in conversion likely to occur from the change in batch to continuous mode. ICPMS analysis, Figure 3.3.5.2, of several samples of the organic phase collected over the course of the reaction showed a remarkably high concentration of Rh ~300 ppm within the first hours of the reaction. This large loss of rhodium from the system may explain the significant reduction in conversion observed as the reactor was set to continuous flow.

Why such a considerable loss of rhodium occurs so early in the reaction is unclear. One hypothesis could be that mixing both the catalyst solution and the substrate at room temperature with CO/H$_2$ does not allow all the [Rh(acac)(CO)$_2$] to react with the perfluorinated ligand so the Rh is not anchored within the fluorous phase but can dissolve into the organic octene, and as the batch reactions have shown hydroformylation begins before reaching 70 °C in this case, it is possible that the
[Rh(acac)(CO)\(_2\)] can pass into the immiscible nonanal phase, and never see any fluorinated ligand, before being removed from the system.

![Figure 3.3.5.2 Rhodium leaching levels to organic phase during final continuous experiment](image)

GC analysis of the product samples indicated a slight leaching of fluorous solvent (0.4 mole % of organic phase) to the organic phase and this was also observed by a gradual drop of the fluorous level in the separator. It was therefore, necessary to replace this fluorous phase during the continuous flow. This was done by adding more catalyst solution from the stock bottle at 8 h 50 min (5.1 cm\(^3\)) and 9 h 20 min (7.8 cm\(^3\)). This led to an increase in conversion, a drop in isomerisation and a higher l:b ratio. The latter two observations are in concordance with the higher ligand concentration introduced by further addition of catalyst solution increasing the concentration of [RhH(CO)\(_2\)L\(_2\)] and [RhH(CO)L\(_3\)], which are both known to give higher linear selectivity and lower isomerisation. It should be noted here that the delay between the addition of more catalyst solution and the observation of the increased rates in the product analysis is due to the volume of liquid in the connecting
tubes and the separator (about 70 cm$^3$) giving rise to a time lag of about 100 minutes before observing the expected changes.

The reaction again showed a steady state at about 40% conversion with high isomerisation and a high l:b (11.7). More catalyst solution was added at 15 h 50 min (5.7 cm$^3$) and 18 h 50 min (9.0 cm$^3$), again with an increase in conversion to 70% due to the increase of catalyst concentration. It was observed that the l:b ratio decreased as the conversion increased, which suggests that it was the loss of phosphine to the organic phase, rather than rhodium, that was occurring at these higher conversions. As previously reported by van Leeuwen et al$^4$, the rate of hydroformylation is negative order in [P], which means loss of phosphine will increase the rate and so the conversion, but the l:b will drop. A further addition of catalyst solution was made at 22 h 20 min (5.7 cm$^3$), and caused a rise in conversion and l:b ratio and a drop in isomerisation. When pure fluororous solvent was added at 24 h (9.6 cm$^3$), 33 h 23 min (7.8 cm$^3$) and 36 h 34 min (9.6 cm$^3$) very little change to the steady reduction in conversion was observed. The decrease in l:b with increased isomerisation confirms the formation of the unmodified Rh species which causes higher isomerisation. Unfortunately, this uncomplexed rhodium is also more soluble in the organic phase and so more Rh is lost to the product phase. This extraction of Rh to the organic phase is equal to a drop in the catalyst concentration and hence accounts for the overall drop in conversion at the end of the reaction. The indication of loss of Rh to the organic phase implies substantial loss of phosphine to the organic phase causing unmodified rhodium to be present and soluble in the organic product phase. In order to prevent the leaching of the phosphine it is likely that significant alterations to the phosphine ligand may be required and that reactions must be carried out at much higher conversion.
3.3.6 Optimising the Continuous Flow system; Semi-continuous Runs

A substantial loss of Rh to the organic phase was observed in all of the continuous flow reactions. Previous studies had shown that in order to reduce this loss we needed to increase the overall conversion and in order to do this we needed to increase the residence time in the reactor. The most straightforward way to do this was to switch from continuous operation to a semi-continuous series of batch reactions. Running the rig in this way meant that we could run consecutive batch reactions and recycle the catalyst solution under anaerobic conditions, whilst easily separating and collecting the product / organic phase. As the catalyst solution and octene were still being added to the reactor simultaneously, each batch reaction was run for 2 hours under a constant gas pressure of 15 bar CO/H\textsubscript{2} and at 70 °C. After which time the gas inlet was closed and the reactor outlet was opened, the dip-tube of the outlet sat slightly above the stirrer in the reactor leaving 11 cm\textsuperscript{3} of reaction mixture in the reactor. By continuing stirring whilst emptying the reactor, we assume that a 1:1 mixture of organic: flourous solvent was removed. Once the gas pressure had dropped to 1 bar in the reactor and the outlet was closed, the reactor was refilled with 64 cm\textsuperscript{3} total volume of octene and catalyst solution. After the second batch reaction, the catalyst solution was recycled from the separator and samples were collected from the overflow after every batch reaction.

During the first two runs of this system, a gas leak was noticed through the stirring mechanism, which must have been caused by solvent degradation of the o-ring and was the possible reason for poor conversion results throughout.

The first experiment run in this semi-continuous mode gave the results depicted in Figure 3.3.6.1.
Figure 3.3.6.1 Semi-Continuous Experiment Results of Each Batch Reaction

In this reaction, the liquid collected in the separator was very dark and the organic samples collected were dark yellow in colour. The first two batch reactions were run on day one with two days between these and the third and fourth runs. Oxidation in the tubing from the stock bottle into the pump occurred during this time and it was therefore necessary to move the fresh catalyst solution into the third stock bottle. Emptying the reactor proved very difficult through the capillaries, a high pressure in the reactor was necessary but the flow rate was still very slow. The nature of running in this series of batch reactions means that we do not need to specifically control the flow rate of liquid from the reactor and so the capillaries are not required, although careful opening of the reactor to the separator will have to be undertaken. The catalyst solution was pumped in fresh from the stock bottle for each reaction because there was only a small amount of fluorous phase observed in the separator. However, there was a significant drop in conversion to nonanal after the first very promising batch reaction. The branched aldehyde and isomerised octenes remain relatively low throughout the final three consecutive reactions. Due to the drop in
conversion and the need to remove the capillaries from the system, the reaction was stopped after the fourth run and the necessary alterations were made to the system before continuing.

### 3.3.6.1 Semi-continuous Flow Reaction without capillaries

The second semi-continuous flow reaction was carried out with a reassembled rig, omitting the capillaries between the reactor and separator. This allowed a quicker emptying of the reactor, with the separator vented out to the back of the fume-cupboard as all gas pressure is released through the separator at this point. The volume of liquid left in the reactor below the end of the dip-tube was measured and found to be 11 cm$^3$. We assume a 1:1 solvent ratio when emptying the reactor as the stirring is not stopped, thus equal volumes of catalyst solution (0.103 g [Rh(acac)(CO)$_2$] and 2.423 g P(C$_6$H$_4$C$_6$F$_{13}$)$_3$ in 100 cm$^3$ PFMC) and substrate were pumped into the reactor at the start of each batch reaction topping up the reactor to the original 75 cm$^3$ volume of liquid.

The first two batch reactions used fresh catalyst solution, fed straight from the stock bottle to the reactor, but the batch reactions 3-7 used recycled fluorous phase from the separator. Batch 7 had a lower volume of reaction mixture (66 cm$^3$), due to there only being 27.5 cm$^3$ fluorous phase in the separator. The final batch reaction was filled with recycled fluorous phase (27.5 cm$^3$) and fresh catalyst solution from the fluorous stock bottle (7.5 cm$^3$) and an equal volume of octene (35 cm$^3$). The GC-FID analysis of the collected samples is shown below in Figure 3.3.6.2, the early samples were collected by syringe before the separator had filled sufficiently to overflow subsequent samples were collected from the overflow of the separator.
The initial results appeared encouraging, with the first three runs achieving over 60% nonanal selectivity. The similarity in results between the first and third batch reaction are reassuring as this third batch reaction was the first recycle of catalyst, a slight drop in isomerised product is observed, probably due to the preformation of the catalyst solution in this run. By the fourth run however, the conversion had dropped considerably.

The fifth run was carried out on day two of the experiment, the reactor had been filled with substrate and catalyst solution and was pressurised with CO/H\textsubscript{2} (12 bar) and was left unstirred, at room temperature overnight, before reacting. The sixth batch reaction had a slightly lower volume, due to some loss of fluorous phase from the separator.

It is assumed that this loss of the fluorous phase occurs during the emptying of the reactor because the fluorinated solvent is quite volatile and is removed with the vented CO / H\textsubscript{2}, through the separator. GC analysis of the organic phase shows that relatively little fluorous solvent (1.1%) is lost due to solubility in the organic phase.
The second peak in conversion occurred with the seventh batch reaction and upon emptying this batch to the separator; both phases were observed to be much darker in colour. This suggested a similar pattern to the continuous flow reactions, where an increase in conversion was observed once the excess phosphine had leached to the organic phase. The dark colour observed suggests that rhodium metal is now dissolving at greater rates because it is no longer anchored into the fluorinated solvent. This agreed with the observed drop in conversion in the final reaction and the ICPMS analysis for Rh leaching, Figure 3.3.6.3, showed that the maximum leaching did occur simultaneously with the lowest conversion in batch reaction 5. We have shown separately that the extent of rhodium leaching is highest at low conversion (chapter 3.2).

![Figure 3.3.6.3 ICPMS data for Rh Leaching in Semi-continuous flow experiment](image)

Unfortunately, the leaching was relatively high from the beginning of the reaction. It may be that high levels of phosphine leaching occurred in the first four reactions, which lead to the high loss of Rh in the fifth reaction. The method of running this series of batch reactions meant that we could not directly compare to the
initial studies by Horváth. He reported ten recyclers of his catalyst phase, but although we used the same stock solution we effectively had two separate batches of the catalyst solution in the first two reactions which mixed for the third and following reactions and eventually more of the original stock solution was added. All of which may distort our results. Re-design of the semi-continuous method was required to allow this direct comparison.

3.3.6.2 The Next Semi-continuous experiment

In order to monitor the recycling of the catalyst solution, it was only necessary to remove the product phase after every batch reaction, but to do this the dip-tube had to be shortened so that it only removed the organic phase from the reactor and left the fluorous phase. By doing this, the catalyst would effectively be preformed for all subsequent reactions after the initial two-hour reaction and so batch reactions 2-9 were reacted for just one hour each.

The separation was carried out without cooling, but with the heater turned off during removal of the organic phase to prevent overheating of the catalyst solution.

The GC-FID analysis of the product phases is shown in Figure 3.3.6.4 and the Rh leaching data of selected samples are shown in Figure 3.3.6.5. The initial conversion is lower than the previous experiment. Nevertheless, the differences between conversions in the first five reactions are much less and appear to have reached a steady level of conversion of around 40 % nonanal, and although this is nowhere near the anticipated >90 % conversions we would expect for individual batch reactions. The GC analysis of the final 4 batch reactions shows a steady drop in conversion which, as before, is attributed to the loss of rhodium to the organic phase, and assuming the leaching of phosphine over the initial reactions.
Encouragingly, the leaching levels were much lower in this second experiment, but corresponded to lower conversions which were in disagreement with the previously reported work by Huang et al^5^ which stated that higher conversion to nonanal decreased the rhodium leaching levels in the organic phase. A similarity in pattern of leaching was observed between this semi-continuous experiment and the
previous one, an initial low loss of rhodium, which rose to a peak after five reactions and then dropped away after that.

This pattern of leaching is much easier to explain in the second experiment due to there being only one addition of catalyst phase to the reactor and no topping-up occurred throughout the reaction. An initially low [Rh] in the organic phase was expected from the previous batch reactions carried out in the kinetic experiments. There was an obvious loss of phosphine in the third and fourth batch reactions, which was determined by the strong yellow colour of the collected product see Figure 3.3.6.6.

We eventually reached a peak (batch 5) of [Rh] in the product phase that reduced after this because of the overall drop in [Rh] in the reactor. There was simply not enough Rh left in the reactor to maintain these high concentrations.

![Figure 3.3.6.6 Product phase collected after each batch reaction](image)

From this photograph of the product phases collected, the extent of Rh leaching is obvious. Samples 2 and 5 also show a small amount of the fluorous phase that had been removed from the reactor during separation. It is interesting to note the change in colour of these two samples.
The small amount of fluorous phase collected in 2 was a bright orange colour as expected when emptying the kinetic rig or HPIR equipment after heating the catalyst solution under CO / H₂. By the fifth run, however, the catalyst phase had turned very dark brown, almost black. This had also been observed before when the HPIR cell was overheated and the catalyst destroyed.

The Rh leaching was obvious from the colour of these samples. The large loss of Rh in the sixth reaction can perhaps be explained by both the large loss of Rh measured in the fifth reaction and the dark colour of the catalyst phase, which is suggestive of free Rh metal, which would occur upon large losses of phosphine leaching (likely to have occurred prior to the Rh leaching).

When the ninth reaction had been run and the analysis showed less than 20 % conversion the experiment was stopped and the reactor opened. It was obvious that there was very little fluorous phase in the reactor. The contents of the reactor were almost entirely pale yellow organic phase. This loss of fluorinated phase throughout the experiment does not concur with the small amounts of fluorous phase collected with the product phase. It is likely that this loss of the fluorinated solvent occurs during the emptying of the organic phase to the separator. When the reactor was first opened to the separator along with the liquid a cloud of vapour was observed and it is likely that this was partly PFMC. This might have been proved by condensing the vapour from the vent, but was not carried out, because the problem was not realised until the reactor was opened.

To try to prevent the loss of PFMC during the experiment, it was considered worthwhile to cool the reaction mixtures before separation of the organic phase and this was done in the final semi-continuous flow experiment that was carried out.
3.3.6.3 Semi-continuous flow with Cold Separation

The series of batch reactions for this experiment were carried out over three days; batches 1-4 on the first, 5-8 on the second and the ninth reaction on the third. The rig was assembled as before and the initial reaction was left stirring under 15 bar CO/ H₂ and 70 °C for two hours, with the subsequent reactions only reacting for 1 hour.

After the reaction time the heater was removed and the stirring slowed. Once the reactor was observed to be cooling down, the stirring was stopped to allow separation. The reactor was emptied once the temperature was below 35 °C, and this was generally about 1 hour after the heater had been removed. The product phase was collected in the separator and removed after every batch reaction to sample vials. The GC-FID analysis of these samples is shown in Figure 3.3.6.7. The results from this experiment appear quite similar to the previous semi-continuous flow experiments.

![Graph showing GC-FID analysis for the semi-continuous experiment with cold product separation.](image)
The results are quite understandable; there is the expected initial high conversion (84%) for the first reaction, which drops down to around 60% for the further reactions run on the first day. It is worth noting that this apparent steady state of conversion over these three reactions has a higher conversion to nonanal than is seen in the steady state range of the continuous flow experiments (~30%). The reactor was then emptied of the organic phase and left to cool at 10 bar CO / H₂ overnight. Batch reaction number 5 was run on the following morning, but a fault with the gas pressure controller had to be fixed and involved the reaction being stopped and cooled. The reaction time for this batch was therefore extended by 30 minutes to account for this and may explain the rise in conversion for this batch reaction. The alternative explanation follows the pattern seen in the continuous flow experiments where we observe a steady state of conversion followed by a rise in conversion due to the leaching of phosphine from the catalyst phase and subsequently a drop in conversion as we lose the unliganded Rh to the organic phase as well.

After the final batch reaction, the reactor was opened and emptied and found to contain 37 cm³ liquid of which < 4 cm³ was the fluorous phase, which had turned a dark orange colour. This indicates that there is still a loss of the fluorous phase through the separation process. The possibility of PFMC dissolving into the organic phase has been disproved by the GC analysis which shows ~1% of the product phase to be PFMC. It is possible that 30-35 °C was still too hot for separation and that cooling to room temperature or below would be necessary for further experiments.

The Rh leaching data for this experiment, Figure 3.3.6.8, initially looked to be very good with 5 ppm [Rh] observed in the first batch reaction, however this quickly increased and by the seventh reaction was nearly 350 ppm. Again, by simply
observing the colour of the collected product phase, Figure 3.3.6.9, a similar assumption of Rh leaching can be made.

![Graph showing Rh leaching to the organic phase](image)

Figure 3.3.6.8 ICPMS analysis of Rh leaching to the organic phase

![Image of collected product from semi-continuous experiment](image)

Figure 3.3.6.9 Collected product from semi-continuous experiment with cold separation

After the third batch reaction, a much darker colouration of the organic phase is observed with the final batch reactions very dark indeed. In this experiment 315 cm$^3$ of octene was used. In comparison, the continuous flow operation of the reactor could use over a litre of octene in 24 hours.
3.4 Conclusions

This study demonstrates the transference of a simple batch reaction to the continuous flow process and that the specifically designed reactor works effectively for this reaction. However, to optimise the reaction it is evident that maximum mixing of the gas and liquid phases are required to achieve high conversions. Further ligand design may improve the conversions and selectivity, as under these conditions leaching of the catalyst to the organic phase is still a major hindrance to the continued running of the reactor system. The continuous process may be improved further by the addition of a second reactor, so that any unreacted alkene can be converted. However, working two reactors in series, on our small-scale rig was not a viable option.

3.5 Reference List


Chapter 4
Experimental
4 Experimental

4.1 Techniques and Equipment

4.1.1 Laboratory Reagents

Air sensitive experiments were carried out under a dried argon atmosphere using a vacuum line and standard Schlenk tube techniques. The argon was dried by passing over a column packed with silica treated with chromium (VI) trioxide and reduced to Cr(II) using CO and H₂.

Solutions were transferred between flasks via cannula or by syringe, using Suba seals as the septa through which to inject. Air sensitive solids were weighed out in a glove box under an argon atmosphere.

All gases were purchased from BOC gases. The synthesis gas was supplied as a 1:1 CO:H₂ ratio (99.9% purity).

Deuterated solvents were purchased from Cambridge Isotope Laboratories, except hexane-d₁₄ which was purchased from Acros Organics, and were degassed by freeze-pump-thawing three times and stored under argon. Toluene-d₈ was degassed under vacuum and backfilling the Schlenk tube with argon three times.

Perfluoro (methylcyclohexane) and perfluoro (1,3-dimethylcyclohexane) were purchased from Apollo Scientific and were degassed by freeze-pump-thawing several times before use. Perfluorohexane was purchased from Aldrich and degassed by pumping under vacuum and refilling with argon three times.

[Rh(acac)(CO)₂] (Strem) was used as received. Tris (4-tridecfluorophenyl)phosphine was initially prepared and provided by E.G. Hope and co-workers by the published method¹, but was subsequently synthesised by the method described in section 4.2.1 and 4.2.2.
1-bromo-4-iodobenzene, copper bronze (for organic synthesis), 2,2'-bipyridine, dimethyl sulfoxide, ammonium hydroxide solution (10 % aq) and n-butyllithium (1.6 M in hexane) were purchased from Aldrich and used as received except the ammonium hydroxide solution which was degassed by stirring under vacuum for a few seconds and backfilling with argon six times. Perfluoro-n-hexyl iodide and fluorobenzene were both purchased from Fluorochem and were used as received. Phosphorus trichloride was purchased from Aldrich and was distilled under argon before use. Diethyl ether was dried using an Innovative Technology Solvent Purification System and degassed by the freeze-pump-thaw method. Dichloromethane was purified by refluxing over calcium hydride.

4.1.1.1 Removal of Peroxides from Oct-1-ene

Oct-1-ene was purchased from Aldrich. Before use, it had to be treated to remove any hydroperoxides, which are known to form in alkenes once they have been exposed to air and can cause unwanted oxidation of products during reactions\(^2\). Oct-1-ene was degassed by bubbling argon through it for 30 minutes. An equal volume of distilled water was degassed by placing under vacuum with occasional (careful) shaking for 30 minutes and back filled with argon, then evacuated and refilled with argon three times. A third large Schlenk tube containing ferrous ammonium sulfate was degassed by evacuating and back filling with argon three times. The ferrous ammonium sulfate was then dissolved in enough water to make a saturated, pale green solution and stirred for complete dissolution. The octene was transferred via cannula, the Schlenk tube was shaken, the phases allowed to separate and the organic phase was removed via cannula and run through a degassed column packed with alumina,
under a stream of argon. The octene was collected and stored under argon until required.

4.1.1.2 Freeze-pump-thaw of Fluorinated Solvents

A Schlenk tube was half-filled with the required solvent; evacuated for a few seconds before being back filled with argon three times; then evacuated once more and closed. The Schlenk tube was cooled in liquid nitrogen by submerging it to the solvent level. Once the solvent was entirely frozen, the Schlenk tube was reopened to the vacuum for 10-20 minutes, then closed and removed from the liquid nitrogen and immediately placed into warm water until completely thawed.

The freeze-pump-thaw process was repeated until no bubbles were observed escaping from the solvent as it thawed. Once no bubbles were observed upon thawing, the Schlenk tube and contents were brought to room temperature before being back-filled with argon and stored until required.

4.1.2 Spectroscopic Techniques

Gas Chromatography Mass Spectrometry was carried out using a Hewlett Packard HP6890 System fitted with a Supelco MDN-35 35 % phenyl / 65 % methylpolysiloxane capillary column for qualitative GCMS.

The temperature programme was as follows: Started at 50 °C held for 4 minutes, ramped at 20 °C / minute to 130 °C, held for 2 minutes, then ramped at 20 °C / minute to 260 °C where it was held for 13.5 minutes. The carrier gas was helium at a flow rate of 1.4 ml / minute, with a split ratio of 100:1. Gas Chromatography Flame Ionisation Detection was used to analyse the product samples collected from the continuous and semi-continuous flow hydroformylation reactions.
Proton and phosphorus NMR spectra were recorded on a Varian 300 MHz NMR spectrometer and a Bruker AM 300 NMR spectrometer. $^1$H spectra were referenced internally to deuterated solvents, which were referenced relative to TMS $\delta = 0$ ppm. CDCl$_3$: $\delta$ 7.27 ppm, C$_7$D$_8$: $\delta$ 2.09 ppm, C$_6$D$_{14}$: $\delta$ 0.8 ppm. C$_6$D$_6$: $\delta$ 7.16 ppm and CD$_3$COCD$_3$: $\delta$ 2.05 ppm. $^{31}$P NMR spectra were referenced externally to phosphoric acid 85 % H$_3$PO$_4$.

4.1.2.1 High-pressure NMR

The high-pressure NMR (HP-NMR) cell consists of a sapphire tube (supplied by Saphikon, OD 10 mm, ID 8 mm, internal volume = 4.7±0.1 cm$^3$), Figure 4.1.2.1. The sapphire tube was sealed at one end by the manufacturers. A titanium head and screw cap fitted with a PTFE seal were built and fitted in the School of Chemistry Workshop at the University of St Andrews. The cell had been pressure tested to 100 bar and 100 °C. The Ti-screw cap acted as a valve through which the cell was connected to an ordinary gas cylinder tube and pressurised. Along with the cell, a brass and aluminium housing was designed which allowed the cell to be pressurised, transported and stored safely.

Due to the increased weight of this NMR cell compared to a conventional one, the airflow in the spectrometer was not powerful enough to raise and lower the cell so an extendable clamp was built which fitted over the top of the probe and could lower and raise the cell in the spectrometer safely. The cell was placed in a spinner to ensure that it sat in the correct position within the magnet. Unfortunately, the airflow was insufficient to spin the cell.

This type of cell has a number of disadvantages; its weight means that it cannot spin within the magnet and the increased wall thickness of the cell results in lower sensitivity than in a normal 10 mm NMR tube.
The small volume and sealed cell limits the gas volume for \textit{in situ} studies of reactions and with no stirring, there is poor mass transport of gas into the reaction mixture.

\subsection*{4.1.2.2 General Procedure}

The solutions containing the desired species were prepared as described below in section 4.2.3.1. Using [Rh(acac)(CO)\textsubscript{2}] and triphenylphosphine or tris(4-tridecafluorophenyl)phosphine with various Rh:P ratios (1:1, 1:5, 1:10). The high-pressure NMR cell was degassed by capping the sapphire tube with a large Suba-seal and purging with argon for 15-30 minutes. The solution (2.5 cm\textsuperscript{3}) was then transferred to the HPNMR cell via cannula under a stream of argon. The cell was sealed by screwing on the cap fully, whilst holding the cell in the brass housing fitted with the brass top, permitting a secure hold of the cell.

To pressurise the cell the spiral hose was connected to the cell cap at one end and the other end was attached to a cylinder of the desired gas mixture. The gas hose was vented and degassed three times, leaving the hose under a pressure of the gas
mixture. The cell was then opened by turning the screw cap one whole turn anticlockwise and pressurised to 20 bar CO/H₂. The cell was closed after a few seconds by turning the screw cap an entire clockwise turn. The cylinder was then closed and the hose vented before removing from the cell.

Using the extendable clamp the cell was removed from the housing in order to swap the brass top with the spinner, allowing the cell to be safely placed into the spinner without ever exposing the worker directly to the pressurised sapphire cell. The cell was then ready to be lowered into the NMR spectrometer, using the extendable clamp, whilst watching the lock signal to ensure release of the cell before removal of the clamp. No lift or spin air was required for these experiments due to the increased weight of this cell. The NMR spectra were acquired with the cell stationary within the probe.

In all spectra recorded the [Rh] remained constant (10 mmol dm⁻³). But due to the poor stability of the solution, no stock solution was prepared so some deviation will have occurred.

Spectra were recorded between –60 °C and 70 °C and at pressures of 1 bar argon and 20 bar CO/H₂ or CO.

For experiments investigating the hydroformylation of 1-octene, the octene (0.2-0.5 cm³) was added after the cell had been heated to 70 °C for an hour and cooled to RT.

4.1.2.3 High-pressure Infrared (HPIR)

The infrared spectra were recorded on a Thermo Nicolet Avatar 360 FTIR ESP spectrometer equipped with a mercury cadmium telluride (HgCdTe) detector, which required cooling with liquid nitrogen before use. This spectrometer was interfaced with a PC running OMNIC software for recording spectra.
All high-pressure infrared spectra were obtained using a Parr autoclave (50 cm$^3$), fitted with two CaF$_2$ windows, stirrer (1500 rpm), a pressure gauge, injection port, thermocouple, gas inlet and heater. The windows used throughout these experiments gave a path length through the solution of ~4 mm. See Figure 4.1.2.2.

![High-pressure IR equipment](image)

**Figure 4.1.2.2 High-pressure IR equipment**

### 4.1.2.4 General procedure

Solutions containing the desired Rh: P ratios were prepared as described elsewhere. The autoclave was degassed by pressurising with 4 bar nitrogen (directly from the cylinder) and then by venting to the atmosphere three times. The injection port was opened with a stream of nitrogen flowing out and the solution was introduced to the autoclave by injection under nitrogen. The substrate was later introduced through this port under an over-pressure of gas, once the autoclave was at pressure and reaction temperature and the catalyst had been preformed.

The autoclave was sealed and placed into the spectrometer on a platform, which had been built in the School of Chemistry Workshop to position the cell windows correctly into the beam of the spectrometer. The cell was heated to the
required temperature. Spectra were recorded at room temperature and prior to pressurising with CO/H\textsubscript{2}. In later experiments, once the autoclave was at the required pressure and temperature, spectra were recorded in series.

4.1.3 Kinetic Studies of the Reaction System

The kinetic measurement experiments were carried out on a specially designed autoclave owned by CATS (Catalytic Evaluation and Optimisation Service). It comprises a small autoclave (Baskerville) fitted with an injection arm, thermocouple, a pressure controller and transducer and a ballast vessel. It is possible to isolate each section of the set-up.

4.1.3.1 Procedure

The autoclave was initially pressurised to slightly below the required reaction pressure and vented three times before the catalyst solution (2.5 cm\textsuperscript{3}, 4 mmol dm\textsuperscript{-3} [Rh], 20 mmol dm\textsuperscript{-3} [P]) was added through the injection port. The autoclave was pressurised to slightly less than reaction pressure and heated to reaction temperature (70 °C). The catalyst was either allowed to preform for 40 minutes before injection of the substrate, 1-octene (2.5 cm\textsuperscript{3}) under a stream of synthesis gas at reaction pressure or the 1-octene was added with the catalyst solution to the autoclave before pressurising and heating. The ballast vessel was closed to the cylinder but the pressure controller maintained a constant pressure in the autoclave and injection port. A pressure transducer monitored the pressure in the autoclave and injection port so that the volume of gas consumed was measured and recorded on a PC using data logging hardware through a Pico monitor, model ADC16, fitted to a PC through a com port. The data logging software was PicoLog for Windows version 5.04.02.
The reaction was determined to have finished once no more gas was consumed. The contents of the reactor were removed on cooling and ICPMS analysis was carried out on the organic phase to monitor the amount of rhodium and phosphorus leaching along with GC analysis to obtain the conversion and selectivities of the reactions.

4.2 Synthesis

4.2.1 Preparation of 4-(tridecafluorohexyl)bromobenzene

This was prepared following the literature method and further advice provided by Dr D. Adams from University of Leicester.

1-bromo-4-iodobenzene (25.0 g, 88.34 mmol), copper bronze (12.36 g, 193.13 mmol), 2,2’-bipyridine (0.98 g, 6.36 mmol), DMSO (200 cm$^3$) and fluorobenzene (150 cm$^3$) were mixed under nitrogen and heated to 70 $^\circ$C. To this was added a solution of perfluoro-$n$-hexyliodide (39.42 g, 88.4 mmol) in perfluorobenzene (50 cm$^3$) dropwise over the course of 7 hours. By careful monitoring the temperature of the reaction solution was maintained at 70 $^\circ$C. The mixture was then left stirring at 70 $^\circ$C for 120 hours after which the mixture was cooled overnight.

The reaction mixture was added to a large conical flask containing water (200 cm$^3$) and diethyl ether (500 cm$^3$). This solution was filtered to remove the precipitate, which was washed with diethyl ether (2x 50 cm$^3$). The organic layer was separated and washed with water (5x 250 cm$^3$); dried over magnesium sulfate; filtered and the solvent removed using a rotary evaporator. This resulted in a brown oil. Leaving this overnight, crystals (1-bromo-4-iodobenzene) formed in the oil. The oil was filtered and then heated in a kugelröhr at 65$^\circ$C to remove unreacted 1-bromo-4-iodobenzene, the oven temperature was then raised to 100$^\circ$C to distil the 4-(tridecafluorohexyl)bromobenzene and 1,4-bis (tridecafluorohexyl)bromobenzene as a
clear oil. This clear oil was distilled using microfine distillation apparatus to give 4-(tridecafluoro)bromobenzene as a colourless oil (b.p. 89-92 °C at 10 mbar) (17.8 g, 42.3 %) $^1$H (300 MHz, CDCl$_3$) 7.5 (2H, d, $^3J_{HH}$=8.2 Hz), 7.3 (2H, d, $^3J_{HH}$= 8.2 Hz). Literature values $^1$H(250 MHz, CDCl$_3$) 7.90 (2H, d, $^3J_{HH}$=8.5 Hz), 7.70 (2H, d, $^3J_{HH}$= 8.5 Hz).

4.2.2 Synthesis of Tris(4-tridecafluorohexylphenyl)phosphine

4-(Tridecafluorohexyl)bromobenzene (24.0 g, 50.53 mmol) was degassed under high vacuum before backfilling the flame-dried Schlenk tube with argon and adding dry diethyl ether (300 cm$^3$). This solution was stirred and cooled to –78 °C with a dry ice/acetone bath. A solution of 1.6 M n-BuLi in hexane (31.5 cm$^3$, 50.4 mmol) in dry diethyl ether (30 cm$^3$) was added to the main flask dropwise over 60 minutes, ensuring the internal temperature never rose above –75 °C. The mixture was stirred for 5 hours at –78 °C, at which point the dropping funnel was rinsed with dry diethyl ether (10 cm$^3$) then charged with dry diethyl ether (30 cm$^3$) and phosphorus trichloride (2.29 g, 16.72 mmol). This solution was added dropwise over 60 minutes with the temperature maintained below –75 °C. The reaction mixture was then allowed to warm to room temperature overnight. Ammonium hydroxide solution (10 % in water, 100 cm$^3$) was added to the reaction mixture and stirred for 20 minutes. The organic solution was then separated and transferred to a flame-dried Schlenk tube containing MgSO$_4$ via cannula. This mixture was stirred for a further 20 minutes before removing the solution to a flame-dried Schlenk tube using a filter stick. The solvent was removed in vacuo, resulting in a yellow oil, which solidified when left overnight. The resulting solid was dissolved in dry, degassed DCM, the solution transferred to a Schlenk tube containing silica and the solvent removed in vacuo –
adsorbing the impure ligand onto the surface of the silica. This silica was transferred under argon to a column already containing some pure silica, with care being taken to ensure the yellow silica remained on the top of the column. The product was eluted with petrol (b.p. 40-60 °C) and the solvent was removed in vacuo resulting in a white powder. The product/petrol solution was passed over a second column of pure silica, if it retained the yellow impurity. The yield for this step is very low ~26 %. $^{31}$P NMR: (300 MHz, CDCl$_3$) $\delta$: -5.2 Literature $^{31}$P NMR (101Hz,CDCl$_3$) –6.3.

4.2.3 Reduction of Tris(4-tridecafluorohexylphenyl)phosphine oxide$^3$

Tris(4-tridecafluorohexylphenyl)phosphine oxide (2.5 g, 2.1 mmol) (obtained through oxidation of tris(4-tridecafluorohexylphenyl)phosphine during synthesis), triethylamine (6.3 cm$^3$, 45.2 mmol), trichlorosilane (3.0 cm$^3$, 29.7 mmol) and toluene (20 cm$^3$) were added to a 100 cm$^3$ flask. Stirring the flask vigorously under an argon atmosphere, the reaction mixture was heated to 120 °C for 6 hours. The mixture was cooled to RT and then cooled further with an ice bath. A saturated NaHCO$_3$ aqueous solution (1 cm$^3$) was added to the reaction mixture and stirred for 10 minutes. The yellow solution was filtered through a silica column and washed with hexane. The solvent was removed in vacuo and a clear colourless oil was obtained this was left in the glove box to solidify to a white powdery solid.

4.2.4 HPNMR solutions

4.2.4.1 Toluene-d$_8$ Solutions

P(-4-C$_6$H$_4$C$_6$F$_{13}$)$_3$ (0.1215 g, 0.1 mmol) was weighed into a Schlenk tube containing [Rh(acac)(CO)$_2$] ( 0.0052 g, 0.02 mmol) in the glove box. To this was added degassed toluene-d$_8$ (2 cm$^3$) and the solution was stirred until all solid had dissolved and was then transferred to the degassed HPNMR cell.
After preforming the catalyst at 70 °C under 20 bar CO/H₂, the 1-octene (0.5 cm³) was added under a stream of argon and the cell re-pressurised. All triphenylphosphine solutions were prepared in this way, but both the Rh precursor and triphenylphosphine could be weighed out in air.

### 4.2.4.2 Hexane-d₁₄ Solutions

P(-4-C₆H₄C₆F₁₃)₃ (0.1215 g, 0.1 mmol) was weighed into a Schlenk tube containing [Rh(acac)(CO)₂] (0.0052 g, 0.02 mmol) in the glove box. This was then dissolved in perfluoro(1,3-dimethylcyclohexane) (PFDMC, 1.5 cm³). Hexane-d₁₄ (0.5 cm³) was added to the solution, which was stirred under argon until all solid had dissolved. Both solvents had been previously freeze-pump-thawed.

### 4.2.5 HPIR Solutions

Triphenylphosphine and [Rh(acac)(CO)₂] were weighed directly in to the HPIR cell which was then sealed and degassed by purging with N₂ gas (direct from cylinder) for 30 minutes. Then dry degassed hexane (30 cm³) was added by syringe through the injection port under a stream of nitrogen.

Solutions of tris(4-tridecafluorohexylphenyl)phosphine were made up by weighing the [Rh(acac)(CO)₂] into a Schlenk tube before taking this into the glove box and weighing out the P(C₆H₄C₆F₁₃)₃ into that Schlenk tube and finally dissolving in degassed hexane. The mixture was stirred and some heating (hot air gun) was often required to ensure total dissolution of the solids. The solution was then injected into the previously degassed HPIR cell under a stream of nitrogen. The cell was sealed and placed into the spectrometer. The spectra were collected as detailed in section 4.1.4.1.
4.3 The Continuous Flow Rig

4.3.1 Apparatus

As part of a collaboration with the Chemical Engineering School of University College London (UCL), a specially designed continuous-flow biphasic rig had been commissioned and built. This rig was transported to the University of St Andrews Chemistry Department where testing of continuous flow hydroformylation was carried out.

The continuous flow apparatus, Figure 4.3.1.1, comprised three feed bottles, two HPLC pumps (organic and fluorous phases), a Parr continuous stirred tank reactor (CSTR) (100 cm³): fitted with a thermocouple, stirrer (1700 rpm), pressure gauge, inlet for liquid and gas, a liquid outlet, a gas purge port, a cold finger and a bursting disc; a heat exchanger (later removed), capillaries for flow control, separator (connected to allow recycling of the fluorous phase) and a collection vessel. The reactor was filled by pumping the catalyst in the fluorous phase and the octene substrate through a Jasco PU-2080 HPLC pump and a Waters 515 HPLC pump...
respectively. The feed from the two pumps mixed at a T-junction of tubing and passed through a heat exchanger before it reached the liquid inlet of the reactor. The reactor was pressurised using a Brooks pressure controller (5866 series) coupled to a Brooks Microprocessor control and read out unit (model 0154), this maintained the pressure within the reactor as gas was consumed in the reaction and fed gas directly from the cylinder. The contents of the reactor were stirred by a mechanical stirrer with a Parr motor (1700 rpm) and heated using a Parr heating mantle controlled by a Watlow Microprocessor-based temperature controller (series 987). The reactor was emptied through a dip tube, which sat inside the CSTR just above the stirrer, through the heat exchanger and through a Brooks mass flow controller, which metered the flow of liquid throughout the experiment. In order to control the flow of liquid from the CSTR a set of four capillaries of different length were introduced with two two-way valves to allow selection of an individual capillary, by increasing the length of the capillary the rate of flow was slowed down and the residence time in the CSTR was increased.

4.3.2 Continuous Flow Operation Procedure

The entire system was connected and left under argon overnight and each section purged separately with argon. The catalyst solution was prepared in a Schlenk tube containing the Rh precursor (0.1548 g, 0.6 mmol), which was taken into the glove-box to add the phosphine ligand (3.6492 g, 3.0 mmol). The perfluorinated solvent, PFMC (150 cm$^3$), was added to the Schlenk tube by syringe and the contents were stirred until all solid had dissolved. During this stage it was possible to see the evolution of CO as the [Rh(acac)(CO)$_2$] and phosphine reacted. This solution and the octene feedstock were transferred to their respective feed-bottles via cannula under an argon atmosphere. The organic substrate and the fluorous solvent from the initial feed
Chapter 4: Experimental

177 bottles were pumped into the CSTR, using the two HPLC pumps to deliver the liquids at constant and identical flow rates (to ensure a 50/50 mix within the reactor (75 cm$^3$)). The pumping was stopped and the reactor was pressurised to 12 bar CO / H$_2$ before it was heated to 70ºC with vigorous stirring (1000 rpm). Once at temperature, the pressure was increased to 15 bar through the pressure controller, maintaining the reactor pressure throughout. The homogeneous mixture in the reactor was left to react as a batch reaction for 2 hours before the gas inlet was closed and the reactor outlet was opened to the separator. Once liquid was observed in the separator, the outlet valve and the gas inlet valve were closed and the stirring stopped. The pumps were started, feeding the liquids into the reactor to compensate for the volume of liquid removed to the tubing and separator; this was calculated by returning the pressure of the reactor to 15 bar and recording the length of time to reach this along with the flow rate of the pumps. Again, the reactor was left under batch conditions for a further 2 hours. After 2 hrs the reactor outlet was opened and the pumps started to deliver catalyst solution and substrate to the reactor at a slow rate (0.6 cm$^3$ min$^{-1}$). Initially there was no product collection, as the separator had to fill to approximately 60 cm$^3$ before the liquid reached the overflow tube. Once the product had started overflowing and the level of fluorous solvent had equilibrated, the recycling of the catalyst was started simply by turning to the second inlet on the fluorous pump, which was connected to the recycling tube on the underneath of the separator. The fluorous level was monitored throughout the experiment to ensure equal levels of both phases in the entire system and adjustment made to the flow rate when necessary. The system was run continuously with the organic phase being sampled every 30 min and analysed by GC-FID. Samples throughout the reaction were also monitored by ICPMS for Rh leaching to the organic phase.
4.3.3 Semi-Continuous Flow Operation of Rig

The equipment was set up as for a continuous flow reaction but without the capillaries and shorter connecting tubing into and out of the reactor. The reactor was filled with the required volume of each liquid by pumping the two liquids through the respective HPLC pumps. The reactor was then pressurised to 12 bar CO / H₂ and heated with stirring to 70°C, with the reactor open to the CO / H₂ cylinder. Once at reaction temperature the pressure was increased to 15 bar CO / H₂ and the timer started. The stirrer was set to maximum (1700 rpm).

After the required time the reactor was closed, the separator gas vent was opened and the outlet from reactor to separator was carefully opened and closed once no more liquid was observed entering the separator. The reactor was then refilled with the required liquid and the process repeated. Samples of the organic phase were collected by syringe through the injection port in the separator and were analysed by GC-FID and the entire experiment was stopped once the overall conversion had dropped below 25%.

4.3.3.1 Alterations to Semi-Continuous Flow Method

In an attempt to lengthen the catalyst life, during the semi-continuous flow reactions, the dip tube was shortened so that it only removed the organic phase from the reactor. The theory being that the catalyst solution would remain in the reactor whilst just collecting pure product phase after each batch reaction.

Initially this was carried out with the contents of the reactor kept at reaction temperature, although the heater was turned off during separation to avoid any overheating and eventual decomposition of the catalyst.
In the second experiment removing only the organic phase, the reactor was cooled to 30 °C before opening to the separator, in an attempt to reduce the decomposition of the catalytic species and the removal of the fluorous phase through the venting of the reactor.

With only the organic phase being removed to the separator, the entire contents of the separator were collected after each batch reaction. These samples were analysed by GC-FID for the conversion data and ICPMS analysis was carried out to obtain the amounts of Rh leaching to the organic phase.

4.4 Reference List


Chapter 5

Conclusions and Further Work
Chapter 5: Conclusions and Further Work

5 Conclusions

5.1 Conclusions and Further Work

The improved rates and selectivities of our ligand \{P(C_6H_4C_6F_{13})_3\}, compared to PPh_3 have been shown to arise from the better complexation of Rh under catalytic conditions. With the \textit{bis} and \textit{tris}-phosphine complexes existing under relatively low concentrations of free ligand in the fluorinated case, whereas triphenylphosphine, as is used in industry, is required in large excess to achieve high selectivities. This has been explained to a degree by the strongly electron-withdrawing perfluorinated poynetails on our ligands.

The existence of the tris-phosphine complex in the separator of the CFR also explains the low leaching levels of our ligand and rhodium to the organic phase, however the extremely low values observed in the original batch reactions were never repeated in the CFR. This was possibly in part due to the difference in charging the two reactors, but also because of the low conversion in the CFR, resulting in a higher concentration of leaching to the organic phase.

The CFR has provided proof of concept and is, to the best of our knowledge, the first example of a fluorous biphasic system operated in continuous mode under high pressure. The overall activity of the reactions was lower than expected compared with preliminary work done in this group, but this was explained by the difference in volume, efficiency of stirring / mass-transport limitations and residence time of the substrate in the reactor.

An efficient mass balance of the reactions, especially the semi-continuous experiments may have provided better evidence as to where the fluorous solvent was
being lost. As an extremely expensive solvent, reducing the volume used and especially lost, is imperative to the running of this system. Initial studies of the vent gas, by passing through a cold trap, showed that both the fluorous and organic solvents were stripped off by the gas flow in the separator, further work may include a more quantitative analysis of this observation. The importance of maintaining the solvents in the liquid phase was emphasised by the semi-continuous experiments, which eventually lost almost all of the fluorous phase and resulted in much higher levels of leaching to the organic phase.

The CFR itself may also benefit from a number of modifications; introducing a second liquid inlet to allow for separate loading of the catalyst solution and substrate to the reactor. Even though the kinetic reactions showed that this change would simply increase the rate of the reaction it may be found to improve the overall running of the system: introducing a second CSTR might increase the yields for the reactions, creating a series of reactors, with either the whole reaction mixture being moved into a second reactor or just the organic phase being removed to the next reactor containing “fresh” catalyst.

The mechanistic study of the catalyst showed that it performed quite similarly to triphenyl phosphine and we surmise that hydroformylation with a perfluorinated phosphine catalyst follows a similar mechanism to that of triphenyl phosphine. The most obvious difference is the electron-withdrawing effect of the fluorous ponytail on the Rh atom, decreasing the back bonding to the other ligands, CO.

Throughout this work, it has been apparent that in order for the FBC system to become industrially viable, the activity and selectivity of the catalyst would require to be much higher than that of the existing industrial catalysts, in order to overcome the major hurdle which faces this technology: cost. The volume of literature published
involving FBS is testimony to the perceived advantages that this system may eventually afford. Nevertheless, from the results of the continuous-flow reactor, which have proved the concept, application to industry lies some time in the future, if at all.

This system at the time of writing, is not yet commercially viable and would require further investigation before it could be so. This would probably include the identification of a more efficient ligand, with efficiency including improved performance and lower solubility in the organic phase as well as easier preparation because the synthesis of \( \text{P(C}_6\text{H}_4\text{C}_6\text{F}_{13})_3 \) was particularly time consuming with a relatively low yield. A study of alternative fluorous solvents may also provide a cheaper alternative to PFMC.

It would have been of interest to investigate further the rhodium dimer complex formed in the HPIR solution and perhaps understand the apparent loss of an aryl group from the bridging phosphorus atom. Had time allowed an investigation of this complex including an attempt to synthesise it would have been carried out.

Investigation of the unassigned bands and peaks in the HPIR and HPNMR may provide further information in the mechanism of the hydroformylation reaction, alternatively some of these peaks may have arisen from the isolated dimer complex. However, no isolated spectroscopy was carried out on the complex.

From what was observed and identified, it does appear clear that the mechanism of the perfluorinated ligand system is very similar to that of triphenylphosphine, but with the strongly electron withdrawing nature of the perfluorinated ligand, the activity and selectivity of this ligand are better than those for the triphenylphosphine system.

The continuous rig may also require some minor alterations to improve its efficiency and overall performance; the introduction of a second reactor either to
preform the catalyst or to be used as a second reactor to increase the overall conversion and the reintroduction of a heat exchanger ought to be investigated. Improvement of the separator or inclusion of a cold trap, to limit the loss of solvent through the vent gas may also improve the economics of the reactor, if the recovered solvent could be recycled.

Ni and co-workers have developed an oscillatory-baffled reactor (OBR)\(^1\) that provides a novel method of mixing a reactor containing a series of baffles, which create eddies when the reaction mixture/fluid passes through them. This alternative method of stirring may improve the activity of the reaction, by providing better mixing within the reactor and is a possible area of further research, as the improvement in conversion upon introduction of the gas entrainment stirrer was notable.

This process is not yet ready to compete with current methods of industrial hydroformylation and the high cost of the perfluorinated ligands and solvents may prevent this ever becoming a large-scale industrial process. Yet, this work has shown that fluorous biphasic catalysis is a feasible method of hydroformylation, which provides high selectivity and conversion, with a facile method of catalyst recovery. Other uses, such as small-scale organic synthesis, may benefit from the fluorous biphasic principal better than larger scale processes.

The work described shows the realisation of the concept and the first reported high-pressure continuous-flow fluorous biphasic reaction in a custom built rig.

### 5.2 Reference List

Appendices
6 Appendices

6.1 Appendix 1

From the synthesis of P(C₆H₄-4-C₆F₁₃)₃, the final step after the purification is to leave the obtained clear, colourless oil to solidify in the glove-box. In one batch, small rectangular, colourless crystals were observed to grow, instead of the expected white powder. These crystals gave the following crystal structure and data.
### Table 1. Crystal data and structure refinement for CMDCH2.

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Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for CMDCH2. $U(eq)$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

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Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å² x 10³) for CMDCH₂. The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [ h^2 a^2 U_{11} + \ldots + 2hk a^* b^* U_{12} ]\)

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Symmetry transformations used to generate equivalent atoms:
6.2 Appendix 2

The crystal structure of the crystal collected after HPIR experiment of [Rh(acac)(CO)$_2$] with P(C$_6$H$_4$-4-C$_6$F$_{13}$)$_3$ (1: 5) in hexanes. The contents of the reactor were collected and stored in a sample vial. After a week small rectangular, orange crystals were observed in the vial. They were found to be a rhodium dimer with some evidence of decomposition of the ligand.
Table 1. Crystal data and structure refinement for CMDCH3.

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<tr>
<td></td>
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<td>Data / restraints / parameters</td>
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Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for CMDCH3. U(eq) is defined as one third of the trace of the orthogonalized U^ij tensor.

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| Symmetry transformations used to generate equivalent atoms: |
| #1 -x+1,-y,-z+1 | #2 -x+1,-y-1,-z |
Table 4. Anisotropic displacement parameters (Å² x 10³) for CMDCH3. The anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁ + ... + 2hk a* b* U₁₂]

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for CMDCH3.

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Symmetry transformations used to generate equivalent atoms:
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