Measuring the electronic effect of some phosphines and phosphites

By

Sanaa Moftah Ali Abushhewa

A dissertation submitted to the University of Manchester for the degree of Master of Science by research in the Faculty of Engineering and Physical Sciences.

School of Chemistry

2010
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>6</td>
</tr>
<tr>
<td>Declaration</td>
<td>7</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>8</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>9</td>
</tr>
<tr>
<td>1.1 History of Phosphorus</td>
<td>9</td>
</tr>
<tr>
<td>1.2 Phosphorus (III) compounds</td>
<td>10</td>
</tr>
<tr>
<td>1.3 Preparation and Properties of Phosphines</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Preparation and Properties of Phosphites</td>
<td>12</td>
</tr>
<tr>
<td>1.5 Bonding of phosphorus (III) ligands</td>
<td>14</td>
</tr>
<tr>
<td>1.6 Measurement of Electronic and Steric Effects</td>
<td>15</td>
</tr>
<tr>
<td>1.7 Steric parameter</td>
<td>17</td>
</tr>
<tr>
<td>1.8 Electronic parameter</td>
<td>17</td>
</tr>
<tr>
<td>1.9 Effects of electronegative substituents</td>
<td>21</td>
</tr>
<tr>
<td>1.10 Phosphines and Phosphites ligand effects</td>
<td>21</td>
</tr>
<tr>
<td>2. Experimental section</td>
<td>24</td>
</tr>
<tr>
<td>General conditions</td>
<td>25</td>
</tr>
<tr>
<td>2.1- Preparation of phosphites</td>
<td>25</td>
</tr>
<tr>
<td>2.1.1- Synthesis of 2, 2’- Biphenyl Chlorophosphite</td>
<td>25</td>
</tr>
<tr>
<td>2.1.2- Synthesis of 1H,1H,2H,2H-perfluorodecyldiphenyl phosphinite</td>
<td>25</td>
</tr>
</tbody>
</table>
2.1.3- Synthesis of 3-fluorophenylidiphenyl phosphinite 26
2.1.4- Synthesis of 2-fluorophenylidiphenyl phosphinite 26
2.1.5- Synthesis of 2, 2-biphenyltrifluoroethyl phosphinite 27
2.1.6- Synthesis of 2, 2'-biphenylhexafluoroisopropyl phosphinite 27
2.1.7- Synthesis of 2, 2'-biphenylpropyl phosphite 28
2.2- Preparation of P(III) Selenides 28
2.2.1- Synthesis of triphenylphosphine selenide 28
2.2.2- Synthesis of triphenylphosphite selenide 29
2.2.3- Synthesis of tris(2,4,6-trimethylphenyl)phosphite selenide 29
2.2.4- Synthesis of diphenyl(o-tolyl) phosphine selenide 30
2.2.5- Synthesis of 2, 2'-biphenyl chlorophosphite selenide 30
2.2.6- Synthesis of diphenyl hexafluoroisopropyl phosphinite selenide 30
2.2.7- Synthesis of 1H,1H,2H,2H-perfluorodecyl diphenyl phosphinite selenide 31
2.2.8- Synthesis of 2, 2'-biphenyltrifluoroethyl phosphite selenide 31
2.2.9- Synthesis of 3- fluorophenylidiphenyl phosphinite selenide 32
2.2.10- Synthesis of 2-fluorophenylidiphenyl phosphinite selenide 33
2.2.11- Synthesis of tris(2-cyanoethyl)phosphine selenide 33
3- Preparation of molybdenum pentacarbonyl P(III) complexes 33
2.3.1- Synthesis of triphenylphosphine molybdenum pentacarbonyl 33
2.3.2- Synthesis of Diphenyl(o-tolyl) phosphine molybdenum pentacarbonyl 33
2.3.3- Synthesis of 1H,1H,2H,2H-perfluorodecylidiphenyl phosphinite molybdenum pentacarbonyl. 34
2.3.4- Synthesis of 2, 2'-biphenylchloro phosphite molybdenum pentacarbonyl 34
2.3.5- Synthesis of tris(2,4,6-trimethylphenyl) phosphite molybdenum pentacarbonyl

2.3.6- Synthesis of diphenyl(ethyl)phosphinite molybdenum pentacarbonyl.

3- Results and discussion

3.1 - Reaction of hexafluoro-isopropanol with chloro-diphenyphosphine

3.2- Reaction of 1H,1H,2H,2H-perfluorodecan-1-ol with chlorodiphenyl phosphine

3.3- Reaction of 3-fluorophenol with chlorodiphenylphosphine

3.4- Reaction of 2- fluorophenol with chlorodiphenyl phosphite

3.5- Reaction of 2, 2′-biphenol with phosphorus trichloride.

3.6- Reaction of 2, 2′-biphenyl chlorophosphite with trifluoroethanol

3.7- Reaction of chlorobiphenyl phosphite with propanol.

3.8- Reaction of triphenylphosphine with selenium

3.9- Reaction of diphenyl(o-tolyl)phosphine with selenium.

3.10- Reaction of tris(2-cyanoethyl)phosphine with selenium

3.11- Reaction of triphenylphosphite with selenium

3.12- Reaction of tris(2,4,6-trimethylphenyl)phosphite with selenium.

3.13- Reaction of 2, 2′-biphenylchlorophosphite with selenium

3.14- Reaction of diphenyl hexafluoroisopropyl phosphite with selenium

3.15- Reaction of diphenyl 1H, 1H, 2H, 2H-perfluorodecylphosphite with selenium

3.16- Reaction of 2, 2-biphenyl (trifluoroethyl) phosphite with selenium.

3.17- Reaction of 3-fluorophenylidiphenylphosphinite with selenium

3.18- Reaction of 2-fluorophenylidiphenylphosphinite with selenium
3.19- Synthesis of triphenylphosphine with molybdenum hexaacarbonyl 53  
3.20- Reaction of diphenyl(o-toly)phosphine with molybdenum hexacarbonyl 54  
3.21- Reaction of $1H$, $1H$, $2H$, $2H$-perfluorodecyldiphenyl phosphinite with molybdenum hexacarbonyl 55  
3.22- Reaction of 2, 2'-biphenylchloro phosphite with molybdenum hexacarbonyl 55  
3.23- Synthesis of tris(2,4,6-trimethylphenyl) phosphite molybdenum pentacarbonyl 56  
3.24 - Synthesis of diphenyl(ethyl)phosphinite with molybdenum hexacarbonyl 57  
Discussion 58  
References 62
This project is concerned with ways of making an assessment of the electronic properties of some phosphine (PR$_3$), phosphinite (R$_2$POR) and phosphite (P(OR)$_3$) ligands. The phosphines studied were PPh$_3$, tris(mesityl)phosphine, PPh$_2$C$_6$H$_4$OCH$_3$ and (NCCH$_2$CH$_2$)$_3$P. Phosphites and phosphinites were prepared by reaction of PCl$_3$ and Ph$_2$PCl or 2, 2’-biphenyl chlorophosphite, respectively, with alcohols under nitrogen conditions at ice temperature. The compounds 1H, 1H, 2H, 2H-perfluorodecylidiphenyl phosphinite, 3-fluorophenylidiphenyl phosphinite, 2-fluorophenylidiphenyl phosphinite, diphenyltrifluoroethyl phosphinite, diphenylhexafluoroisopropyl phosphinite and propyldiphenyl phosphinite were prepared.

Characterisation, by phosphorus, proton and fluorine NMR spectroscopy confirmed the identity of the P(III) ligands.

The selenides of these phosphorus (III) ligands were synthesised by reaction with selenium in toluene at reflux. The $^{1}$J(PSe) coupling constants were measured from the $^{31}$P{$^{1}$H} NMR spectra, and ranged from 720 Hz in diphenyl(o-tolyl)phosphine selenide to 1044 Hz in 2-2’biphenyltrifluoroethyl phosphinite selenide.

The [Mo(CO)$_5$P] complexes (P = phosphorus(III) ligand) were also synthesised by the reaction of the ligand with molybdenum hexacarbonyl in toluene at reflux over a period of time.

A comparison of the $^{1}$J(PSe) coupling constants of the phosphine and phosphite selenides and highest A$_1$ ν(CO) stretching frequency of the [Mo(CO)$_5$P] complexes was undertaken.
DECLARATION

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning;

COPYRIGHT STATEMENT

i. The author of this dissertation (including any appendices and/or schedules to this dissertation) owns any copyright in it (the “Copyright”) and she has given The University of Manchester the right to use such Copyright for any administrative, promotional, educational and/or teaching purposes.

ii. Copies of this dissertation, either in full or in extracts, may be made only in accordance with the regulations of the John Rylands University Library of Manchester. Details of these regulations may be obtained from the Librarian. This page must form part of any such copies made.

iii. The ownership of any patents, designs, trade marks and any and all other intellectual property rights except for the Copyright (the “Intellectual Property Rights”) and any reproductions of copyright works, for example graphs and tables (“Reproductions”), which may be described in this dissertation, may not be owned by the author and may be owned by third parties. Such Intellectual Property Rights and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property Rights and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and exploitation of this dissertation, the Copyright and any Intellectual Property Rights and/or Reproductions described in it may take place is available from the Head of School of Chemistry.
AKCNOWLEDGMENT

It is difficult to overstate my gratitude to my MSc. supervisor, Dr Alan Brisdon. With his inspiration and enthusiasm, he helped to make chemistry fun for me. Throughout my dissertation-writing period, he provided support, sound advice, and a lot of good ideas. I would have been lost without him.

In particular, I wish to express my gratitude to my parents, Mr Moftah and Mrs Aisha, who have been a continuous source of support – moral, emotional and of course financial – during my life, and this dissertation would certainly not have existed without them.

Words cannot explain how extremely grateful I am to have had my beloved husband (Ali Elfurgani) beside me throughout this dissertation. He has been, always, my joy, my pillar and my guiding light, and I thank him.

I am heartily thankful to my sisters and my brothers for never-ending support, especially my sister (Hameda), who was the reason for me to complete my postgraduate study at Manchester University, even when the road to my graduate degree has been long and winding.

Over all, I would to thanks my little angel (Malak) for giving me happiness and joy. She is a powerful source of inspiration and energy during this work.

Finally, thanks to Mrs Lorraine Onabanjo and Dr Robin Pritchard for their support and help. Also I offer my regards and blessings to all of those who supported me in any respect during the completion of the dissertation.
Introduction

1.1 History of Phosphorus

Hennig Brand is attributed with the discovery of phosphorus in Hamburg in 1669, although previously the element may have discovered by Arabian alchemists.\(^1\), \(^2\) Brandt obtained the substance by distilling urine, to give a substance which, when exposed to air, glowed in the dark and burst into flame. It was consequently named “phosphorus” derived from two Greek words, “\(\pi\omega\zeta\)” phos, meaning light and “\(\pi\omega\rho\zeta\)” phoros meaning to bring before sunrise.\(^3\), \(^4\)

However the name “phosphorus” was not just applied to materials containing phosphorus but was often used for a variety of light-emitting materials, such as luminescent barium sulphide which was called “Bologna phosphorus”.\(^1\), \(^2\)

The easiest process to prepare elemental phosphorus was by reducing compounds containing phosphorus. Initially this was based on the reduction of a mixture of dried urines with charcoal and sand. By the end of the eighteenth century urine, which had been the only source used to obtain the element for nearly 100 years after its discovery, was replaced by bones.\(^3\) Today the method is similar, but based on various phosphate rocks which are reduced by a mixture of sand and coke in an electric furnace. Because of the range of compositions of phosphate rocks, it is not feasible to write a simple general equation to describe this reaction. However the equation shown is often given, eq (1).\(^5\)

\[
\text{Ca(OH)(PO}_4\text{)}_3 + 5\text{SiO}_2 + 7\text{C} \rightarrow 5\text{CaSiO}_3 + 7\text{CO} + \frac{1}{2}\text{H}_2\text{O} + 3\text{P}
\]

In 1811 the first organic phosphorus compound “lethicin” was isolated by Vauquelin from brain fat and it was characterised by Gobley in 1850 as a phosphorus-containing lipid.\(^1\) Another naturally-occurring organic phosphorus compound, “nuclein”, was isolated by Mieschem in 1868 from pus cells, obtained from surgical bandages. These findings resulted in the association of phosphorus compounds with living tissues.\(^3\)

It is now established that phosphorus is one of the most important elements for life,\(^6\) being very important to a variety of body functions; it plays a vital role to protect cell
membranes and it is involved in the formation of energy-storing materials such as ATP (adenosine triphosphate).\(^7\)\(^\text{2}\) Phosphorus-containing compounds also help to buffer acids and bases in blood and it is essential for platelet function and that of white and red blood cells. Moreover, phosphorus plays a crucial role with calcium in the formation of healthy teeth and bones.\(^7\)\(^\text{2}\)

Organo-phosphorus compounds also play an important part in modern organic synthetic chemistry. For example, the Wittig reaction, discovered in 1954 by Georg Wittig\(^8\) is used for the formation of new C-C bonds. It involves a carbonyl compound as an electrophile and a phosphorus–stabilized carbanion (ylid) as a nucleophile. In general, the ylid is prepared in situ from a triphenylphosphonium salt and a strong base, for example alkyl lithium or LDA (eq 2):\(^9\)

\[
\begin{align*}
\text{R-CH}_2\text{Br} + \text{P(C}_6\text{H}_5)_3 & \rightarrow \text{RCH}_2\text{P(C}_6\text{H}_5)_3 \quad \text{LDA} \\
\text{RCH}_2\text{P(C}_6\text{H}_5)_3 & \rightarrow \text{RCH} \equiv \text{P(C}_6\text{H}_5)_2
\end{align*}
\]

However, one of the most widespread uses of P (III) systems is as ligands in transition metal systems which are subsequently used for catalysis. Triphenylphosphine complexes of Rh, Pd, and Ru play an important role in homogeneous catalysis for a large range of transformations. Palladium complex with PPh\(_3\) are particularly valuable in organic synthesis.\(^{10}\) The formation and properties of P(III) ligands is reviewed in the remainder of this section.

### 1.2 Phosphorus (III) compounds:

The entry point for many P(III) compounds is PCl\(_3\), which is formed by the reaction of elemental phosphorus with chlorine.\(^{11}\) From this is formed three major categories of P(III) compounds, the first type containing P–R (where R is aryl or alkyl) bonds, the second with P–ER linkages (where E is heteroatom such as, N, O, R = aryl, alkyl), such as the triorganophosphites P(OR)\(_3\); the third containing a combination of the other two, for example phosphonites, R’P(OR)\(_2\), and phosphinites (R’\(_2\)POR). A range of halo-containing phosphorus(III) compounds are also known, which are used mainly as starting materials for the generation of other P(III) compounds, but some have also been used as ligands, such as PF\(_3\).\(^{12}\)
1.3 Preparation and Properties of Phosphines:

The most general methods for preparation of tertiary phosphines are:

1.3.1 Using Grignard reagents:

This synthetic method is usually limited to tertiary phosphines such as triphenylphosphine (PPh$_3$), and involves treatment of a phosphorus halide with a Grignard reagent at room temperature, under refluxing conditions in tetrahydrofuran or diethylether (eq 3): $^{10,13}$

\[
P X_3 + 3R MgX \rightarrow PR_3+3MgX_2\]

As a result of its favourable physical properties, such as being easy to handle, air-stable and its solubility in organic media, PPh$_3$ is one of the most common ligands formed in this way, and it has been applied in many applications, for example as a reagent in organic synthesis or as a ligand in organometallic and coordination chemistry. $^{10}$

1.3.2 Using organolithium reagents or other active organometallic compounds on halides:

Organolithium reagents are similar to Grignard reagents in their reactions (see eq 4-5) but Grignard reagents are less reactive because the C-Mg bond is less ionic than the C-Li bond. $^{10,13}$

\[
P X_3 + 3LiR \rightarrow PR_3+3LiX\]

Organometallic compounds can be used to obtain mixed halo-organo-P(III) species by using a weaker alkylating or arylating agent as shown below in eq (6-7). $^{13}$

\[
P Cl_3 + LiR \rightarrow RPCl_2 + LiCl\]
In some cases, mixed derivatives may be prepared directly by heating phosphorus with an alkyl iodide, for example (eq 8):  

$$\text{PCl}_3 + 2\text{HgR}_2 \rightarrow \text{R}_2\text{PCl} + 2\text{RHgCl}$$

Tertiary phosphines are generally oxidatively sensitive and malodorous, although less so when aryl rather than alkyl groups are attached to the phosphorus centre. They can react as bases, and can be quaternised by reaction with R'X compounds. However, their major uses are as ligands for transition metal complexes, which is described in more detail below.

1.4 Preparation and Properties of Phosphites

The general method used for the preparation of phosphites is by reaction of phosphorus trichloride with an alcohol in the presence of nitrogen base (eq 9).  

$$\text{PCl}_3 + 3\text{C}_2\text{H}_5\text{OH} + 3\text{C}_5\text{H}_5\text{N} \rightarrow (\text{C}_2\text{H}_5\text{O})_3\text{P} + 3\text{C}_5\text{H}_5\text{N}\text{HCl}$$

An alternative approach is to use a transesterification reaction of either an alcohol ROH or phenol PhOH with trimethyl phosphate P(OCH$_3$)$_3$ under acid catalysed conditions to give rise to high molecular-weight phosphites (eq10).  

$$\text{P(OCH}_3)_3 + 3\text{ROH} \rightarrow \text{P(OR)}_3 + 3\text{CH}_3\text{OH}$$

Triaryl phosphites react to produce triaryl or trialkyl (RO)$_2$P(=O)H as given in reactions (11),(12),(13).  

$$\text{P(OR)}_3 + \text{H}_2\text{O} \rightarrow (\text{RO})_2\text{P(=O)H} + \text{ROH}$$

$$\text{P(OR)}_3 + \text{HCl} \rightarrow (\text{RO})_2\text{P(=O)H} + \text{RCl}$$

$$2\text{P(OR)}_3 + \text{HP(=O)(OH)}_2 \rightarrow 3(\text{RO})_2\text{P(=O)H}$$
In the presence of hydrogen chloride acceptors such as pyridine, and by carrying out the previous reactions, the separation of mono, di, and trialkyl phosphites is possible.\(^{(15)}\)

Triaryl phosphites and trialkyl phosphites are liquids with a smell. In general, phosphites when exposed to moisture in the air or humidity tend to hydrolyse. The rate of hydrolysis is usually greater for the lower molecular weight phosphites.\(^{(15)}\)

Phosphites when heated may produce phosphonates, as shown in eq (14) below:

\[
P(OR)_3 \xrightarrow{\text{Heat}} P(=O)R(OR)_2\]

Trialkyl phosphites react with a catalytic amount of methyl iodide at 200°C, to give alkyl phosphonates in practically quantitative yield. The mechanism for this reaction involves two consecutive S\(_{\text{N}}\)2 steps (eq 15):

\[
(\text{CH}_3\text{O})_3\text{P}: + \text{CH}_3\text{I} \xrightarrow{200°C} \text{CH}_3\text{P(OCH}_3\text{)}_2
\]

\(\text{Trimethyl phosphite} \quad \text{dimethyl methylphosphonate}\)

In the first step, iodide is displaced from the alkyl iodide to give an alkyl trialkoxyphosphonium salt, eq(16). The iodide ion liberated then attacks one of the methoxy groups, resulting in the formation of a neutral dialkyl phosphonate, eq (17).

\[
1- (\text{CH}_3\text{O})_3\text{P}: + \text{CH}_3\text{I} \xrightarrow{} (\text{CH}_3\text{O})_3\text{P}^+\text{CH}_3\text{I} \]

\(\text{Methyltrimethoxyphosphonium iodide}\)

\[
2- \text{CH}_3\text{I} \xrightarrow{} \text{CH}_3\text{I}
\]

\(\text{Dimethyl methylphosphonate}\)
Because the alkyl halide is regenerated in the second step, only a catalytic amount of alkyl iodide is required in order to initiate the reaction. This Arbuzov reaction has been used in the synthesis of many dialkyl phosphonates. When a full equivalent of alkyl halide is used, dialkyl phosphonates with different groups attached to phosphorus and oxygen can be produced, eq (18).\(^{(14)}\)

\[
\text{O} \quad \text{O} \\
\text{(CH}_3\text{CH}_2\text{O})_3\text{P} + \text{BrCH}_2\text{CO}_2\text{C}_2\text{H}_5 \overset{200^\circ}{\longrightarrow} \text{C}_2\text{H}_5\text{OCCH}_2\text{P}(\text{OC}_2\text{H}_5)_2 \
\]

Phosphites find applications in a number of important roles. Their ability to reduce peroxy and alkoxy radicals and hydroperoxides, and to help reduce photodegradation means that they are common additives for lubricants,\(^{(15)}\) as stabilisers,\(^{(16)}\) and polymers.\(^{(17)}\)

### 1.5 Bonding of phosphorus (III) ligands

By appropriate use of various R groups it is possible to tune the organophosphorus compound in terms of electronic and steric effect; as a result phosphorus(III) systems are considered as one of the most versatile ancillary ligands in organometallic and inorganic chemistry.\(^{(12)}\)

As a result of the lone pair of the phosphorus atom, phosphorus (III) ligands are good \(\sigma\)-donors; they are also moderate \(\pi\)-acceptors, at least for the majority of common phosphines (such as, triaryl and trialkyl phosphines).\(^{(18)}\) As a result the trends for \(\sigma\)-donating abilities follow the order below.\(^{(19, 20)}\)

\[
P\text{Me}_3 = \text{P} (\text{NR}_2)_3 < \text{PAr}_3 < \text{P(OMe)}_3 < \text{P(OR)}_3 < \text{PCl}_3 < \text{PF}_3 = \text{CO} \\
\]

Alkyl phosphines are good \(\sigma\)-donor ligands and good bases, because of the lone pair of electrons. However, phosphites, because of the presence of oxygen, are \(\pi\)-acceptors, forming stable complexes with electron rich transition metals.\(^{(21)}\) Phosphines can also act as \(\pi\)-acceptors, previously this was thought to involve the d-orbitals of phosphorus, but it is proposed that the \(\sigma^*\) (P-R) orbital can also act as a \(\pi\)-acceptor orbital.\(^{(18, 19, 20)}\)
When electron withdrawing substituents are present on the phosphorus, the energy of the $\sigma^*$ (P-R) orbital is lowered (figure 1). As a consequence it has been suggested that \( \pi \)-bonding could be dominant in phosphines of the type PX$_3$ (X = halogen), and to a lesser extent the phosphites.

1.6 Measurement of Electronic and Steric Effects:

It is useful first to consider what is meant by an electronic and a steric effect.

**Electronic effect:** means modifying the molecule so as to change its electron donor or acceptor properties. This usually arises as a result of transmission along chemical bonds due to the addition of a strong electron donating or electron withdrawing atom or group, for example, changing P(\( \rho \)-C$_6$H$_4$OCH$_3$)$_3$ to P(\( \rho \)-C$_6$H$_4$Cl)$_3$. \(^{23, 24}\)

**Steric effects:** are the results of non-bonding forces arising from changing parts of a molecule with a smaller or larger group, for instance, changing P(\( \rho \)-CH$_3$C$_6$H$_4$)$_3$ to P(\( \sigma \)-CH$_3$C$_6$H$_4$)$_3$. \(^{23, 24}\)

A pictorial representation of both is shown in Figure 2. \(^{24}\)
However, it is very important to realize that electronic effects can have important steric consequences and vice versa. For instance, changing the angles between substituents will change the percentage of s-character of the phosphorus lone pair (see figure 3). Also changing the electronegativity of atoms can have an effect on angles and bond distances. Therefore, electronic and steric effects are very strongly related and difficult to separate from each other (figure 2).

Figure 2- A schematic definition of electronic and steric effects. (10)

In order to quantify the effects described above steric and electronic parameters have been proposed.

Figure 3 - Substituent effects on the lone pairs of phosphorus in phosphines. (23)
1.7 Steric parameter:

By changing the substituents attached to the phosphorus centre it is possible to control the bulkiness of the ligand, for example on going from PMe₃ to P'Bu₃ the size of the phosphine increases. The most widely used measure of the size of each ligand is made using the Tolman cone angle, θ, which is the angle of the cone at the metal centre of the [Ni(CO)₃PR₃] complex, which completely encloses the ligand and just touches the van der Waals radii of the outermost atoms of the R-substituents. This is shown in figure 4 (a) and (b).

![Tolman cone angle measurement](image)

(a) (b)

Figure 4- (a) – Tolman cone angle measurement for symmetrical ligand. (b)- Cone angle measurement for an unsymmetrical ligand, where the cone angle is taken as two thirds of the sum of the individual cone half angles.

\[ \theta = \frac{2}{3} \sum_{i=1}^{3} \theta_i / 2 \]

1.8 Electronic parameter:

Infrared (IR) frequencies of metal complexes can be very useful as a reliable yardstick of the electronic properties of phosphorus ligands that are co-ordinated to a particular metal and provides an alternative to phosphorus-based parameters, for example the proton basicity scale.

Tolman’s electronic parameter (TEP) is the simplest and still one of the best–known parameters for the measurement of the electronic effects of phosphorus ligands, which is based upon the vibration spectra of [Ni(CO)₃PR₃] complexes. The stretching frequencies of the co-ordinated carbon monoxide ligands in complexes has
been used in this way because an increase in the electron density on the metal, resulting from strong $\sigma$-donor ligands, increases the back donation into the CO ligand $\pi^*$ orbital, which lowers the CO stretching frequency, (as illustrated in figure 5). \(^{(22, 21)}\)

![Diagram showing strong and weak back donation](image)

**Strong back-donation**  
low $\nu$(CO)

**weak back-donation**  
high $\nu$(CO)

Figure 5- An illustration of how the extent of backbonding from a phosphine ligand effects the CO stretching frequency. \(^{(21, 22)}\)

From data for a series of complexes containing different phosphines an electronic parameter $\chi$(chi) can be obtained as the difference in the IR frequencies of the symmetric stretches of one complex against that containing P(t-Bu)$_3$. \(^{(22)}\)

In view of the extreme toxicity of nickel tetracarbonyl [Ni(CO)$_4$] \(^{(27)}\) a number of substitute metal complexes have been used, such as those of [Rh(CO)ClP$_2$] and [Mo(CO)$_5$P], whilst Strohmeier and Horrocks compared the CO stretching frequency in [CrL(CO)$_3$] complexes for a series of phosphorus ligands.\(^{(22)}\) Other measures have also been used, including NMR-derived coupling constants, such as $^1$J(PSe) and $^1$J(PtP) from the phosphine selenides and platinum complexes of the ligands.

Although different numbers are obtained from different complexes they demonstrate the same trends {as shown in figure 6 (a) - (b)} and the values can be experimentally inter-related. \(^{(27)}\)
TEP = 1.116 ν(CO)Mo – 243 cm$^{-1}$ \hspace{1cm} (1.1)

TEP = 0.226 ν(CO)Rh + 1621 cm$^{-1}$ \hspace{1cm} (1.2)$^{(27)}$

Table 1- Electronic and steric properties of some monodentate P(III) compounds.$^{(22)}$

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Cone angle</th>
<th>ν(CO)$_{Ni}$/cm$^{-1}$</th>
<th>ν(CO)$_{Mo}$/cm$^{-1}$</th>
<th>ν(CO)$_{Rh}$/cm$^{-1}$</th>
<th>$^1$J(SeP)/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe$_3$</td>
<td>118</td>
<td>2064.1</td>
<td>2071</td>
<td>1976</td>
<td>684</td>
</tr>
<tr>
<td>PEt$_3$</td>
<td>132</td>
<td>2061.7</td>
<td>2069</td>
<td>1958</td>
<td>686</td>
</tr>
<tr>
<td>P(n-Bu)$_3$</td>
<td>132</td>
<td>2060.3</td>
<td>2070</td>
<td>1955</td>
<td>689</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>145</td>
<td>2068.9</td>
<td>2073</td>
<td>1979</td>
<td>731</td>
</tr>
<tr>
<td>P(o-Tol)$_3$</td>
<td>194</td>
<td>2066.6</td>
<td>2066</td>
<td>1974</td>
<td>706</td>
</tr>
<tr>
<td>P(p-Tol)$_3$</td>
<td>145</td>
<td>2066.7</td>
<td>2070</td>
<td>1976</td>
<td>719</td>
</tr>
<tr>
<td>PMe$_2$Ph</td>
<td>122</td>
<td>2065.3</td>
<td>2071</td>
<td>1968</td>
<td>710</td>
</tr>
<tr>
<td>PMePh$_2$</td>
<td>136</td>
<td>2067</td>
<td>2073</td>
<td>1974</td>
<td>725</td>
</tr>
<tr>
<td>POEtPh$_2$</td>
<td>133</td>
<td>2071.6</td>
<td>2071.8</td>
<td></td>
<td>796</td>
</tr>
<tr>
<td>P(OMe)$_3$</td>
<td>107</td>
<td>2079.5</td>
<td>2080</td>
<td>2014</td>
<td>945</td>
</tr>
<tr>
<td>P(p-FC$_6$H$_4$)$_3$</td>
<td>145</td>
<td>2071.3</td>
<td>2078</td>
<td>1983</td>
<td>741</td>
</tr>
</tbody>
</table>
Figure 6- Correlation plots for ν(CO) in [Ni(CO)$_3$P] against (a) ν(CO) in [Mo(CO)$_5$P], (b) ν(CO) in [Rh(CO)ClP$_2$] and (c) $^1$J(PSe) for SeP ($P = $ monodentate P(III) ligand).
1.9 effects of electronegative substituents:

The $\pi$-acidity of the phosphorus (III) ligand increases by using electronegative substituents; such as perfluoroalkyl groups, so that P(CF$_3$)$_3$ is similar to CO in its $\pi$ acceptor properties. In addition to that, they usually exhibit different bonding properties compared with the organophosphines, as a result of their increased $\pi$ acidity. PF$_3$ was identified in the 1940s by Chatt as one of the strongest $\pi$-acceptor ligands, resulting in its ability to replace carbon monoxide in zero-valent transition metal complexes. (28)

A particular stereoelectronic effect observed mostly by phosphites is the so-called $\alpha$-effect; this is when the neighbouring atom has lone pairs of electrons and results in improved nucleophilicity of the phosphorus (III) centre.

This electronic effect can also be moderated by steric constraints, for example, ring systems such as (a) have a reduced $\alpha$-effect compared with (b) so is a stronger nucleophile than (a). (28)

![Diagram of phosphorus ligands](image)

1.10 Phosphines and Phosphites ligand effects.

Aryl phosphites were amongst the earliest ligands that were widely studied. (22) The complicated effects of ligand structure on the rate of the catalytic reactions and process conditions on the product distribution was recognized in the sixties. Pruett and Smith reported a systematic study of ligand effects on a hydroformylation reaction resulting in the presence of several catalytically-active rhodium complexes, in the reaction mixture, figure 7. All these complexes, which contain a number of phosphorus ligands are in equilibrium, and complexes containing more than three phosphorus ligands can be used as hydroformylation catalysts as shown in figure 7.
In addition, the position of the equilibrium depends on a lot of reaction parameters, for example, concentration, temperature, pressure and type of ligand. (29)

At low ligand concentrations the results obtained with P(OR)₃ and PPh₃ are similar. The phosphites at higher ligand-to-metal ratios may retard the reaction, as its steric and electronic properties have a large effect on selectivity of the reaction and the rate. (22)

![Diagram](Rhodium catalysts containing a variety of phosphorus and carbonyl ligands. (29))

Each complex, illustrated in figure 7, reacts at a different rate and has a different selectivity in the hydroformylation of 1-alkenes. Generally, phosphorus ligands by contrast with CO ligands are weaker π–acceptor and stronger σ-donor than carbonyl ligands, they also have the ability to introduce more steric hindrance around the metal. (22, 29)

Alkene addition is hampered by the stronger bonding of CO and by steric hindrance. Consequently, the general rate of the hydroformylation reaction decreases with the number of phosphorus ligands coordinating to the rhodium centre, whereas, simultaneously, the selectivity increases. (22, 29)

### Table 2- Hydroformation with Rhodium phosphite and phosphine catalysts. (22)

<table>
<thead>
<tr>
<th>Ligand R₃P, R=</th>
<th>χ value</th>
<th>θ value</th>
<th>Linearity of product %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Bu</td>
<td>4</td>
<td>132</td>
<td>71</td>
</tr>
<tr>
<td>n-BuO</td>
<td>20</td>
<td>109</td>
<td>81</td>
</tr>
<tr>
<td>Ph</td>
<td>13</td>
<td>145</td>
<td>82</td>
</tr>
<tr>
<td>PhO</td>
<td>29</td>
<td>128</td>
<td>86</td>
</tr>
<tr>
<td>2,6-Me₂C₆H₃O</td>
<td>28</td>
<td>190</td>
<td>47</td>
</tr>
<tr>
<td>4-Cl-C₆H₄O</td>
<td>33</td>
<td>128</td>
<td>93</td>
</tr>
</tbody>
</table>
A wide variety of phosphite and phosphine ligands were studied by Pruett and Smith, who found the general trend, of decreased selectivity for the linear aldehyde when the electron withdrawing properties of the ligand increase. table 2 summarizes the results of Pruett and Smith with some recent data.

As described above, phosphites possess distinctly different steric and electronic properties, and different applications compared with phosphines.

Their ranges of steric properties are more limited than phosphines, but their electronic properties are more extreme. This can be seen in table 3, where some of the measurements of the steric and electronic properties are listed which can be compared with table 1.

| Phosphite | Cone angle | v(CO)$_{\text{Ni}}$ | J(Se) | v(CO)$_{\text{Mo}}$ | v(CO)$_{\text{Rh}}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(MeO)$_3$P</td>
<td>107</td>
<td>2079.5</td>
<td>945</td>
<td>2080</td>
<td>2014</td>
</tr>
<tr>
<td>(EtO)$_3$P</td>
<td>109</td>
<td>2076.3</td>
<td>940</td>
<td>2078</td>
<td></td>
</tr>
<tr>
<td>(PhO)$_3$P</td>
<td>128</td>
<td>2085.3</td>
<td>1027,1039,1086</td>
<td>2083</td>
<td>2016</td>
</tr>
<tr>
<td>(i-PrO)$_3$P</td>
<td>130</td>
<td>2075.9</td>
<td>924</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MeO)Ph$_2$P</td>
<td>132</td>
<td>2072</td>
<td>881</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MeO)$_2$PhP</td>
<td>120</td>
<td></td>
<td>788</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is clear from the literature, that there are relatively few phosphite selenides, or Ni, Mo and Rh metal complexes containing phosphites, compared with phosphines.
Project Aims

As has been described above modifying the steric and electronic properties of a phosphine can have a significant effect the way it bonds to a metal, and this in turn can alter the properties of that metal complex. This can be have a significant influence in metal-catalysed reactions, where changing the P(III) donor can influence the rate of reaction and the product distribution. Whilst there has been much study of tertiary phosphines of the type PR₃ there is a smaller range of phosphites that have been similarly investigated.

Traditionally the steric parameter of phosphines has been measured from X-ray diffraction work, such as the Tolman cone angle which comes from the structure of a [Ni(CO)₃P] complex (P = mondentate P(III) ligand). The electronic properties of a ligand must be obtained from spectroscopic methods. However, the precursor for the nickel complex, nickel tetracarbonyl, is extremely toxic, so alternatives have been used, such as the CO stretching frequency of molybdenum and rhodium complexes or coupling constants derived from platinum or selenium-containing compounds of the phosphines. These approaches have been successfully used before for phosphines, but not, as far as we are aware, for phosphites.

The aim of this project therefore is to prepare a number of phosphites, some of which are already known, and some of which are new with a range of electron withdrawing substituents. Once characterised these phosphites will be reacted with molybdenum hexacarbonyl to form the [Mo(CO)₅P] complexes and with elemental selenium to give the phosphine selenides. The CO stretching frequencies of the molybdenum carbonyl complexes will be recorded and the data obtained will be compared with that previously published for phosphines and the limited number of phosphites.

The ¹J(PSe) coupling constants will be determined for the phosphite selenides and these values will be compared against those obtained for known phosphine selenides and also compared with the vibrational data. It is hoped in this way to demonstrate that ¹J(PSe) values can be used as a convenient measure of the electronic properties of phosphites as well as phosphines. If successful it is hoped that ¹J(PSe) values obtained from readily-prepared P(III) selenides this will provide chemists with an simple scale that is parallel to Tolman’s in measuring the electronic properties.
Experimental section
General Conditions

Phosphorus, fluorine and proton NMR spectra were recorded on a 400 MHz Bruker instrument at 161.976, 376.698 and 400.131 MHz respectively, as solutions in CDCl₃. Spectra were referenced against TMS (proton), CFCl₃ (fluorine) and 85% H₃PO₄ (phosphorus) Multiplicities are given as follows: s=singlet, m=multiplet, t=triplet, q=quartet. Infrared (IR) spectra were recorded on a Perkin Elmer RX-1 spectrometer. Percentage yields are quoted against the limiting reagent, however in some cases it was not possible to remove all starting materials or solvents and in those cases a percentage yield figure is not reported. Chemical element analyses were performed by the analytical laboratory in the School of Chemistry.

The solvents toluene and diethyl ether were dried over sodium wire for more than 24 hours prior to use. Chloroform was used as supplied. The compounds PPhCl₂, PPh₂Cl and PCl₃ are sensitive to the air so need to be handled appropriately. All glassware was oven-dried before use in an experiment.

1- Preparation of Phosphites:

2.1.1- Synthesis of 2, 2’-biphenyl chlorophosphite.

This was made by the method of Vallee et al, as shown below: \(^{(32)}\)

\[
\text{PCl}_3 + \text{OH} \quad \text{Et}_3 \text{N} \quad \text{OH} \quad \text{Cl}\quad \text{PCl}_3 + \text{Et}_3 \text{N} \cdot \text{HCl}
\]

2, 2’-Biphenol (2.00 g, 10.7 mmol) was dissolved in toluene (25 ml) and the solution was cooled in an ice bath. A solution of phosphorus trichloride (2.21 g, 16.0 mmol) and triethylamine (4.5 ml, 32.0 mmol) in toluene (10 ml) was slowly added. The mixture was allowed to warm to room temperature and was stirred for a further 36 h. It was filtered and concentrated to afford slightly yellow oil; yield: 2.37 g (59 %). \(^{31}\)P{\(^1\)H} NMR: 178.9 ppm. \(^1\)H NMR: 7.0-7.4 (m, 10H, Ar).
2.1.2- Synthesis of 1H,1H,2H,2H-perfluorodecyldiphenyl phosphinite:

A 3-necked round-bottom flask equipped with magnetic stirrer, was charged with a mixture of 1H,1H,2H,2H-perfluorodecan-1-ol (0.2577 g, 2.71 mmol), diethyl ether (45 ml) and N, N-diethyl aniline (0.4 g, 2.71 mmol). After cooling to ice temperature a solution of chlorodiphenylphosphine (0.5 g, 2.71 mmol) dissolved in diethyl ether (5 ml) was added drop wise. The mixture was stirred at ice temperature for 3 hours, and then allowed to warm to room temperature. After filtration through filter paper, the solvent was removed using a rotary evaporator to afford a white solid; yield: 1.64 g, (89 %). $^{31}$P $^{1}$H NMR: 116.1 ppm. $^{1}$H NMR: 2.31 (t, 2H, CH$_2$), 3.88 (t, 2H, CH$_2$), 7.1-7.8 (m, 10H, Ar). $^{19}$F NMR: -80.9 (m, 3F, CF$_3$), -113.6 (m, 2F, CF$_2$), -122.0 (s, 4F, 2CF$_2$), -122.17 (s, 2F, CF$_2$), -123.72 (s, 2F, CF$_2$), -126.14 (s, 2F, CF$_2$).

2.1.3- Synthesis of 3-fluorophenyldiphenyl phosphinite:

A 3-necked round-bottomed flask equipped with magnetic stirrer, was charged with a mixture of 3-fluorophenol (0.3 g, 2.719 mmol), N,N-diethyl aniline (0.4, 2.719 mmol) and dry diethyl ether (45 ml). After cooling to ice temperature a solution of chlorodiphenyl phosphine (0.4 ml, 2.719 mmol) dissolved in diethyl ether (5 ml) was slowly added over 10 minutes. The reaction mixture was stirred at ice temperature over 3 hours under nitrogen and then allowed to warm at room temperature. After filtration through filter paper, the solvent was removed using a rotary evaporator to afford a white liquid, yield: 1.06 g. $^{31}$P $^{1}$H NMR: 112.4 ppm. $^{1}$H NMR: 6.4-7.3 (m, 14H, Ar). $^{19}$F NMR: -112.7 (dt, 12.5 Hz, 10.4 Hz, F)
2.1.4- Synthesis of 2-fluorophenyldiphenyl phosphinite:

\[
\begin{align*}
\text{OH} + \text{PPh}_2\text{Cl} & \xrightarrow{\text{N, N-diethylaniline}} \text{Diethylether} \\
\text{O} - \text{P} & \xrightarrow{} \\
\end{align*}
\]

A 3-necked round-bottomed flask equipped with magnetic stirrer, was charged with a mixture of 2-fluorophenol (0.3 g, 2.719 mmol), \(N, N\)-diethyl aniline (0.4, 2.719 mmol) and dry diethyl ether (45 ml). After being cooled to ice temperature a solution of chlorodiphenyl phosphine (0.4 ml, 2.719 mmol) dissolved in dry diethyl ether (5 ml) was slowly added over 10 minutes. The reaction mixture was stirred at ice temperature for 3 hours under nitrogen. After that time it was allowed to warm to room temperature, filtered through filter paper and the solvent was removed using a rotary evaporator to afford to white liquid, yield: 1.0 g. \(^{31}\text{P}\{\text{^1H}\}\) NMR: 118.7 ppm. \(^{1}\text{H}\) NMR: 6.8-7.8(Ar, 14H). \(^{19}\text{F}\) NMR: -139.78 (s, 1F, F).

2.1.5- Synthesis of 2, 2'-biphenyltrifluoroethyl phosphate:

\[
\begin{align*}
\text{OH} + \text{P-Cl} & \xrightarrow{\text{N, N-diethylaniline}} \text{Diethylether} \\
\text{O} - \text{P} & \xrightarrow{} \\
\text{O} - \text{CH}_2\text{CF}_3 & \xrightarrow{}
\end{align*}
\]

A 250ml 3-necked round-bottom flask equipped with magnetic stirrer was charged with a mixture of 2, 2-trifluoroethanol (0.1 g, 1.2 mmol), \(N, N\)-diethyl aniline (0.17g, 1.2 mmol) and diethyl ether (45 ml). After cooled to ice temperature a solution of 2, 2'-biphenyl chlorophosphite (0.3 g, 1.2 mmol) dissolved in diethyl ether (5 ml) was added slowly over 10 minutes. The reaction mixture was stirred at ice temperature for 3 hours then it was allowed to warm to room temperature. After filtration through filter paper, the solvent was removed using a rotary evaporator to afford a yellow liquid, yield: 1.76g. \(^{31}\text{P}\{\text{^1H}\}\) NMR: 135.2 ppm. \(^{1}\text{H}\) NMR: 3.7(t, 2H, CH$_2$), 7.0-7.4(m, 8H, Ar), \(^{19}\text{F}\) NMR: -76.7 ppm (t, 9.0 Hz, CF$_3$).

2.1.6- Synthesis of 2, 2'-biphenylhexafluoroisopropyl phosphinite:
A 3-necked round-bottomed flask equipped with magnetic stirrer, was charged with a mixture of hexafluoroisopropanol (0.380g, 2.26 mmol), \( N, N \)-diethylaniline (0.27g, 2.266 mmol) and diethyl ether (45 ml). After being cooled to ice temperature a solution of chlorodiphenylphosphine (0.4 g, 2.26 mmol) dissolved in diethyl ether (5 ml) was slowly added over 10 minutes. The reaction mixture was stirred at ice temperature for 3 hours, after that time it was allowed to warm to room temperature. After filtration through filter paper the solvent was removed using a rotary evaporator to afford to yellow solid; yield: 1.86 g. \(^{31}\)P\{\(^1\)H\} NMR: 141.9 ppm. \(^1\)H NMR: 7.2-7.7(m, 10H, Ar), 4.40(sept, 6.5 Hz, 1H, CH), \(^19\)F NMR: -75.3 (d, 6.5 Hz, 2CF\(_3\)).

2.1.7- Synthesis of 2, 2'-biphenylpropyl phosphite:

A 3-necked round-bottomed flask with a magnetic stirrer was charged with a mixture of propanol (0.096 g, 1.6 mmol), \( N, N \)-diethyl aniline (0.23 g, 1.6mmol) and diethyl ether (45 ml). After cooled to ice temperature a solution of 2, 2'-biphenyl chlorophosphite (0.4 g, 1.6mmol) dissolved in diethyl ether (5 ml) was added slowly over 10 minutes. The reaction mixture was stirred at ice temperature for 3 hours. After that time it was allowed to warm at room temperature, filtered and the solvent was removed using a rotary evaporator to afford to yellow liquid; yield: 0.93 g. \(^{31}\)P\{\(^1\)H\} NMR: 143.8 ppm.
2-Preparation of P(III) Selenides:

2.2.1- Synthesis of triphenylphosphine selenide:

\[
\text{Triphenylphosphine (1.0 g, 3.8 mmol) and selenium (0.60 g, 7.6 mmol) were dissolved in toluene (50 ml) and heated at reflux for 6 hours. The product was left to cool to room temperature, after then it was filtered and concentrated to obtain to yellow solid; yield: 0.197g (15 %).}^{31} \text{P} \{^1\text{H}\} \text{ NMR} 35.3 \text{ ppm} \quad 1^J(\text{PSe}) = 728 \text{ Hz.} \quad 1^H \text{ NMR: 7.3-7.5 (m, 15H, Ar), 7.6-7.7 (m, 15H, Ar).}
\]

2.2.2- Synthesis of triphenylphosphite selenide:

\[
\text{Triphenyl phosphite (0.5 g, 1.6 mmol) and selenium (0.2 g, 3.22 mmol) were added to toluene (45 ml) in a round-bottom flask. The reaction mixture was heated to reflux and stirred for 8 hours. After allowing to cool to room temperature the mixture was filtered to remove the excess of selenium and concentrated to afford a yellow oil; 0.52 g (83 %).}^{31} \text{P} \{^1\text{H}\} \text{ NMR: 58.4 ppm,} \quad 1^J(\text{SeP}) = 1024 \text{ Hz.} \quad 1^H \text{ NMR: 7.2-7.5 ppm (m, 15H, Ar)}
\]

2.2.3- Synthesis of tris(2,4,6-trimethylphenyl)phosphite selenide:
To a round bottomed flask with condenser and magnetic stirrer bar was added toluene (45 ml), tris (2, 4, 6-trimethylphenyl) phosphite (0.3 g, 0.687 mmol) and powdered elemental selenium (0.1 g, 1.37 mmol). The solution was stirred and heated in an oil bath over 8 hours. After that time it was left to cool to room temperature. The reaction mixture was filtered and concentrated to remove the solvent. It gave a yellow solid, yield: 0.31 g (88 %). $^{31}$P $^{1}$H NMR: 51.3 ppm, J(SeP) = 1010 Hz. $^{1}$H NMR: 2.15(s, 9H, 3CH$_{3}$), 2.19(s, 12H, 6CH$_{3}$), 7.1(m, 12H, 3Ar).

2.2.4- Synthesis of diphenyl(o-tolyl) phosphine selenide:

Diphenyl(o-tolyl) phosphine (0.5 g, 2.21 mmol) and powdered elemental selenium (0.349 g, 4.42 mmol) were dissolved in toluene (50 ml) in a round bottomed flask fitted with condenser and magnetic stirrer. The solution was stirred and refluxed for 9 hours. After the mixture was allowed to cool to room temperature, it was filtered to remove excess selenium and concentrated using a rotary evaporator to afford a yellow oil, yield: 0.55 g (67 %). $^{31}$P $^{1}$H NMR: 32.2 ppm, J(SeP) = 720 Hz, $^{1}$H NMR: 3.62(s, 3H, OCH$_{3}$), 6.9-7.5(m, 2H, Ar), 7.5-7.7 (m, 12H, Ar). Elemental analysis (calculated for C$_{19}$H$_{17}$OPSe): C: 61.96 (61.45), H: 4.62 (4.62) %

2.2.5- Synthesis of 2, 2’-biphenyl chlorophosphite selenide:
To a 250ml round bottomed flask with condenser and magnetic stirrer bar was added powdered elemental selenium (0.8 g, 10 mmol) and a solution of 2,2'-biphenyl chlorophosphite (2.5 g, 10 mmol) dissolving in toluene (50 ml). The mixture was refluxed over 8 hours and then cooled to room temperature. After that time it was filtered through filter paper, and the solvent was removed using a rotary evaporator to afford yellow oil; yield: 1.04 g (32 %) $^{31}$P{$^{1}$H} NMR: 61.5 ppm. $^{1}$J(SeP) = 870 Hz. $^{1}$H NMR: 7.7-7.3 (m, 8H, Ar).

2.2.6- Synthesis of diphenyl(hexafluoroisopropyl)phosphinite selenide:

\[
\text{(CF}_3\text{)}_2\text{HCOPPh}_2 + \text{Se} \xrightarrow{\text{Toluene, Reflux}} \text{(CF}_3\text{)}_2\text{HCOPPh}_2
\]

Into a round bottomed flask with condenser and magnetic stirrer was added powdered elemental selenium (0.2 g, 2.5 mmol) and a solution of diphenyl(hexafluoroisopropyl)phosphinite (2.68 g, 1.81 mmol) dissolving in toluene (50 ml). This was refluxed over 14 hour. The mixture reaction was allowed to cool to room temperature, then filtered and the solvent removed in vacuum. The resulting brown oil was purified through a short silica column using diethyl ether as the eluent, yielding as a yellow oil; yield: 1.58 g (48 %). $^{31}$P{$^{1}$H} NMR: 100.7 ppm, $^{1}$J(SeP) = 843 Hz. $^{1}$H NMR: 5.6-5.8 (d sept, $J_{PH}$=16.3, $J_{HF}$ = 6.1 Hz, 1H, HC (CF$_3$)$_2$), 7.36-7.52 (m, 6H, Ar), 7.65-7.7 (m, 4H, Ar) $^{19}$F NMR: -72.8 ppm (d, 6.0 Hz, 2CF$_3$).

2.2.7- Synthesis of 1H, 1H, 2H, 2H-perfluorodecyl diphenyl phosphinite selenide:

\[
\begin{array}{c}
\text{Ph} \text{P} - \text{O} - \text{CH}_2 - \text{CH}_2 - (\text{CF}_2)\gamma - \text{CF}_3 + \text{Se} \xrightarrow{\text{Toluene, Reflux}} \\
\text{Ph} \text{P} - \text{O} - \text{CH}_2 - \text{CH}_2 - (\text{CF}_2)\gamma - \text{CF}_3
\end{array}
\]

To the previously prepared 1H, 1H, 2H, 2H-perfluorodecyl diphenyl phosphinite was added powdered elemental selenium (0.21 g, 2.6 mmol) and toluene (50 ml). This was refluxed for 11 hours. After the reaction mixture was allowed to cool to room temperature it was filtered and the solvent removed in vacuum. The resulting brown oil was purified through a short silica column using diethyl ether as the eluent, yielding, 1H,1H,2H,2H-perfluorodecyl diphenyl phosphinite selenide as a yellow
oil; yield: 0.51 g, (91 %). $^{31}$P $^1$H NMR: 87.6 ppm, $^1$J(SeP) = 807 Hz. $^1$H NMR: 2.4-2.6(tt, 2H,CH$_2$), 4.2-4.4(q, 2H, CH$_2$), 7.3-7.5(m, 6H,Ar), 7.7-7.9 (m, 4H, Ar). $^{19}$F NMR: -80.7 (t, 9.9Hz, CF$_3$), -113.2 (m, 2F, CF$_2$), -121.6 (m, 2F, CF$_2$), -121.9 (m, 4F, 2CF$_2$), -122.6 (m, 2F, CF$_2$), -122.8 (m, 2F, CF$_2$), -126.0(m, 2F, CF$_2$).

2.2.8- Synthesis of 2, 2’-biphenyltrifluoroethyl phosphite selenide:

![Chemical structure](image)

2, 2’-biphenyltrifluoroethyl phosphite (1.76 g, 5.60 mmol) and powdered selenium (0.88g, 11.20mmol) were dissolved in toluene (50 ml) in a round bottomed flask with condenser and magnetic stirrer. The solution was stirred and refluxed over 7 hours. The solution was left to cool to room temperature. It was filtered to remove excess selenium and concentrated using a rotary evaporator to afford a yellow oil; yield: 0.77 g (35 %). $^{31}$P $^1$H NMR: 79.9 ppm, $^1$J (SeP) = 1044 Hz. $^1$H NMR: 4.5{dq J (PH) = 12, J (FH) = 8 Hz, CH$_2$}, 7.0-7.4(m, Ar). $^{19}$F NMR: -74.3 (t, J (FH) = 8 Hz, CF$_3$).

2.2.9-Synthesis of 3- fluorophenyl(diphenyl)phosphinite selenide:

![Chemical structure](image)

3- fluorophenyl(diphenyl) phosphinite (1.06 g, 3.58 mmol) and powdered selenium (0.43 g, 5.44 mmol) were dissolved in toluene (50 ml) in a round bottomed flask with condenser and magnetic stirrer . The solution was stirred and refluxed over 10 hours. The solution was left to cool to room temperature. It was filtered to remove excess selenium and concentrated by using rotary evaporator to afford yellow oil; yield: 0.88 g. $^{31}$P $^1$H NMR: 87.115 ppm, $^1$J (SeP) = 829 Hz, $^1$H NMR: 6.2-7.9 (m, Ar). $^{19}$F NMR: -111.38 (s, 1F).

2.2.10- Synthesis of 2-fluorophenyl (diphenyl)phosphinite selenide:
2-fluorophenyldiphenyl phosphinite (1.0 g, 2.719 mmol) and powdered selenium (0.43 g, 5.44 mmol) were dissolved in toluene (50 ml) in a round bottomed flask with condenser and magnetic stirrer. The solution was stirred at reflux for 14 hour. The solution was left to cool to room temperature. It was filtered to remove excess selenium and concentrated by using rotary evaporator to afford yellow oil; yield: 1.11g (88 %). $^{31}$P {$^{1}$H} NMR: 62.4 ppm, $^{1}$J(SeP) = 759Hz, $^{1}$H NMR: 6.6-7.8(Ar, 14H). $^{19}$F NMR: -138.23(s, 1F).

2.2.11- Synthesis of tris(2-cyanoethyl)phosphine selenide:

![Chemical structure](image)

Tris(2-cyanoethyl)phosphine (0.3 g, 1.55 mmol) and selenium (0.24 g, 3.10 mmol) were dissolved in toluene (50 ml) in a round bottomed flask with condenser and magnetic stirrer. The solution was stirred and refluxed over 7 hours. The solution was left to cool to room temperature. It was filtered to remove the excess of selenium and concentrated by using rotary evaporator to afford yellow oil; yield: 0.24g (57 %).

$^{31}$P {$^{1}$H} NMR: 100.1 ppm, $^{1}$J(SeP) = 810 Hz.

2.3- Preparation of molybdenum pentacarbonyl P(III) complexes.

2.3.1 -Synthesis of triphenylphosphine molybdenum pentacarbonyl:
PPh₃ (0.3 g, 1.14 mmol) and molybdenum hexacarbonyl (0.3 g, 1.14 mmol) were dissolved in toluene (50 ml), then the reaction mixture was refluxed and stirred for 3 hours. The mixture was left to cool to room temperature then filtered and concentrated to obtain a light green solid. ³¹P {¹H} NMR: 37.7 ppm. ¹H NMR: 7.2-7.6 (m, 15H, Ar). IR: 3062(w), 2071(s), 1992(m) cm⁻¹.

2.3.2- Synthesis of diphenyl(o-tolyl)phosphine molybdenum pentacarbonyl:

Diphenyl(o-tolyl) phosphine (0.5g, 1.71 mmol) and molybdenum hexacarbonyl (0.45g, 1.71 mmol) were dissolved in toluene (45 ml). The reaction mixture was heated to reflux with stirring for 2 hours. After allowing to cool to room temperature the solution was filtered and concentrated by vacuum resulting in a white solid; yield: 0.54 g (60 %). ³¹P {¹H} NMR: 29.8 ppm. ¹H NMR: 3.7(s, 3H, OCH₃), 6.7-6.8(m, 1H, Ar), 6.9-7.0(m, 2H, Ar), 7.3-7.5(m, 11H, Ar). IR: 2068(m), 1904(s), 1243(m), 1091(w), 796(w) cm⁻¹. Elemental analysis (calculated for C₂₄H₁₇OPSe): C: 57.07(54.4), H: 3.28 (3.24)

2.3.3- Synthesis of 1H,1H,2H,2H-perfluorodecyl diphenyl phosphinite molybdenum pentacarbonyl:

To the previously prepared (1H,1H,2H,2H-perfluoro decyl diphenyl phosphinite) was added molybdenum hexacarbonyl (0.3577 g, 2.21 mmol) and toluene (45ml). The mixture was heated to reflux and stirred for 2 hours. After that time the reaction mixture was left to cool to room temperature, and then it was filtered and concentrated to take off the solvent. The resulting white solid was purified through a short silica column using chloroform as the eluent, yield: 1.09 g (56 %). ³¹P {¹H} NMR: 130.26 ppm. ¹H NMR: 2.32(tt, 2H, J = 19.0, 6.4 Hz, CH₂CF₂), 3.9(t, 2H, J = 6.4Hz, OCH₂), 7.4(m, 6H, Ar), 7.6(m, 4H, Ar). IR: 2972(w), 1505(m), 1914 (s),
1353(w), 744(m) cm$^{-1}$. $^{19}$F NMR: -80.72 (t, 3F, 9.9 Hz, CF$_3$), -113.2 (m, 2F, CF$_2$), -121.6 (m, 2F, CF$_2$), -121.9 (m, 4F, 2CF$_2$), -122.8 (m, 2F, CF$_2$), -123.6(m, 2F, CF$_2$), -126.0 (m, 2F, CF$_2$).

2.3.4 - Synthesis of 2,2'-Biphenyl chlorophosphite molybdenum pentacarbonyl:

```
\[
\begin{array}{c}
\text{O} & P - Cl \\
\text{O} & P - Cl
\end{array}
\quad +
\quad \begin{array}{c}
\text{Mo(CO)}_6
\end{array}
\quad \xrightarrow{Toluene \text{ Reflux}}
\quad \begin{array}{c}
\text{O} & P - Cl \\
\text{O} & P - Mo(CO)_5
\end{array}
\]
```

2, 2'-biphenylchlorophosphite (2.55 g, 10.1 mmol) and molybdenum hexacarbonyl (2.68 g, 10.1 mmol) was dissolved in toluene (45 ml). The mixture was heated to reflux and stirred for 2 hours. After that time the reaction mixture was left to cool to room temperature, was filtered and concentrated to take the solvent off resulting in a yellow oil, yield: 2.09 g (45 %). $^{31}$P{$^1$H} NMR: 168.8 ppm. $^1$H NMR: 6.9- 7.05 (m, 8H, Ar). IR: 3063 (w), 2080 (m), 1929(s), 1603(w), 1435 cm$^{-1}$ (m).

2.3.5 - Synthesis of tris(2,4,6-trimethylphenyl) phosphite molybdenum pentacarbonyl:

```
\[
\begin{array}{c}
\text{O} \quad \text{P}_3 \\
\end{array}
\quad +
\quad \begin{array}{c}
\text{Mo(CO)}_6
\end{array}
\quad \xrightarrow{Toluene \text{ Reflux}}
\quad \begin{array}{c}
\text{O} \quad \text{P} - \text{Mo(CO)}_5
\end{array}
\]
```

Into a round-bottomed flask with magnetic stirrer and reflux condenser was placed tris(2,4,6-trimethylphenyl)phosphite (0.3 g, 0.68 mmol) and molybdenum hexacarbonyl (0.18 g, 0.68 mol) in toluene (50 ml). The reaction mixture was stirred and heated to reflux over 2 hours. After cooling to room temperature overnight, the mixture was filtered and the solvent removed on a rotary evaporator to obtain a dark green oil from which the solvent could not be completely removed: yield 1.2 g.
$^{31}$P{$^1$H} NMR: 153.1 ppm. $^1$H NMR= 2.3 (s, 6H, 2CH$_3$), 2.4(s, 3H, CH$_3$), 7.0(s, 2H, Ar).

2.3.6- Synthesis of diphenyl(ethyl)phosphinite molybdenum pentacarbonyl:

$$\text{CH}_3\text{CH}_2\text{OPPh}_2 + \text{Mo(CO)}_6 \xrightarrow{\text{Toluene, Reflux}} \text{Mo(CO)}_5\text{PhOPCH}_2\text{CH}_3$$

To a round-bottomed flask with magnetic stirrer were dissolved (CH$_3$CH$_2$O)PPh$_2$ (0.3 g, 1.30 mmol) and molybdenum hexacarbonyl (0.34 g, 1.30 mmol) in toluene (50 ml). The reaction mixture was stirred and heated to reflux over 2 hours. The solution was left to cool to room temperature overnight, and was then filtered and the solvent removed on a rotary evaporator to give a yellow oil, yield 0.56 g (92 %). $^{31}$P{$^1$H} NMR: 142.2 ppm. $^1$H NMR= 1.2 (t, 3H, CH$_3$), 3.6 (m, 2H, OCH$_2$), 7.2-7.5 (m, 10H, Ar). IR: 2071(m), 1897(s), 1434 (w), 691(m) cm$^{-1}$. 


Results and discussion
A number of phosphines, phosphinites and phosphites were already available within the laboratory; however a number of others needed to be prepared before their complexes could be made. This project required a number of unusual and mixed phosphites in order to test the use of ν(CO) and $^{1}J($PSe) parameters as a measure of their electronic properties. To start with some phosphinites were made by reacting Ph$_2$PCl with alcohols.

3.1 - Reaction of hexafluoro-isopropanol with chlorodiphenylyphosphine:

Hexafluoro-isopropyldiphosphine has been reported once before.\(^{(33)}\) It was prepared by the dropwise addition of diphenylchlorophosphine into a solution of hexafluoro-isopropanol in cold diethyl ether in the presence of $N,N$-diethylaniline as a base which reacts with the HCl formed during the reaction. The resulting salt is filtered off to leave the product dissolved in the diethyl ether. The reaction can be described in the following equation:

The $^{31}P\{^{1}H\}$ NMR spectrum observed for the product of the reaction dissolved in CDCl$_3$ showed a single peak at 141.9 ppm. This can be compared with the starting material, chlorodiphenylphosphine, which has a peak at 82.2 ppm, and with that reported previously (142 ppm)\(^{(33)}\) which confirms that a reaction has occurred. The $^{1}H$ NMR spectrum shows a septet for the CH at 4.40 ppm with coupling 6.5 Hz. This must be due to coupling with the six equivalent fluorine nuclei and is confirmed by the fluorine NMR spectrum which shows a doublet in the CF$_3$ region at -75.3 ppm with coupling of 6.5 Hz due to coupling with the hydrogen.

3.2- Reaction of $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorodecan-1-ol with chlorodiphenyl phosphine:

There are no previous reports of the phosphite containing the long fluorinated chain derived from $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorodecan-1-ol, this was therefore reacted in a
similar way with chlorodiphenyl phosphine in the presence of \(N,N\)-diethyl aniline in diethyl ether was carried out at ice temperature over 3 hours. After warming to room temperature and work-up a white solid resulted.

The reaction as shown below:

\[
\text{H}_2\text{O} - \text{CH}_2 - \text{CH}_2 - (\text{CF}_2)_7 - \text{CF}_3 + \text{PPh}_2\text{Cl} \xrightarrow{\text{Diethyl ether}} \text{N}, \text{N}-\text{diethylaniline} \rightarrow \text{Ph}_2\text{P} - \text{O} - \text{CH}_2 - \text{CH}_2 - (\text{CF}_2)_7 - \text{CF}_3
\]

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum (figure 3.1) shows a single peak at 116.1 ppm, which is not due to the starting chlorophenylphosphine. The \(^1\text{H}\) NMR spectrum shows a triplet of triplets at 2.31 due to one \(\text{CH}_2\) group, another triplet at 3.88 due to the other \(\text{CH}_2\), and a series of multiplets within the range 7.1-7.8 due to aromatic protons. The presence of the long chain is confirmed by the \(^{19}\text{F}\) NMR spectrum, which shows a multiple at -80.9 due to the \(\text{CF}_3\) and other multiples due to the \(\text{CF}_2\) groups at -113.6, -122.0, -122.2, -123.7, -126.1 respectively.

Figure 3.1- The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \text{1H,1H,2H,2H}-perfluorodecyldiphenyl phosphine.

3.3- Reaction of 3-fluorophenol with chlorodiphenylphosphate:

Once again, there are no reports of phosphites which contain a single fluorine substituent on the phenoxy group, therefore the reactions with 3-fluorophenol and 2-fluorophenol with chlorodiphenyl phosphite were carried out over 3 hours at ice
temperature. The first of these (described by the following equation) resulted in a white liquid product:

\[
\begin{align*}
\text{F} & \text{OH} + \text{PPh}_2\text{Cl} \xrightarrow{N, N\text{-diethylaniline}} \text{Diethylether} \\
\end{align*}
\]

Once again, after work-up, the phosphorus NMR spectrum (figure 3.2) showed the disappearance of the peak due to the starting chlorodiphenyl phosphine at approximately 82 ppm, and the rise of a signal new peak at 112.3 ppm. The proton NMR spectrum shows a number of multiplets within the ranges 6.4-7.3 ppm due to the aromatic protons.

The $^{19}$F NMR of the white liquid shows a doublet of triplets at -112.7 with coupling constant measured as 12.49 Hz and 10.41 Hz due to the fluorine atom bound on the aromatic ring.

---

Figure 3.2 - $^{31}$P($^1$H) NMR spectrum of 3-fluorophenyl diphenyl phosphite

3.4- Reaction of 2- fluorophenol with chlorodiphenyl phosphite

The reaction between 2-fluorophenol and chlorodiphenyl phosphite was carried out in a similar way to that for 3-fluorophenol, and is described by the following equation:
The phosphorus NMR spectrum showed a single new peak at 118.7 ppm, which is in a similar position to that found for the isomer 3-fluorophenyldiphenylphosphinite. The proton NMR is also similar, and shows aromatic protons within the ranges 6.8-7.8 ppm, of total intensity of 14 protons. The presence of the fluorine in the product is shown in the $^{19}$F NMR spectrum of the white liquid, which shows a singlet peak at -139.78 ppm due to the fluorine atom.

It has been reported that 2,2′-biphenyl chlorophosphite is a convenient way of preparing phosphites which have different groups. This was prepared following the method of Christophe Vallee et al.\(^{(32)}\)

3.5- Reaction of 2, 2′-biphenol with phosphorus trichloride.

2,2′-Biphenol was reacted with phosphorus trichloride in toluene in the presence of triethyl amine, as shown below to give a yellow-coloured viscous oil.

$$\text{Cl}\ x\ x\ x\ x\ N,\ N\text{-diethylaniline}$$

Figure 3.4 illustrates the $^{31}$P\{\textsuperscript{1}H\} NMR spectrum for this oil, which shows a clear single peak at 179.8 ppm. No starting phosphorus trichloride remained, since there was no longer a peak at approximately 220 ppm. The reaction appears to be successful, since Vallee et al reported the $^{31}$P resonance for the product at 178.9 ppm.\(^{(32)}\) The reduction in chemical shift value (from that of PCl₃) is expected on replacing two of the chlorines with biphenol. The proton NMR spectrum of the product recorded in CDCl₃ shows a multiplet due to the protons on the aromatic ring over the range 7.0-7.4 ppm.
Having successfully prepared 2,2’-biphenyl chlorophosphite this was used to prepare new phosphites by reaction with a series of alcohols.

Figure 3.4- The $^{31}$P {$^1$H} NMR spectrum of 2,2’-biphenyl chlorophosphite

3.6 - Reaction of 2,2’-biphenyl chlorophosphite with trifluoroethanol.

2,2-biphenyltrifluoroethyl phosphite was synthesised at ice temperature over a period of time 3 hours according to the following equation:

\[
\text{PhNEt}_2\cdot\text{HCl} + \text{N, N-diethylaniline} \rightarrow \text{PhNEt}_2\cdot\text{HCl} + \text{N, N-diethylaniline}
\]

The $^{31}$P NMR data observed for the product dissolved in chloroform shows a single peak at 135.2 ppm, which is in the region expected for a phosphite. The $^1$H NMR spectrum of this product shows two sets of signals. One is a triplet at 3.7 ppm, due to the CH$_2$ group and the second is a set of multiplets due to the protons on the aromatic rings in the region 7.0 – 7.4 ppm. The $^{19}$F NMR spectrum shows the expected CF$_3$ group as a triplet at -76.7 ppm with coupling constant of 0.9 Hz.

3.7 -Reaction of 2, 2’-biphenyl chlorophosphite with propanol.

2,2’-Biphenyl propyl phosphite has not been reported previously, according to searches conducted on Reaxys, so this was prepared in a similar way by reacting a
mixture of chlorobiphenyl phosphite to a diethyl ether solution containing propanol and \(N, N\)-diethylaniline.

The resulting yellow coloured, viscous liquid shows a single peak at 143.8 ppm in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum. This is different from the starting material and in the usual region for a phosphite. Unfortunately, the proton NMR spectrum shows the presence of some diethyl ether. However two of the expected signals are visible in the spectrum, a triplet at 1.08 ppm due to methyl group, and a triplet of quartets at 3.3 ppm due to the \(\text{CH}_2\) group, and the protons on the aromatic rings are observed in the region 7.0-7.5 ppm.

Having successfully prepared a number of phosphinites and phosphites their selenides were prepared by reacting them with elemental selenium in toluene in order to measure their \(^1\text{J}(\text{PSe})\) coupling constants. Unless stated otherwise, all of the compounds that follow have not been prepared or characterised before. Comparisons were also to be made with some phosphines, and these reactions were studied first.

3.8- Reaction of triphenylphosphine with selenium:
Following the method of Allen and Taylor,\(^{(34)}\) triphenylphosphine was heated for 6 hours with elemental selenium to afford a yellow solid; as shown by the following equation:

As expected the proton NMR spectrum in figure 3.6 shows multiplets within the range 7.3-7.5 due to aromatic protons. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum, shown in figure
exhibits an intense signal at 35.3 ppm with two weaker peaks either side, marked by *. This pattern arises because selenium has one spin-active nucleus, $^{77}$Se ($I = \frac{1}{2}$, 7.6 %). For (100-7.8) % of the molecules a singlet is observed, but when a molecule contains $^{77}$Se a doublet results. So, the $^1J$(PSe) coupling constant can be measured from the distance between the two weaker, outside, peaks. In this case $^1J$(PSe) = 728 Hz. This coupling constant has previously been reported in the literature by Allen and Taylor as 732 Hz.$^{(34)}$

Figure 3.5: The $^{31}$P{${^1}$H} NMR spectrum of triphenylphosphine selenide.

Figure 3.6: The $^1$H NMR spectrum of triphenylphosphine selenide.
3.9-Reaction of diphenyl(o-tolyl)phosphine with selenium.

\[
\begin{array}{ccc}
   \text{Ph} & \text{P} & \text{Ph} \\
   \text{Ph} & \text{OCH}_3 \\
\end{array}
\quad + \quad \text{Se}
\quad \begin{array}{c}
   \text{Toluene} \\
   \text{Reflux}
\end{array}
\quad \rightarrow
\begin{array}{ccc}
   \text{Ph} & \text{Se} & \text{P} \\
   \text{Ph} & \text{OCH}_3
\end{array}
\]

The reaction between diphenyl(o-tolyl)phosphine and powdered elemental selenium, illustrated above, was carried out over 9 hours at reflux, resulted in a yellow solid in good yield. The NMR spectrum shows to a very clear single peak at 32.2 ppm with selenium satellites, as illustrated in figure 3.7, which gives $^1J(PSe) = 720 \text{ Hz}$. This is similar to that seen in the spectrum of triphenylphosphine selenide.

The proton NMR spectrum confirms the presence of this product. There are seven sets of signals one of them due to the (OCH\textsubscript{3}) group on the aromatic ring which is observed as a singlet, and the other multiplets due to protons on the aromatic rings.

The elemental analysis (calculated for C\textsubscript{19}H\textsubscript{17}OPSe) is shown in table 3.1

<table>
<thead>
<tr>
<th>Atom</th>
<th>Expected %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>61.45</td>
<td>61.96</td>
</tr>
<tr>
<td>H</td>
<td>4.62</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Table 3.1- Elemental analysis figures for diphenyl(o-tolyl)phosphine selenide.
Figure 3.7- The $^{31}$P{$^1$H} NMR spectrum of diphenyl(o-tolyl)phosphine selenide.

3.10- Reaction of tris(2-cyanoethyl)phosphine with selenium:

Tris (2-cyanoethyl) phosphine selenide was synthesised by adding two equivalents of powdered selenium to tris(2-cyanoethyl)phosphine in toluene and refluxing this over 7 hours to afford a yellow oil, as shown in the following equation:

\[
\text{(NCCH}_2\text{CH}_2\text{)}_3\text{P} + \text{Se} \xrightarrow{\text{Toluene Reflux}} \text{(NCCH}_2\text{CH}_2\text{)}_3\text{PSe}
\]

The $^{31}$P{$^1$H} NMR spectrum of the product shows a signal peak at 100.1 ppm that is shifted from the starting phosphine by 34.5 ppm with selenium satellites of 811 Hz.

While there are many phosphine selenides reported in the literature there are not very many phosphite or phosphinite selenides. However (PhO)$_3$P=Se has been reported before, and so this was reaction was repeated first.

3.11- Reaction of triphenylphosphite with selenium.

The reaction between triphenylphosphite and elemental powdered selenium was carried out over 8 hours at reflux, according to the following equation:
The $^{31}$P{$^1$H} NMR spectrum of the isolated product showed the loss of the peak due to triphenylphosphite at 128 ppm and the growth of a signal at 58.4 ppm, which has selenium satellites, $^1$J (PSe) = 1024 Hz.

Previously, Glidewell and Leslie have reported for (PhO)$_3$P=Se the following data $\delta_P$ = 58.6 ppm and $^1$J(PSe) = 1027 Hz$^{(30)}$. This agrees with the data reported here. However, Krawczyk, Skowron'ska and Michalski report a somewhat larger coupling constant of 1086 Hz but with a similar chemical shift value of 58.1 ppm$^{(31)}$.

The $^1$H NMR spectrum only showed multiplets within the region 7.1-7.5 due to aromatic protons. Considering all the data, it is clear that the desired product was formed.

3.12-Reaction of tris(2,4,6-trimethylphenyl)phosphite with selenium.

A yellow solid in good yield was obtained by reacting tris(2,4,6-dimethylphenyl)phosphite with selenium in toluene over 8 hours at reflux. The phosphorus NMR spectrum shows a signal peak at 51.34 ppm and selenium satellite with a phosphorus selenium coupling constant of 1010 Hz. This data can be compared with the starting of tris(2,4,6-dimethylphenyl) phosphite, which has a $^{31}$P{$^1$H} signal at 143.5 ppm.

The proton NMR spectrum shows two peaks at 2.15 ppm and 2.19 ppm due to 3CH$_3$ & 6CH$_3$ environments respectively, a multiplet is also observed at 7.1 due to the protons on the three aromatic rings.

The reaction can be summarised as:

$$\text{P(OPh)$_3$ + Se} \xrightarrow{\text{Toluene, Reflux}} \text{SeP=O}$$
3.13- Reaction of 2, 2’-biphenylchlorophosphite with selenium.

Since we had prepared earlier 2, 2-biphenylchlorophosphite we thought it would be interesting to try to prepare the selenide of that material. This was carried out as shown below in the scheme:

The $^{31}$P NMR spectrum of the product was recorded in CDCl$_3$. As anticipated this spectrum shows a single peak at $\delta = 61.5$ ppm with selenium satellites, $^{1}J$(PSe) = 870 Hz. There is no report of this selenide in the literature, however the coupling constant appears consistent with those for other chlorine-containing P(III) systems, such as 867 Hz in Ph$_2$ClP=Se, and 839 Hz for Et$_2$ClP=Se$^{35}$

Additionally, the proton NMR spectrum confirms the presence of the 2, 2’-biphenyl group with the appearance of signals due to the protons on the aromatic rings which are observed as multiplets in the region 7-7.3 ppm.

3.14- Reaction of diphenyl(hexafluoroisopropyl) phosphinite with selenium.

Two equivalents of powdered selenium were added to a solution of diphenyl(hexafluoroisopropyl)phosphinite in toluene and refluxed over 14 hours under nitrogen. After which was obtained a brown oil that was run down a short silica column using diethyl ether to elute the product. The reaction is as follows:

The $^{31}$P($^1$H) NMR spectrum obtained after work up from this reaction shows only a signal peak at 100.7 ppm with $^{1}J$(SeP) = 843 Hz. None of the starting diphenyl(hexafluoroisopropyl)phosphinite remained, because there was no signal at 141.8 ppm corresponding to this as, illustrated in figure 3.8.
Both the $^1$H and $^{19}$F spectra confirm the presence of the fluorinated side-chain in the product. The proton NMR shows a doublet of septets at 5.7 ppm with $J_{PH} = 16.3$ Hz and $J_{HF} = 6.1$ Hz and the $^{19}$F NMR spectrum shows the a doublet ($\delta = -72.8$ ppm) for the 6F nuclei of the 2 CF$_3$ groups with $J_{PF} = 5.9$ Hz.

Figure 3.8- The $^{31}$P{${^1}$H} NMR spectrum of diphenyl(hexafluoroisopropyl) phosphinite selenide

3.15 - Reaction of diphenyl $^{1}H, {^{1}H}, {^{2}H}, {^{2}H}$-perfluorodecylphosphinite with selenium.

The reaction between diphenyl $^{1}H, {^{1}H}, {^{2}H}, {^{2}H}$-perfluorodecyl phosphinite and selenium in toluene, as shown above, was conducted for 11 hours, after this time it was purified through a short silica column using diethyl ether as the eluent, then the solvent was removed and the sample analysed.

The $^{31}$P{${^1}$H} NMR spectrum shows a single peak at 87.6 ppm and no remaining starting phosphinite at 116.1 ppm. The proton NMR spectrum of the product showed a triplet of triplet due to one of the CH$_2$ groups at 2.5 ppm, the other CH$_2$ signal appears as a complex pattern at 4.3 ppm. A series of multiplets due to the protons on the aromatic ring appear in the range 7.3-7.5 and 7.7-7.9 which by integration against the CH$_2$ signals are of total intensity 10.
The $^{19}$F NMR spectrum exhibits eight signals, the first signal is a triplet at $-80.7$ ppm with a coupling constant of 9.9 Hz due to CF$_3$. The others are multiplets at $-113.2$, $-121.6$, $-121.9$, $-122.6$, $-122.8$ and $-126.0$. These signals confirm the presence of the long fluorinated chain in the product.

3.16 - Reaction of 2, 2-biphenyl (trifluoroethyl)phosphite with selenium.

2,2-biphenyl (trifluoroethyl) phosphite was synthesised at ice temperature over a period of 7 hours according to the following equation:

After work-up a yellow oily product results. The $^{31}$P NMR spectrum of this oil is a single peak at 79.9 ppm with coupling constant $^{1}J_{PSe} = 1044$ Hz. The fact that this is shifted from the starting phosphite (135.2 ppm) and shows the presence of selenium satellites confirms the formation of the selenide.

The $^{1}$H NMR shows two sets of signals. The CH$_2$ group is observed as a quartet at 3.7 ppm in the starting compound. This is shifted to 4.5 ppm in the product, and the pattern also changes to a doublet of quartets with coupling constants of $J$ (FH) = 12 Hz and $J$(FH) = 8 Hz.

The $^{19}$F NMR spectrum of this product recorded in CDCl$_3$, shows, as anticipated, a triplet at chemical shifts appropriate for a CF$_3$ containing compound ($-74.3$ ppm) with J(CH) of 8 Hz.

3.17– Reaction of 3-fluorophenyl(diphenyl)phosphinite with selenium:

The preparation of 3-fluorophenyl(diphenyl)phosphinite selenide was prepared by adding two equivalents of selenium to the phosphite dissolved in toluene resulting in a yellow oil, according to the following scheme:
The $^{31}$P {$^1$H} NMR spectrum shows a peak at 87.1 ppm (this can be compared with the starting phosphinite, 3-fluoro(diphenyl)phosphinite, at 112.3 ppm) with selenium coupling of 829 Hz.

The $^1$H NMR spectrum confirms the presence of the aromatic protons with a set of complex multiplets between 6.2 and 7.9 ppm, and the $^{19}$F NMR spectrum shows a single peak at -111.38 due to the one aromatic fluorine position.

3.18- Reaction of 2-fluorophenyl(diphenyl)phosphinite with selenium:

The preparation of 2-fluorophenyl(diphenyl)phosphinite selenide was carried out over 14 h to afford a yellow oil; as shown in the following equation:

As shown in figure 3.9, the $^{31}$P {$^1$H} NMR spectrum of this oil is a single peak at 62.4 ppm with coupling constant, $^1$J(SeP), of 759 Hz. The $^1$H NMR shows aromatic protons within the range 6.6-7.8 ppm, and the $^{19}$F NMR spectrum of this product recorded in CDCl$_3$, as anticipated, shows a single peak at -138.2 ppm.
Figure 3.9- The $^{31}\text{P}^{(1)}\text{H}$ NMR spectrum of 2-fluoro (diphenyl)phosphinite selenide.

3.19- Synthesis of triphenylphosphine with molybdenum hexaacarbonyl

Triphenylphosphine molybdenum pentacarbonyl was synthesised by adding a mixture of triphenylphosphine and molybdenum hexacarbonyl dissolved in toluene that was heated at reflux over 3 hours resulting in a light green solid. The reaction is shown below:

$$\text{Ph}_{3}\text{P} + \text{Mo(CO)}_6 \xrightarrow{\text{Toluene, Reflux}} \text{Ph}_{3}\text{P(CO)}_5\text{Mo}$$

The phosphorus NMR spectrum (figure 3.10) shows a signal peak at 37.7 ppm, which is shifted from the starting of triphenylphosphine by 43.3 ppm. The proton NMR spectrum shows multiplets within the range 7.2-7.6ppm, due to the aromatic protons of the product.
Figure 3.10- The $^{31}$P{$^{1}$H} NMR spectrum of triphenylphosphine molybdenum pentacarbonyl.

The IR spectrum of triphenylphosphine molybdenum pentacarbonyl shows CO stretching frequencies at 2071 and 1992 cm$^{-1}$ respectively. The lower energy band is broad and intense, the band at 2071 cm$^{-1}$ is weaker, but very sharp. It is this second, $A_{1}$ symmetry, band that is used in assessing the donor ability of a P (III). This complex has been prepared before. In that work the $\nu$(CO) stretching band is reported to be at 2072 cm$^{-1}$ (36). Therefore this experiment was worked.

3.20- Reaction of diphenyl(o-tolyl)phosphine with molybdenum hexacarbonyl.

Diphenyl(o-tolyl)phosphine molybdenum pentacarbonyl was prepared by the reaction of the diphenyl(o-tolyl)phosphine and molybdenum hexacarbonyl in toluene, after heating over 2 hours. The $^{31}$P {$^{1}$H} NMR spectrum, shows a single peak at 29.8 ppm. This data might be compared with the starting material of diphenyl (o-tolyl) phosphine, which has a $^{31}$P{$^{1}$H} NMR chemical shift of -16.8 ppm.

The reaction is shown below:

$$\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_3 + \text{Mo(CO)}_6 \xrightarrow{\text{Toluene, Reflux}} \text{Mo(CO)}_5\text{P} - \text{C}_6\text{H}_4\text{OCH}_3$$

The elemental analysis (calculated for C$_{19}$H$_{17}$OPMo(CO)$_5$) is shown in table 3.2.
Table 3.2- Elemental analysis figures for diphenyl(o-tolyl)phosphine molybdenum pentacarbonyl

<table>
<thead>
<tr>
<th>Element</th>
<th>Expected %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54.4</td>
<td>57.07</td>
</tr>
<tr>
<td>H</td>
<td>3.24</td>
<td>3.28</td>
</tr>
</tbody>
</table>

The IR spectrum of diphenyl(o-tolyl)phosphine molybdenum pentacarbonyl showed a number of absorptions. Two of these are in the CO stretching region of the spectrum with the one at 2068 cm⁻¹ being assigned as the A₁ CO mode.

3.21 – Reaction of 1H,1H,2H,2H-perfluorodecyldiphenyl phosphinite with molybdenum hexacarbonyl.

Heating 1H, 1H, 2H, 2H-perfluorodecyldiphenyl phosphinite and molybdenum hexacarbonyl in toluene at reflux temperatures for 2 hours results in a white coloured viscous solid, after purification through a short silica column using chloroform as the eluent. The reaction was according to the following equation:

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{(CF}_2)_7 & \quad \text{CF}_3 + \text{Mo(CO)}_6 \quad \text{Toluene} & \quad \text{Reflux} & \quad \text{Ph}_2\text{P} & \quad \text{O} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{(CF}_2)_7 & \quad \text{CF}_3 \\
\end{align*}
\]

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of this solid shows a single peak at 130.3 ppm and that no starting 1H,1H,2H,2H-perfluorodecyldiphenyl phosphinite remained.

The \(^1\text{H}\) NMR spectrum shows a CH₂ triplet of triplet at 2.32 ppm with coupling constants of 19.0 and 6.4 Hz and the other OCH₂ signal as a triplet at 3.9 ppm with \(J = 6.4\) Hz and signals for the aromatic protons between 7.4 and 7.6 ppm.

The fluorine NMR data shows the presence of a triplet due to the CF₃ group at -80.7 ppm with a coupling constant of 9.9 Hz, each of the CF₂ signals is a multiplet two of which overlap these are seen at -113.2, -121.6, -121.9, -122.8, -123.6 and -126.0 ppm.
Taken together the $^{31}$P and $^1$H NMR data suggested that reaction of $^{1}H,^{1}H,^{2}H,^{2}H$-perfluorodecyldiphenyl phosphinite has occurred with molybdenum hexacarbonyl to give the expected product, \([\text{Ph}_2\text{POCH}_2(\text{CF}_2)_7\text{CF}_3]\text{Mo(CO)}_5\].

3.22 - Reaction of 2, 2’-Biphenylchlorophosphite with molybdenum hexacarbonyl.

2, 2’-Biphenylchlorophosphite molybdenum pentacarbonyl was synthesised by adding 2, 2’-Biphenylchlorophosphite to molybdenum hexacarbonyl dissolved in toluene as shown in the following reaction:

\[
\begin{align*}
\text{P-Cl} + \text{Mo(CO)}_6 & \rightarrow \text{Mo(CO)}_5 \text{P-Cl} \\
\text{Toluene} \quad \text{Reflux} & 
\end{align*}
\]

The product of the reaction shows a singlet at 168.8 ppm in the $^{31}$P{$^1$H} NMR spectrum, figure 3.11. This can be compared with 178.9 ppm for the starting chlorobiphenyl phosphite. The IR spectrum of 2, 2’-Biphenyl chlorophosphite molybdenum pentacarbonyl showed a number of absorptions with the one at 2080 cm$^{-1}$ being assigned as the A$_1$ CO mode.

Figure 3.11 - The $^{31}$P{$^1$H} NMR spectrum of 2,2’-Biphenyl chlorophosphite molybdenum pentacarbonyl.

3.23- Synthesis of tris(2,4,6-trimethylphenyl) phosphite molybdenum pentacarbonyl:

A dark green oil was obtained in good yield after reacting tris(2, 4, 6-trimethylphenyl) phosphite with molybdenum hexacarbonyl in toluene after 2 hours of heating at reflux. The phosphorus NMR spectrum shows a single peak at 153.1
ppm. This data can be compared with the starting phosphite of tris (2,4,6-trimethylphenyl) phosphite which has a signal at 143.5 ppm.

The proton NMR spectrum shows a signal peaks at 2.3 ppm due to two methyl groups and a signal peak at 2.4 ppm due to the other methyl group in the product (as shown in the scheme below) a signal is also observed for the protons on the aromatic rings.

![Chemical Structure](image)

3.24 - Synthesis of diphenyl(ethyl)phosphinite with molybdenum hexacarbonyl:

Diphenyl(ethyl)phosphinite molybdenum pentacarbonyl was synthesised by adding diphenyl(ethyl)phosphinite and molybdenum hexacarbonyl to toluene and heating this to reflux for 2 hours. The reaction is shown below:

![Chemical Structure](image)

The phosphorus NMR spectrum shows a signal peak at 142.2 ppm, this can be compared with the starting diphenyl(ethyl)phosphinite which shows a peak at 110.9 ppm. The proton NMR spectrum shows a triplet due to the methyl group of the product at 1.2, a multiplet at 3.6 ppm due to the OCH₂ group and multiplets within the range 7.2-7.5 due to the aromatic protons. The IR spectrum of diphenyl(ethyl)phosphinite molybdenum pentacarbonyl shows CO stretching frequencies at 2071 and 1897 cm⁻¹ with the higher energy band being assigned to the A₁ mode.
Discussion

As described in the introduction a formula exists that allows the \([\text{Mo(CO)}_5\text{L}]\) complexes to be related to the \(\nu(\text{CO})\) value for \([\text{Ni(CO)}_3\text{L}]\) complexes. This is:

\[
\text{TEP} = 1.116 \nu(\text{CO})_{\text{Mo}} - 243 \text{ cm}^{-1}
\]

These calculated values are shown in the next to last column of table 3.3. These calculated values can be compared with the observed values for the limited known \([\text{Ni(CO)}_3\text{P}]\) complexes. For example, when \(P = \text{PPh}_3\) the reported value of \(\nu(\text{CO})\) for the nickel complex is 2068.9 cm\(^{-1}\), this can be compared with 2067.9 cm\(^{-1}\) calculated from the carbonyl stretching frequency of \([\text{Mo(CO)}_5\{\text{PPh}_3\}]\). However, there are not very many reported \(\text{Mo(CO)}_5\)-phosphite complexes. Also, the range of \(\nu(\text{CO})\) frequencies is rather small.

An alternative, as described in the introduction is based on the \(^1\text{J}(\text{PSe})\) values of the selenides. For a series of phosphines the equation:

\[
\text{TEP} = 0.159 \text{J}(\text{PSe}) + 1952.3 \text{ cm}^{-1}
\]

gives a good fit to the observed data for phosphines. While this method has been used before for phosphines, it does not appear to have applied to phosphites.

Using this formula for triphenylphosphite suggests that based on a \(^1\text{J}(\text{PSe})\) value of 1024 Hz the \(\nu(\text{CO})\) value of the \([\text{Ni(CO)}_3\text{P}\{\text{OPh}_3\}]\) complex should be over 2115 cm\(^{-1}\). This compares poorly with the real value of 2085.3 cm\(^{-1}\). However, based on a wide range of phosphines and phosphites a more complex formula has been obtained:

\[
\text{TEP} = 0.307 \text{J}(\text{PSe}) - 0.000137 \text{J}(\text{PSe})^2 + 1915.7 \text{ cm}^{-1}
\]

When this formula is used a \(^1\text{J}(\text{PSe})\) value of 1024 Hz gives 2086.7 cm\(^{-1}\), 1.4 cm\(^{-1}\) higher than the real value.

A summary of the spectroscopic data obtained for the selenide and molybdenum pentacarbonyl compounds of the P(III) ligand in this project is given in table 3.3. Also the \(\nu(\text{CO})_{\text{Ni}}\) (TEP) values calculated from the \([\text{Mo(CO)}_5\text{P}]\) stretching frequency and the \(^1\text{J}(\text{PSe})\) values are listed.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}\text{P}^1\text{H}$</th>
<th>J(PSe)</th>
<th>Calc. $\nu$(CO)$_\text{Ni}$</th>
<th>$\nu$(CO)$_\text{Ni}$</th>
<th>Calc. $\nu$(CO)$_\text{Mo}$</th>
<th>$\nu$(CO)$_{\text{(37)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>triphenylphosphite selenide</td>
<td>58.4</td>
<td>1024</td>
<td>2086.7</td>
<td></td>
<td></td>
<td>2085.3</td>
</tr>
<tr>
<td>tris(2,4,6-trimethylphenyl)phosphite selenide</td>
<td>51.3</td>
<td>1010</td>
<td>2086.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diphenyl(o-tolyl)phosphine selenide</td>
<td>32.2</td>
<td>720</td>
<td>2065.9</td>
<td>2066.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2, 2′-Biphenyl chlorophosphite selenide</td>
<td>61.5</td>
<td>870</td>
<td>2079.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diphenyl hexafluoroisopropyl phosphinite selenide</td>
<td>100.7</td>
<td>842</td>
<td>2077.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1H,1H,2H,2H$-perfluorodecyl diphenyl phosphinite selenide</td>
<td>87.5</td>
<td>807</td>
<td>2074.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2′-biphenyltrifluoroethyl phosphinite selenide</td>
<td>79.9</td>
<td>1044</td>
<td>2087.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-fluorophenyl diphenyl phosphinite selenide</td>
<td>87.1</td>
<td>829</td>
<td>2076.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-fluorophenyl diphenyl phosphinite selenide</td>
<td>62.4</td>
<td>759</td>
<td>2069.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>triphenylphosphine selenide</td>
<td>35.3</td>
<td>728</td>
<td>2066.8</td>
<td>2068.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2-cyanoethyl)phosphine selenide</td>
<td>100.1</td>
<td>810</td>
<td>2074.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenyl(o-tolyl) phosphine molybdenum pentacarbonyl</td>
<td>29.8</td>
<td></td>
<td>2067.6</td>
<td>2064.5</td>
<td>2066.1</td>
<td></td>
</tr>
<tr>
<td>$1H,1H,2H,2H$-perfluorodecyl diphenyl phosphinite molybdenum pentacarbonyl</td>
<td>80.7</td>
<td></td>
<td>2071.2</td>
<td>2067.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2-biphenylchlorodiphenyl phosphite molybdenum pentacarbonyl</td>
<td>168.8</td>
<td></td>
<td>2080.3</td>
<td>2077.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diphenyl(ethyl)phosphinite molybdenum pentacarbonyl</td>
<td>142.1</td>
<td></td>
<td>2071.8</td>
<td>2068.5</td>
<td>2071.6</td>
<td></td>
</tr>
<tr>
<td>triphenylphosphine molybdenum pentacarbonyl</td>
<td>37.7</td>
<td></td>
<td>2071.2</td>
<td>2067.9</td>
<td>2068.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3- A summary of the spectroscopic data for P(III) phosphines, phosphinites and phosphites obtained in this project, and comparison with known $\nu$(CO)$_\text{Ni}$ values.
For ligands where both the selenide and molybdenum pentacarbonyl complex have been prepared the two calculated TEP values agree well. For example, for diphenyl(o-toly)phosphine the TEP value calculated from the selenium-phosphorus coupling constant is 2065.9 cm\(^{-1}\), and that calculated from the Mo\((\text{CO})_5\)-phosphine complex is 2064.5 cm\(^{-1}\), a difference of 1.5 cm\(^{-1}\). The observed value for the real complex is 2066.1 cm\(^{-1}\) which is remarkably close to that calculated from the \(^1\)J(PSe) coupling constant.

At this stage it is difficult to make a more extensive comparison because there is very little data for nickel tricarbonyl phosphite complexes. However, for ligands where both selenide and molybdenum carbonyl complexes have been prepared we can compare the values obtained in this work against each other. For 2,2-biphenylchlorophosphite we observe only a small difference in the TEP values predicted based on ν\((\text{CO})\)Mo and \(^1\)J(PSe) (2079.3 and 2077.3 cm\(^{-1}\), a difference of 2.0 cm\(^{-1}\)). But, for \(1H,1H,2H,2H\)-perfluorodecylphenyl phosphinite there is a significant difference between the two values (2074.4 and 2067.8 cm\(^{-1}\), a difference 6.6 cm\(^{-1}\)). Unfortunately because of the toxicity of Ni(CO)\(_4\) any attempt to prepare the [Ni(CO)\(_3\)P] complexes could not form part of this project. However, both sets of figures show the same order, 2,2-biphenylchlorophosphite > \(1H,1H,2H,2H\)-perfluorodecylphenyl phosphinite > diphenyl(o-toly)phosphine which is as expected based on the electronegativity of the groups surrounding phosphorus.

In conclusion, a number of phosphites have been prepared. After characterisation their selenides and molybdenum pentacarbonyl complexes have been synthesised, from which \(^1\)J(PSe) and ν\((\text{CO})\) values were obtained. These values have been used in previously reported relationships to give Tolman ν\((\text{CO})\) values. Where data exists this suggests a good agreement between the data derived from the nickel complex, and that based on these other derivatives. However, the amount of existing data to which comparisons can be made is very limited. This suggests that further work should be done in this area, but it appears that both ν\((\text{CO})\) and \(^1\)J(PSe) values can be used as a reliable guide to the electronic properties of phosphites as well as for phosphines, and that this should be of interest to chemists seeking to determine the
electronic properties of P(III) ligands, such as those used in metal complexes for catalysis.
References


10- Comprehensive Coordination Chemistry II, Elsevier, 2004, 1, 253-296


12- C. Herbert, 2nd yr PhD report, university of Manchester, 2008.


36- Personal communication, A. K. Brisdon.