

Measuring the electronic and steric effect of some phosphine ligands

By

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ABSTRACT

This project describes and compares two methods of assessing the electronic properties of some phosphine ligands. The ligands PPh_3 , $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{-3-CH}_3)$, $\text{PPh}_2\text{C}_6\text{H}_4\text{-4-Cl}$, $\text{P}(\text{C}_6\text{H}_4\text{-4-Cl})_3$, $\text{PPh}(\text{C}_6\text{H}_4\text{-4-SCH}_3)_2$, $\text{P}(\text{C}_6\text{H}_4\text{-4-OCH}_3)_3$ were investigated. Additionally ligands of the type Ph_2PR and PhPR_2 where R = mesityl, cyclohexyl or adamantly were prepared by the reaction of Ph_2PCl , PhPCl_2 with the appropriate Grignard reagents.

The selenides of these P(III) ligands were obtained by reaction of the phosphine with selenium in toluene under reflux over a period of a few hours. The $^1\text{J}(\text{PSe})$ coupling constants were determined for these compounds and ranged from 833 Hz in dimesityl phosphine selenide to 714 Hz in tris(p-anisyl)phosphine selenide.

$[\text{Mo}(\text{CO})_5\text{P}]$ complexes (P = P(III) ligand) were also obtained by the reaction of the phosphine with molybdenum hexacarbonyl in toluene with heating for 2 hours. The $\nu(\text{CO})$ stretching frequencies varied from 2072 cm^{-1} in tri-phenylphosphine molybdenum pentacarbonyl to 2069 cm^{-1} in *bis*(p-thioanisyl)phenylphosphine molybdenum pentacarbonyl.

A comparison of the $^1\text{J}(\text{PSe})$ coupling constants of the phosphine selenides and $\nu(\text{CO})$ stretching frequency of the $[\text{Mo}(\text{CO})_5\text{P}]$ complexes for these ligands, and others reported in the literature is made. From this it is shown the $^1\text{J}(\text{PSe})$ is a useful probe of the electronic effects of a phosphine ligand.

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.

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1. Introduction

1.1 Phosphorus background

Phosphorus is a non-metallic chemical element, which is essential for all living organisms. This element does not naturally exist alone on Earth, but is always found combined with other elements such as oxygen.⁽¹⁾

Hennig Brandt was the first person to have discovered phosphorus; he obtained it by the process of distilling urine. The element which he discovered has the unusual feature of glowing in the dark, and when it is exposed to the air, it bursts into flames.

It got the name “phosphorus” from the Greek language, the word consists of two parts; 'Phos' that means “the light” and 'phorus' that means “it bears when it appears before the sunrise”.^(2,3)

The element Phosphorus has an atomic number which is 15, and a relative atomic weight of 30.97376. Across the cosmos phosphorus has a relative abundance to 3.2×10^{-7} while in crustal rocks on Earth it is the 11th element in order of abundance.⁽⁴⁾

1.2 Chemistry of phosphorus

Since its first isolation in its elemental form as white phosphorus obtained from the distillation of human urine⁽⁵⁾ in the late 17th century phosphorus instilled much curiosity in the minds of early chemists.

The first organic phosphorus compound was isolated from brain fat in 1811 by Vauquelin. In 1850, Gobley characterized it as a phosphorus-containing liquid.⁽⁶⁾ Another natural organic phosphorus compound, 'nuclein', was isolated from pus cells obtained from surgical bandages in 1868 by Mieschem. This could be considered as an important step in the history of associating phosphorus compounds with living tissues.⁽²⁾

By the end of the 18th century, chemists realized that phosphorus existed in animal bones and that plants relied on the element to grow properly. These discoveries

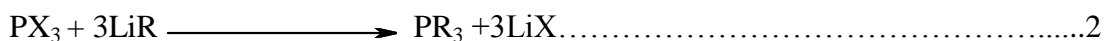
inspired people to develop the fertilizer industry early in the 19th century. ⁽⁵⁾ Originally, the production of phosphorus was achieved by reducing a mixture of desiccated urines with sand and charcoal. ⁽⁶⁾ Until about 1890, the main method to obtain phosphorus was from bone and phosphate rock by reaction with sulphuric acid (H₂SO₄) and carbon. ⁽⁵⁾ In the mid-twentieth century, phosphorus chemistry developed rapidly, because of the discovery by Schrader and Saunders of insecticidal and toxic properties of certain esters containing phosphorus. The economic implications of phosphorus-based pesticides continue to stimulate much work. ⁽⁷⁾

1.3 Preparation and properties of phosphorus and its organic compounds

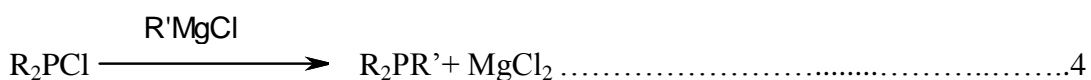
The method used to obtain phosphorus today is not fundamentally different from that used before, but now the starting materials are various phosphate rocks which are reduced by a mixture of sand and coke in an electric furnace. ⁽⁶⁾

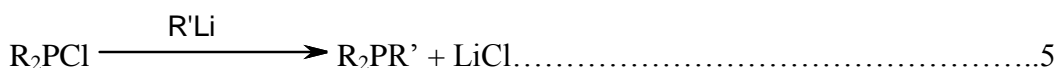
Phosphorus forms a variety of organo-phosphorus compounds, the majority of which have the general formula PR₃ bearing alkyl and aryl substituents on the phosphorus atom. In a more general sense, R may also a halogen atom (e.g. phosphorus halides, PX₃) or, for example, an OR group to give phosphites P(OR)₃. ⁽⁸⁾

Probably the most common P(III) compound used for preparing derivatives of phosphorus is PCl₃, prepared by the reaction of P₄ with chlorine. This can then be reacted with Grignard reagents or other reactive organometallic compounds to give the organic derivatives. ⁽⁹⁾



Mixed phosphines can also be prepared in a similar way:



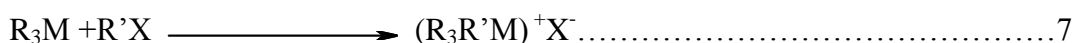


Phosphines are generally sensitive to oxidation, for example trimethylphosphine is spontaneously flammable in air. However, oxidation occurs more slowly for the heavier trialkyl and triaryl phosphines. ⁽¹⁰⁾

The oxidation of phosphines with oxygen, sulfur or selenium can be described by the equation:



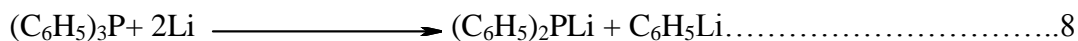
Phosphines also form quaternary salts, e.g. trialkyl and triarylphosphines, -arsines, and -stibines generally react with alkyl and aryl halides:



The tetraphenylphosphonium and arsonium ions can be used for precipitating large anions such as ReO_4^- and ClO_4^- , and complex metal anions. ⁽¹⁰⁾

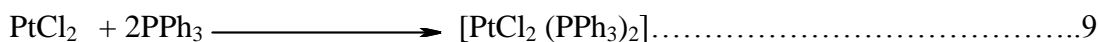
1.4 Reaction of P-C bonds

The phosphorus-carbon bond is not easily cleaved and is relatively strong, so in general P-C bonds are preserved even under reactive conditions. On the other hand, if a relatively stable carbonion can be formed, then P-C bond cleavage, can occur for example: ⁽¹¹⁾



1.5 Phosphorus (III) ligands

Organic phosphines (or phosphanes), PR_3 , play a major role in coordination and organometallic chemistry as ligands. ⁽⁸⁾ The complexes of organophosphines can frequently be simply made from a stoichiometric mixture of a phosphine ligand and a metal salt. Triphenylphosphine, which is a white crystalline solid (m.p 80°C), is a particularly common ligand for transition metal complexes. ⁽¹⁰⁾



Changing the substituents on a phosphorus ligand has long been known to cause marked changes in the properties of the transition metal complexes and the free ligands themselves. Before 1970, almost all changes were considered in terms of electronic effects, while there were fewer references to steric effects. However, in that year, quantitative measures of both steric and electronic effects were suggested based on the A_1 carbonyl stretching vibration (ν) in $\text{Ni}(\text{CO})_3\text{L}$ complexes and the cone angle, θ , of ligands obtained from space-filling CPK molecular models.⁽¹¹⁾

1.6 Definition of Electronic and Steric Effects

An electronic effect arises if changes to part of molecule result in a different electronic distribution within the molecule. This effect usually occurs via transmission along chemical bonds. A steric effect results when the size or shape of the molecule changes. For example, on going from $\text{P}(\text{p-C}_6\text{H}_4\text{Cl})_3$ to $\text{P}(\text{p-C}_6\text{H}_4\text{CH}_3)_3$ a change in electronic effect would be expected, whilst for $\text{P}(\text{p-C}_6\text{H}_4\text{CH}_3)_3$ and $\text{P}(\text{o-C}_6\text{H}_4\text{CH}_3)_3$ the major change should be steric.⁽¹²⁾

However, changing the steric effects can have significant electronic influence and vice versa. For example, greater angles between substituents because of increased bulk will reduce the amount of s-character in the phosphorus lone pair, so changing the electronic properties of the ligand. Changing the electronegativity of the attached atoms or groups may also affect the bond distances and angles at phosphorus. Consequently, electronic and steric effects are inter-related and difficult to separate.

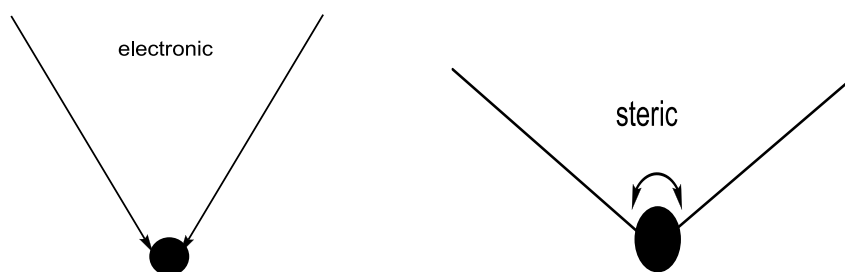


Figure 1. A schematic definition of electronic and steric effects.⁽⁴⁾

1.7 Electronic parameter, ν

In 1977 Tolman reported a parameter based on the vibrational spectra of $[\text{NiL}(\text{CO})_3]$ complexes as a measure of the electronic properties of a ligand – he proposed using the highest CO stretching frequency, ν , of the phosphine-substituted transition metal carbonyl complex. He found that the IR frequencies can be measured with sufficient accuracy to give different values for common substituents. From a series of such measurements he obtained a group electronic parameter χ (chi) by measuring the difference in the CO frequencies of the complexes with different phosphines. Typical values of χ for carbon substituents range from 0 to 20, some values are shown in table 1; ⁽¹³⁾

Table (1) typical values of χ for carbon substituents range from 0 to 20.

Ligand R_3P , R=	χ value for R	θ for PR_3
n-Bu	1.3	132
n-BuO	6.7	109
Ph	4.3	145
PhO	10	128
2,6-Me ₂ C ₆ H ₃ O	9.3	190
4-Cl-C ₆ H ₄ O	11	128
CF ₃ CH ₂ O	13	115
(CF ₃) ₂ CHO	17	135

The $\nu(\text{CO})$ stretching frequency for a $[\text{Ni}(\text{CO})_3\text{L}]$ complex is then given by the sum of the individual χ -value contributions of the groups :

$$\nu = 2056.1 + \chi_1 + \chi_2 + \chi_3 \text{ cm}^{-1}$$

This additively rule may not always apply but it remains a useful approximation. ⁽¹³⁾

Since then a number of computational studies of ligands have been undertaken. A quantitative analysis of ligand effects (QALE) of phosphines was described by Giering and co-workers.⁽¹⁴⁾ Crabtree et al. have reported a method for quantifying the electronic effect of phosphines through *ab initio* calculations on $[\text{Ni}(\text{CO})_3(\text{PR}_3)]$ complexes and obtained computationally derived ligand electronic parameters. Suresh and Koga quantified the electronic effects of substituted phosphines in terms of their molecular electrostatic potential minimum (V_{min}).⁽¹⁵⁾

Kuhl has reviewed a variety of methods for predicting the electronic effect of phosphine ligands and also used the V_{min} parameter for the quantification of the electronic effect of phosphine ligands. The V_{min} in $\text{NH}_2\text{-X}$ system is used as a measure of the electron-attracting tendencies of a substituent and is described by Murray and Politzer. They evaluated the electronic shape of phosphines on the basis of the semiempirical electronic parameter (SEP) of a series of rhodium Vaska-type complexes.^(12, 16)

On changing from one metal to another there may be some difference in the electronic parameters determined for phosphine ligands. For example, Strohmeier and Horrocks,⁽¹⁷⁾ measured the CO stretching frequencies in $[\text{CrL}(\text{CO})_5]$ rather than $[\text{Ni}(\text{CO})_3\text{L}]$ complexes in order to compare phosphorus ligand properties. Generally, there have been few attempts to link the data obtained from one metal complex to that from another. So when plotting a series of properties of metal complexes e.g. stability constants, rate spectral, data rate constants against ligands electronic parameter this is best done by using the electronic parameter property as determined for the same metal.⁽¹³⁾

1.8 Steric effects of phosphine

In 1977 the steric demand of phosphines were quantified by Tolman based on the Corey-Pauling-Koltun model of ligand-metal complexes, and has since become known as the Tolman cone angle, θ . This is defined as the apex angle of a cylindrical cone centered 2.28 Å from the centre of the phosphorus atom that just touches the van der Waals radii of the molecules outermost atoms. ⁽⁴⁾ This method was very practical, even if a rather basic method.

Consequently, attempts were made by a variety of groups to quantify phosphines steric effect and to improve the Tolman model by using the geometry parameters obtained from crystallographic structure and from the quantum mechanically calculated structure of the ligand-metal complex. For example: ⁽¹²⁾ Brown and co-workers derived the ligand repulsive energy parameter (ER) from molecular mechanics (MM) studies, an alternative measurement of the size of a phosphine, which is easier to apply, especially from crystallographic data is the S_4 value. This is calculated as the difference between the sum of the three M-P-C angles and the sum of the three C-P-C angles. Because of this definition a sterically demanding ligand has small S_4 values, and vice versa.

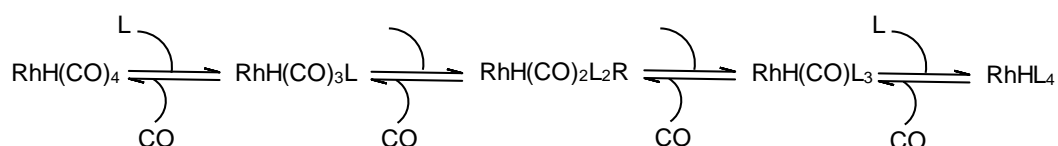
1.9 Applications of phosphines

Organophosphorus compounds have been employed widely as ligands and reagents in the synthesis of bulk chemicals and numerous fine chemical intermediates and are applied in homogenous catalysis, organometallic chemistry and organic synthesis as well as finding widespread use as ligands in co-ordination chemistry, and used for separating lanthanide and actinide mixtures. Phosphorus (III) ligands of the type PR_3 are probably the most widely studied transition metal ligand systems, and they, or their derivatives, have applications in many areas of chemistry, including as functional materials, such as phase-transfer reagents and electrolytes, as organocatalysts, such as PCy_3 and as ligands in many metal-catalysed C–C bond forming reactions. ⁽¹⁸⁾

The application of organophosphorus-containing compounds falls into three main areas; phosphines as ligands in catalytic systems, phosphines as bases and phosphines as reagents.

1.10 Phosphines in catalysis

There are a very large number of applications of phosphines in catalysis, with many hundreds of research papers being published each year on the synthesis and use of phosphines in catalysis. It has been suggested that the steric profile of the phosphine can impart an important amount of control over the transition metal-mediated reactions.⁽¹²⁾ In the 1960s, Pruet and Smith described the effects of ligand structure on the product distribution and the reaction rate of some metal catalysed reactions the existence of a number of catalytically-active rhodium compounds in the reaction makes systematic studies of ligand effects on the hydroformylation reaction difficult. The complexes with a varied number of phosphorus ligands are in equilibrium, and complexes containing up to three phosphorus ligands can all be active as hydroformylation catalysts. The equilibrium mixture composition is based on a large number of parameters, such as type of ligand, concentration temperature and pressure.⁽¹⁹⁾



Scheme 2 Rhodium catalysts containing various phosphorus and carbonyl ligands involves in the hydroformylation of 1-alkenes.

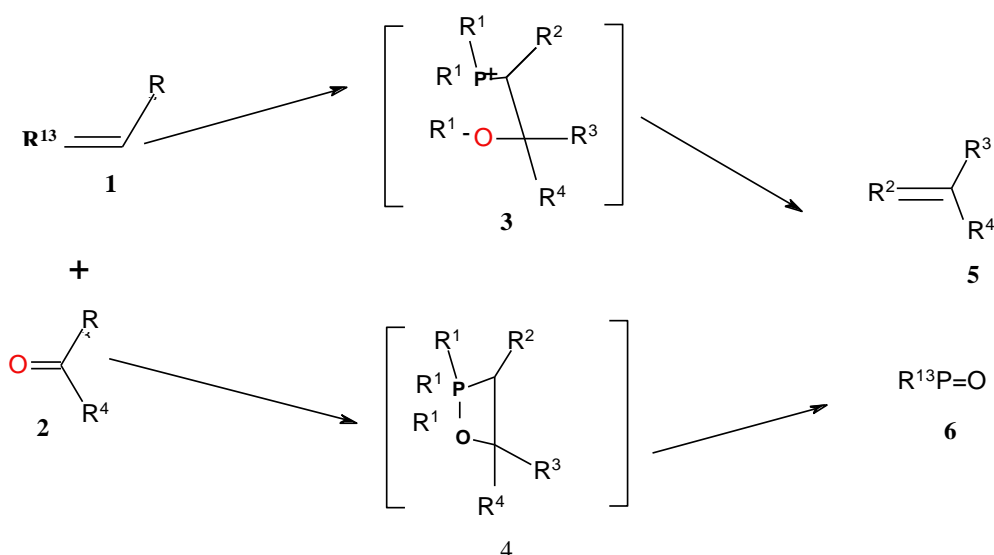
1.11 Phosphines as bases

Organophosphines with the lone pair of electrons can act as nucleophiles and as bases. Their base strength is based on the degree and nature of substitution to a greater extent than is the case with amines. In general, for comparable alkyl R groups, the basicities of phosphines lie in the order: $\text{R}_3\text{P} > \text{R}_2\text{PH} > \text{RPH}_2 > \text{PH}_3$.⁽²⁰⁾ Recently the use of bulky, basic phosphines, such as PCy_3 , has found a number of applications in organic synthesis. Such systems are often called organocatalysts.

1.12 Phosphines as Reagents

The Wittig reaction can be considered as one of the most significant methods for the preparation of carbon–carbon double bonds and is employed as a key step in numerous natural product syntheses owing to its stereo-selective formation of a double bond. ⁽²¹⁾ The Wittig reaction results in the regio-selective formation of a double bond at the position of a former carbonyl group, and the possibility to control the stereo-selectivity by applying special reaction conditions. ⁽²²⁾

The stereo-selectivity and mechanism of the Wittig reaction have been studied for a long time; previously betanes were believed to be the major intermediates in these reactions (Scheme 1). ⁽²¹⁾



Scheme 1: Wittig reaction, taken from reference 21.

Now it is known that the conditions needed for maximum Z or E-alkene selectivity are strongly dependent on the nature of the ylide used. ⁽²²⁾

1.13 Project aims

As described above, the area of designing and synthesis P(III) ligands for use in organometallic catalysts is extremely active both synthetically and computationally. A major application of phosphine-containing metal complexes is in homogeneous catalysis. Since the original work by Wilkinson on the use of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ as a catalyst for hydrogenation reactions, new phosphine complexes have been developed and they are now used in carbonylation, hydroformylation, isomerisation and other organic syntheses.⁽²³⁾

As described above changing the electronic parameter of a phosphine ligand can modify its reactivity/application. There is continued interest in being able to determine these properties for a phosphine easily. Tolman's electronic parameter, based on $\nu(\text{CO})$ stretching frequencies of a nickel carbonyl complex are inconvenient because of the toxicity of $\text{Ni}(\text{CO})_4$. Therefore alternatives have been sought, such as using other useful complexes, or spectroscopic parameters.

The table and figures below show how $\nu(\text{CO})$ from $[\text{Ni}(\text{CO})_3\text{P}]$ complexes compare with $\nu(\text{CO})$ from $[\text{Mo}(\text{CO})_5\text{P}]$, $[\text{Rh}(\text{O})\text{ClP}_2]$ and $^1\text{J}(\text{PSe})$ from $\text{P}=\text{Se}$ compounds. Generally the agreement is good.

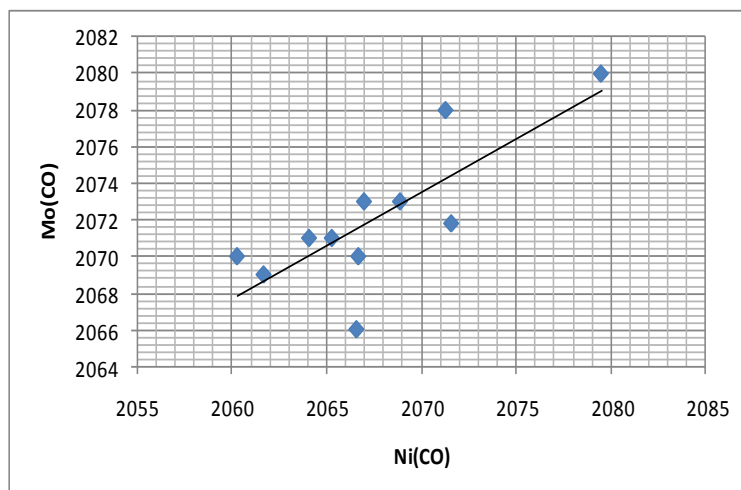
Phosphine	Cone angle	$\nu(\text{CO})\text{Ni}$ / cm^{-1}	$\nu(\text{CO})\text{Mo}$ / cm^{-1}	$\nu(\text{CO})\text{Rh}$ / cm^{-1}	$\text{J}(\text{SeP})$ / Hz
PMe_3	118	2064.1	2071	1976	684
PEt_3	132	2061.7	2069	1958	686
$\text{P}(\text{n-Bu})_3$	132	2060.3	2070	1955	689
PPh_3	145	2068.9	2073	1979	731
$\text{P}(\text{o-Tol})_3$	194	2066.6	2066	1974	706

P(p-Tol) ₃	145	2066.7	2070	1976	719
PMe ₂ Ph	122	2065.3	2071	1968	710
PMePh ₂	136	2067	2073	1974	725
POEtPh ₂	133	2071.6	2071.8	-	796
P(OMe) ₃	107	2079.5	2080	2014	945
P(p-FC ₆ H ₄) ₃	145	2071.3	2078	1983	741

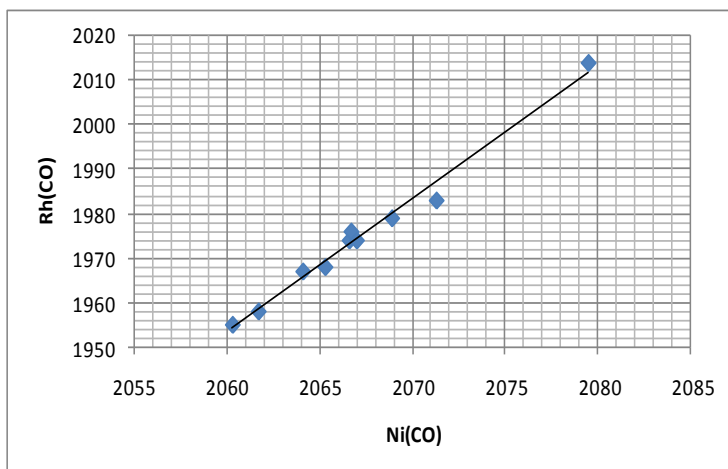
Table (2)

$$\text{TEP} = 1.116 \nu(\text{CO})_{\text{Mo}} - 243 \text{ cm}^{-1} \quad (1.1)$$

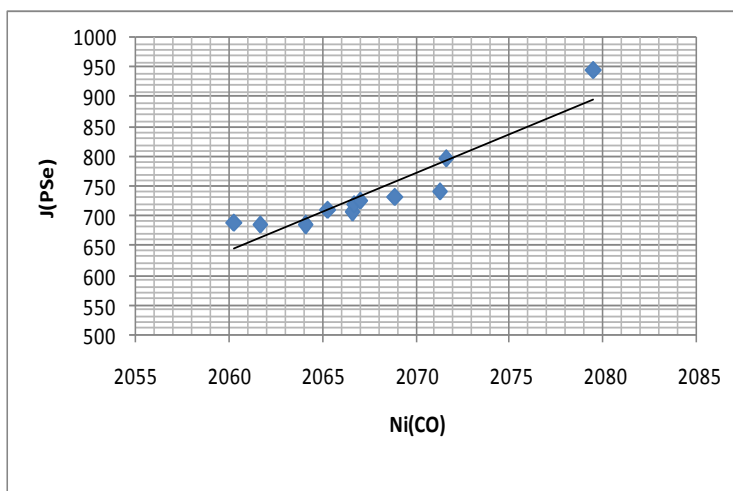
$$\text{TEP} = 0.226 \nu(\text{CO})_{\text{Rh}} + 1621 \text{ cm}^{-1} \quad (1.2) \quad (18)$$



Graph (1)



Graph (2)



Graph (3)

Correlation between $\nu(\text{CO})$ in $[\text{NiCO})_3\text{P}]$ and graph (1) $[\text{Mo}(\text{CO})_5\text{P}]$, graph (2) $[\text{Rh}(\text{CO})\text{ClP}_2]$ and graph (3) $^1\text{J}(\text{PSe})$ (P= monodentate P(III) ligand).

The aim of this project is to prepare some new phosphine ligands and investigate using the $\nu(\text{CO})$ stretching frequency of the $[\text{Mo}(\text{CO})_5\text{L}]$ complex and the $^1\text{J}(\text{PSe})$ coupling constant of the phosphine selenide as a more convenient measure of the electronic properties of these phosphine ligands.

Experimental section

2. Experimental section

2.1 Introduction:

All reagents were obtained from standard suppliers and were used as supplied; reactions were performed under a nitrogen atmosphere, non-chlorinated solvents were dried using sodium wire prior to use. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I spectrometer and NMR were spectra recorded on 400 MHz Bruker and 200 MHz Bruker spectrometers in CDCl₃, and referenced against H₃PO₄ (³¹P) and TMS (¹H).

2.2 Synthesis of selenium and molybdenum hexacarbonyl compounds:

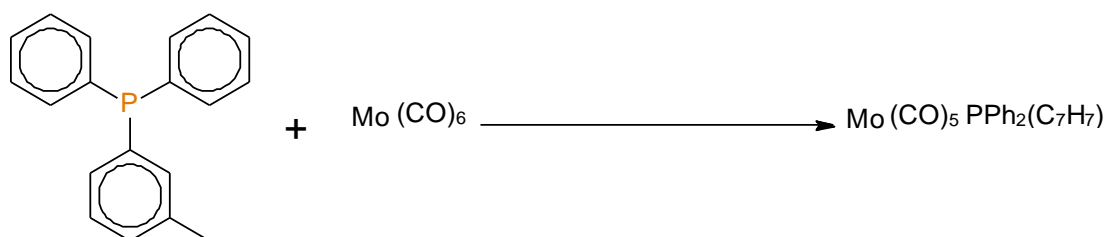
2.3 Synthesis of meta-tolyldiphenylphosphine selenide.



In a typical procedure to a one necked round bottomed flask, equipped with magnetic stirrer, was added toluene (40 ml), meta-tolyldiphenylphosphine (0.5 g, 1.8 mmol) and selenium (0.284 g, 3.6 mmol). The mixture was heated to reflux and stirred for 6 hours. After cooling to room temperature the reaction mixture was filtered and concentrated to afford a white solid; yield: 0.63 g. (93%)

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 35.3 ppm $^1\text{J}(\text{PSe}) = 727$ Hz ^1H NMR: 2.3(s, 3H, CH_3), 7.2-7.7(m, 14H, Ar).

2.4 Synthesis of meta-tolyldiphenylphosphine molybdenumpentacarbonyl.

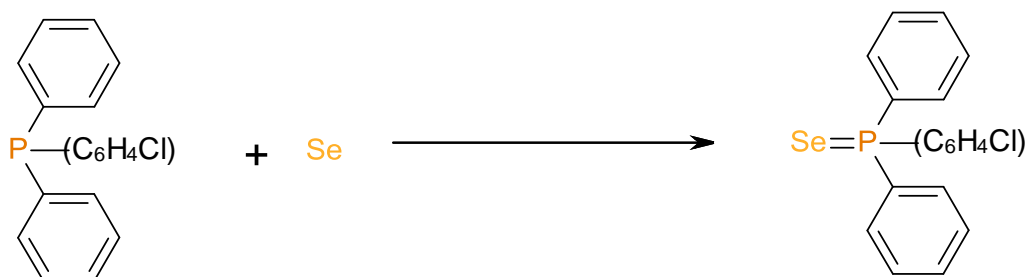


Meta-tolyldiphenylphosphine (0.5 g, 1.8 mmol), and molybdenum hexacarbonyl (0.475 g, 1.8 mmol) were introduced into a one-necked round-bottom flask with a stirrer. Toluene (40 ml) was added and the reaction heated at reflux for 2 hours in an oil bath. After that the mixture was left to cool to room temperature, then it was filtered and concentrated on a rotary evaporator to obtain a dark green solid, yield; 1.97g. (47 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 37.4 ppm ^1H NMR: 2.3(s, 3H, CH_3), 7.1-7.7(m, 14H, Ar).

IR: 3062.21(w), 2071.0 (s), 1992.02(m) cm^{-1} .

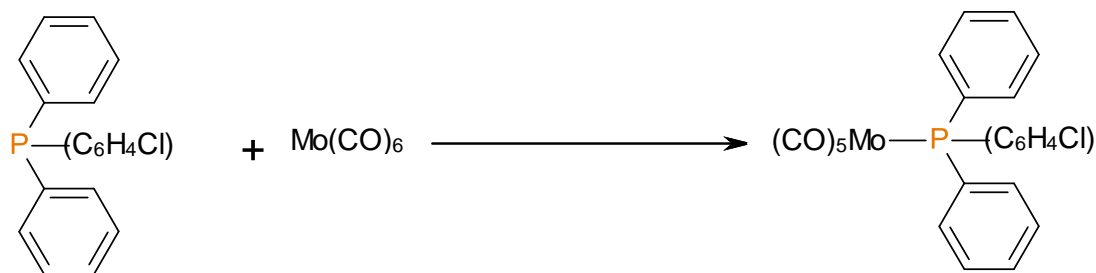
2.5 Synthesis of (p-chlorophenyl)diphenylphosphine selenide.



To a 250 ml round bottom flask was added (p-chlorophenyl)diphenylphosphine (0.5 g, 1.68 mmol) and selenium (0.265 g, 3.36 mmol) dissolved in toluene (50ml), then the solution was heated under reflux for 6 hours. The reaction was left to cool, after that it was filtered through filter paper and the solvent removed under vacuum to afford a yellow solid; yield: 1.15g. (55 %)

^{31}P { ^1H } NMR δ 34.6 ppm ^1J (PSe) = 737 Hz. ^1H NMR: 7.1-7.8(m, 14H, Ar)

2.6 Synthesis of (p-chlorophenyl)diphenylphosphine molybdenumpentacarbonyl.

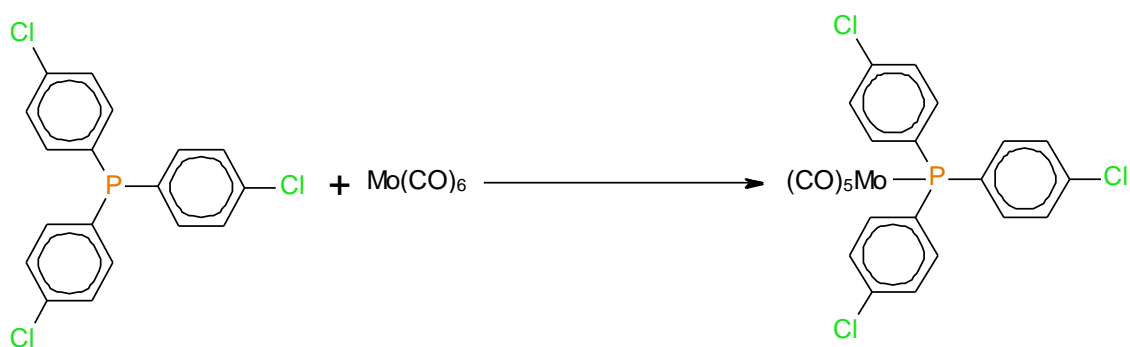


To a round-bottomed flask was added toluene (40 ml) (p-chlorophenyl)diphenylphosphine (0.5 g, 1.68 mmol), and molybdenum hexacarbonyl (0.443 g, 1.68 mmol). The reaction mixture was stirred and heated for 2 hours. After that time the solution was left to cool to room temperature, it was filtered and concentrated to afford a green solid, yield: 1.21 g (74%).

^{31}P { ^1H } NMR δ 37.8 ppm ^1H NMR: 7.2-7.7(m, 14H, Ar).

IR: 3000 (w), 2070.2 (s), 1979.7 (m), 1560.6 (w), 1189.7 (w), 819.6 cm^{-1} (w).

2.7 Synthesis of tris(p-chlorophenyl)phosphine molybdenumpentacarbonyl

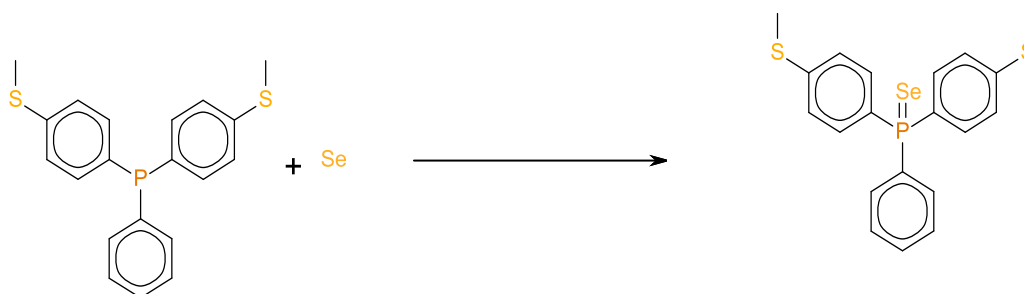


To a one-necked round-bottomed flask, was added tris(p-chlorophenyl)phosphine (0.21 g, 0.575 mmol) and molybdenumhexacarbonyl (0.152g, 0.575 mmol), and toluene (40 ml). The mixture was refluxed for 2 hours. After cooling the reaction mixture was filtered and concentrated to afford a dark green solid, yield; 0.3 g. (63 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 37.7 ppm ^1H NMR: 7.0-7.4(m, 12H, Ar).

IR: 3025.4(w), 2919.6(w), 2072.2(s), 1920.1(m), 1574.8(m) cm^{-1}

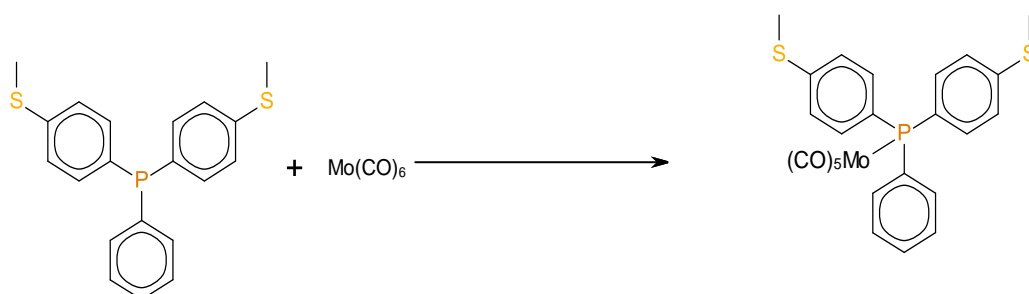
2.8 Synthesis of bis(p-thioanisyl) phenyl phosphine selenide.



A mixture of bis(p-thioanisyl)phenyl phosphine (0.3 g, 0.84 mmol), selenium (0.133 g, 1.68 mmol) and toluene (40 ml) were added to a 250 ml round bottom flask and heated in an oil bath for 6 hours. After that time the mixture was left to cool, filtered and the solvent evaporated, to afford a thick yellow oily, yield: 0.53 g. (83 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 33.8 ppm ^1J (PSe) = 727 Hz ^1H NMR: 2.5(s, 6H, CH_3), 7.4-7.8(m, 13H, Ar)

2.9 Synthesis of bis(p-thioanisyl) phenylphosphine molybdenumpentacarbonyl.

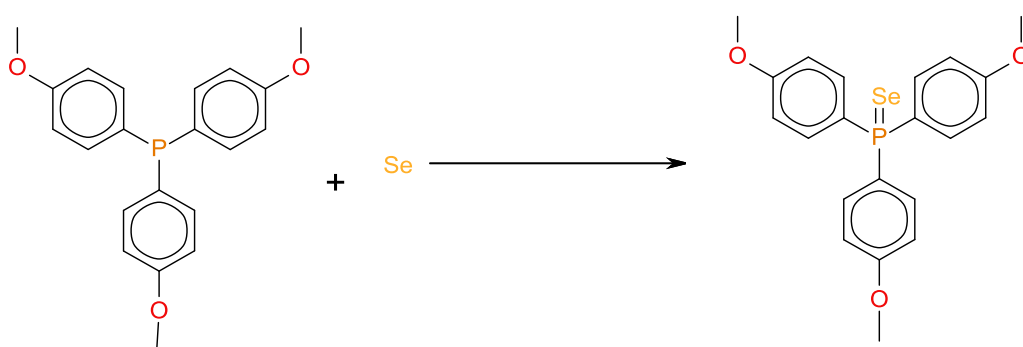


To a mixture of bis(p-thioanisyl) phenyl phosphine (0.3 g, 0.841 mmol) and molybdenum hexacarbonyl (0.221 g, 0.841 mmol) in a one-necked round-bottomed flask was added toluene (40 ml). The mixture was heated and stirred at reflux for 2 hours. After cooling to room temperature the reaction mixture was filtered and concentrated to afford a black solid, yield; 0.51 g (50 %).

$^{31}\text{P}\{^1\text{H}\}$ δ 35.97ppm ^1H NMR: 2.4(s, 6H, SCH₃), 7.2-7.4(m, 13H, Ar)

IR result: 2599 (w), 2069.7 (s), 1910.6 (m), 1577.7 (w), 1070.6 cm⁻¹(w).

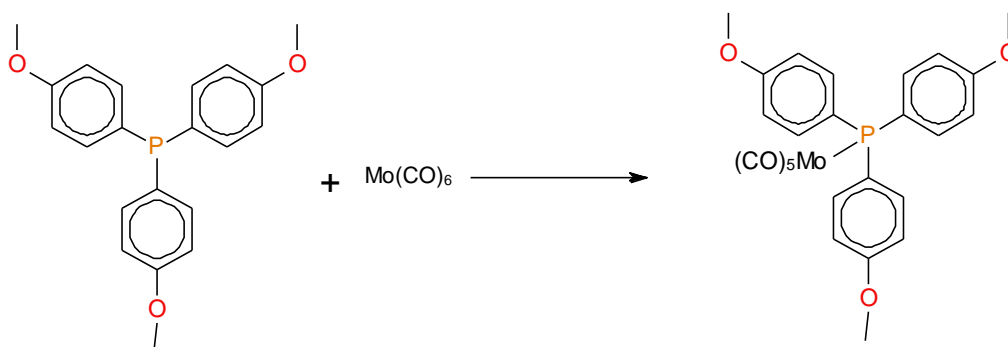
2.10 Synthesis of tris(p-anisyl)phosphine selenide.



Selenium (0.134 g, 1.7 mmol), and tris(p-anisyl)phosphine (0.3 g, 0.85mol) were dissolved in toluene (40 ml). The reaction mixture was heated and stirred to reflux for 6 hours. It was allowed it to cool to room temperature then it was filtered and concentrated to afford a white oily solid, yield; 1.23 g (30 %).

^{31}P $\{^1\text{H}\}$ NMR δ 31.6 ppm ^1J (PSe) = 714 Hz ^1H NMR: 3.9(s, 3H, CH₃), 6.8-6.9(m, 2H, Ar), 7.5-7.7(m, 2H, Ar).

2.11 Synthesis of tris(p-anisyl)phosphine molybdenumpentacarbonyl

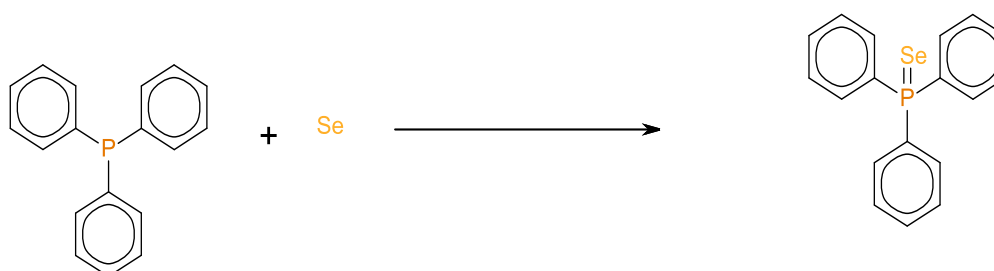


flask equipped with magnetic stirrer, were dissolved tris(p-anisyl)phosphine (0.3 g, 0.85 mmol) and molybdenum hexacarbonyl (0.224 g, 0.85 mmol) in toluene (40 ml), then the reaction mixture was stirred and heated to reflux for 2 hours in a oil bath. The mixture was left to cool and then was filtered and concentrated to afford a light green solid, yield: 0.41g (50 %)

NMR: ^{31}P $\{^1\text{H}\}$ NMR δ 32.2 ppm ^1H NMR: 3.8(s, 3H, CH₃). 6.8-7.6(m, 4H, Ar)

IR: 3000 (w), 2069.0 (s), 1915.3 (m), 1567.6 cm⁻¹ (m)

2.12 Synthesis of triphenylphosphine selenide.

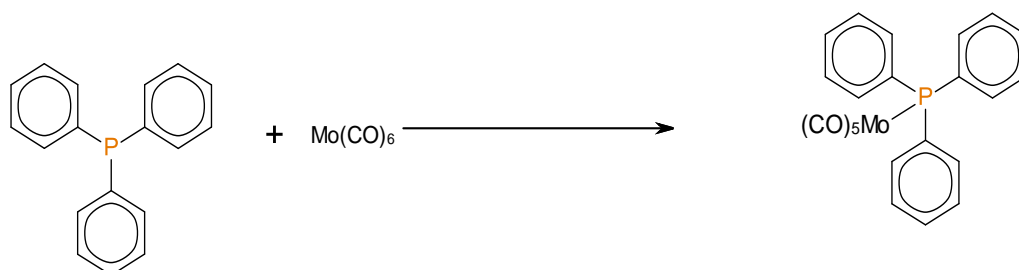


To a 250 ml round bottom flask was added PPh₃ (1.0 g, 3.8 mmol) and selenium (0.6 g, 7.6 mmol) dissolved in toluene (50 ml), then the solution was heated under reflux

for 6 hours. The product was left to cool, after that it was filtered through filter paper and concentrated to afford to yellow solid, yield: 0.197g. (15.27%)

^{31}P $\{^1\text{H}\}$ NMR δ 35.3 ppm ^1J (PSe) = 728 Hz ^1H NMR: 7.3-7.5 (m, 15H, Ar), 7.6-7.7 (m, 15H, Ar).

2.13 Synthesis of triphenylphosphine molybdenum pentacarbonyl.

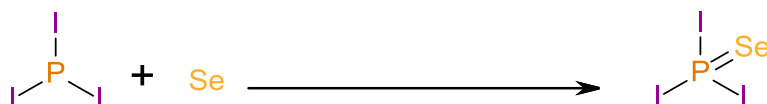


To round bottomed flask equipped with magnetic stirrer, were dissolved PPh₃ (0.3gm, 1.14 mmol) and molybdenum hexacarbonyl (0.3 g, 1.14 mmol) in toluene (50 ml), then the reaction mixture was stirred at reflux for 2 hours in an oil bath. The mixture was left to cool then filtered and concentrated to afford a light green solid yield;

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 37.7 ppm ^1H NMR: 7.2-7.6 (m, 15H, Ar).

IR: 3062.21(w), 2071.2 (s), 1992.0 cm^{-1} (m)

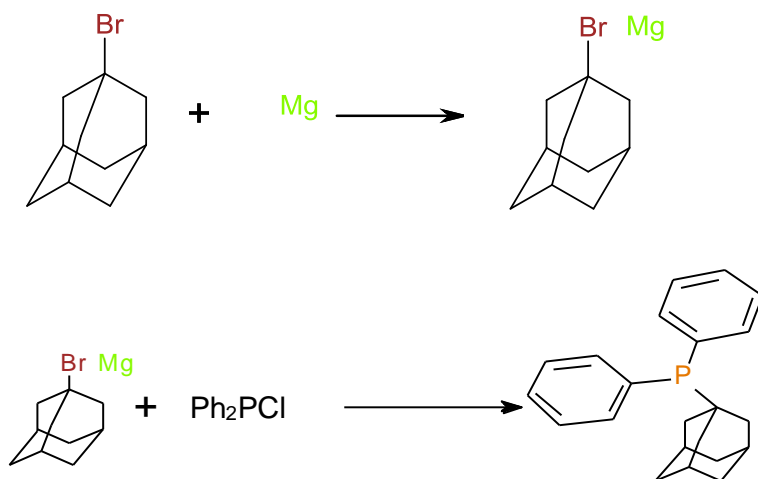
2.14 Attempted synthesis of phosphorus triiodide selenide



In a typical reaction, PI₃ (0.5 g, 1.2 mmol), and selenium (0.19 g, 2.4 mmol) were introduced into a one-necked round bottom flask. Toluene (40 ml) was added to the flask and the reaction was heated at reflux for 6 hours. After that time the mixture was left to cool to room temperature. It was filtered and concentrated on a rotary evaporator to obtain a black solid.

2.15 Synthesis of Grignard reagents:

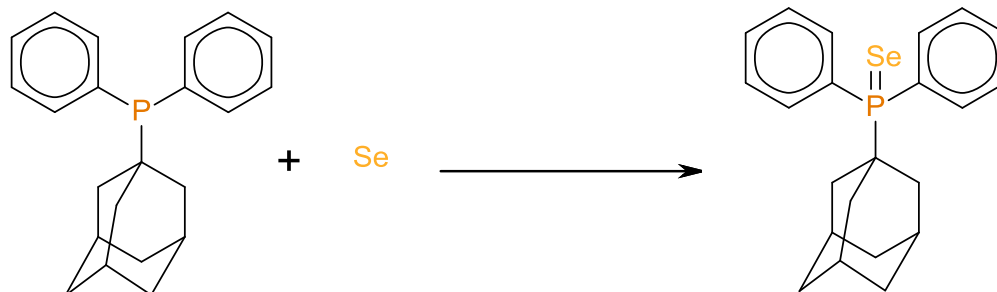
2.16 Synthesis of adamantyldiphenylphosphine



In a three-necked round-bottomed flask equipped with a magnetic stirrer bar, rubber septum, reflux condenser and dropping funnel was placed a few small crystals of iodine, diethyl ether (40 ml), dried magnesium (0.1 g, 2 mmol), and a little of the 1-bromoadamantane. The reaction was heated until the iodine colour was discharged. After the reaction had started, 1-bromoadamantane (0.5 g, 2 mmol) was added with stirring at a rate not faster than one drop every second. The mixture was allowed to stir over a period of ½ hour. After that time the mixture was heated for another ½ hour. Chlorodiphenylphosphine (0.4 ml, 2 mmol), dissolved in diethyl ether (40 ml) was added slowly, and the reaction mixture was stirred for 1 hour. After that time it was worked up, filtered and concentrated to afford a light yellow oil yield; 1.33 g.

NMR: ³¹P{¹H} NMR δ 29.0 ppm ¹H NMR: 7-7.9(m, 10H, Ar), 2.5(s, 3H, CH₂), 2.0 (s, 6H, CH₂), 1.7(s, 6H, CH₂).

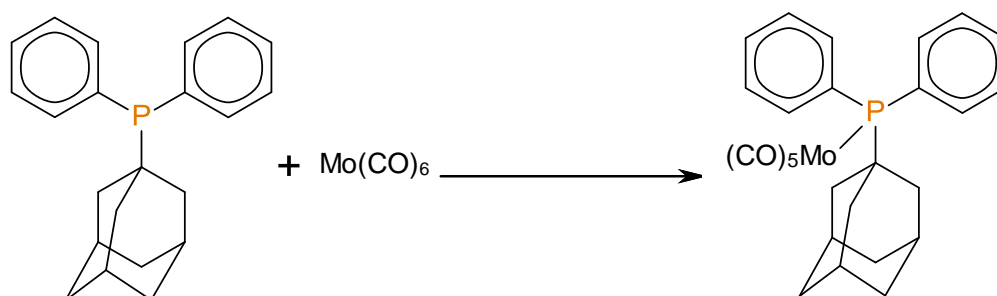
2.17 Synthesis of adamantyldiphenylphosphine selenide.



In a typical procedure, to a one-necked round bottomed flask, equipped with magnetic stirrer, was added toluene (40 ml), adamantyldiphenylphosphine (0.68 g, 1.56 mmol) and selenium (0.246g, 3.12 mmol). The mixture was heated to reflux for 6 hours under a nitrogen atmosphere. After cooling to room temperature the reaction mixture was filtered and concentrated to afford to yellow oily; yield: 0.6g.

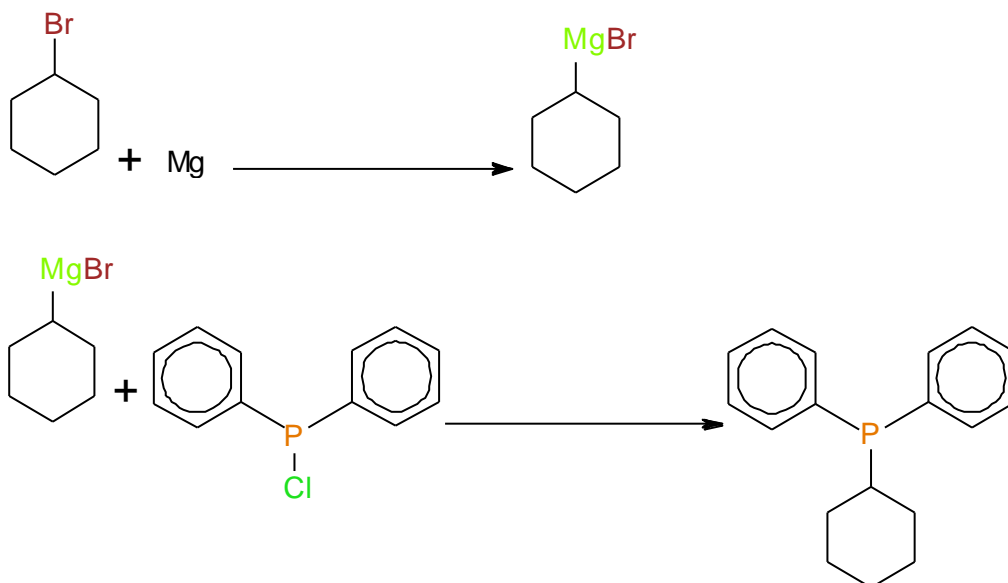
$^{31}\text{P}\{^1\text{H}\}$ NMR δ 52.3 ppm $^1\text{J}(\text{PSe}) = 833$ Hz ^1H NMR: 7.1-7.9(m, 10H, Ar), 2.5(s, 3H, CH_2), 2.0(s, 6H, CH_2), 1.7(s, 6H, CH_2).

2.18 Synthesis of adamantayldiphenylphosphine molybdenumpentacarbonyl



In a dried a round-bottomed flask with condenser and magnetic bar was placed toluene (40 ml), adamantyldiphenylphosphine (0.96 g, 2.2 mmol) and molybdenum hexacarbonyl (0.581 g, 2.2 mmol). The solution was stirred and heated for 2 hours. After that time it was left to cool to room temperature. The reaction mixture was filtered and concentrated to obtain a dark-green solid;

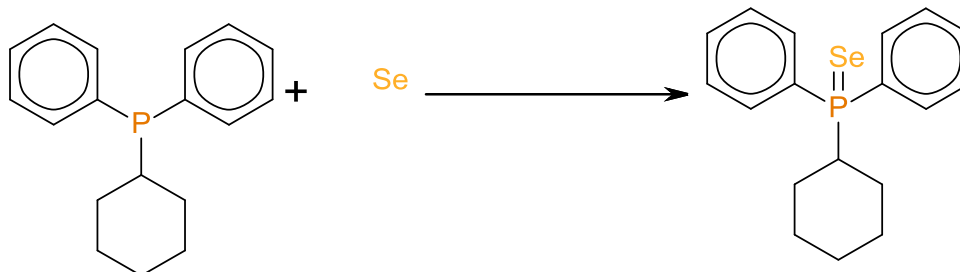
2.19 Synthesis of cyclohexyl diphenylphosphine.



In a three-necked round-bottomed flask equipped with a magnetic stirrer bar, rubber septum, reflux condenser and dropping funnel was placed a few small crystals of iodine, dried diethyl ether (50 ml), dried magnesium (0.1 g, 3 mmol), and a little of the bromocyclohexane. The reaction was heated until the iodine colour was discharged. After the reaction had started, bromocyclohexane (0.5 g, 3 mmol) was added with stirring at a rate not faster than one drop every second. The mixture was allowed to stir over a period of ½ hour. After that time the mixture was heated for another 1½ hours. Chlorodiphenylphosphine (0.4 ml, 3 mmol), dissolved in dry diethyl ether (50 ml) was added slowly, and the reaction mixture was stirred for 1 hour. After that time it was worked up, filtered and concentrated to afford oil yellow yield; 0.8 g.

$^{31}\text{P}\{^1\text{H}\}$ NMR: 41.1(s), 328 (s), 22.4(s), -40.5(s).

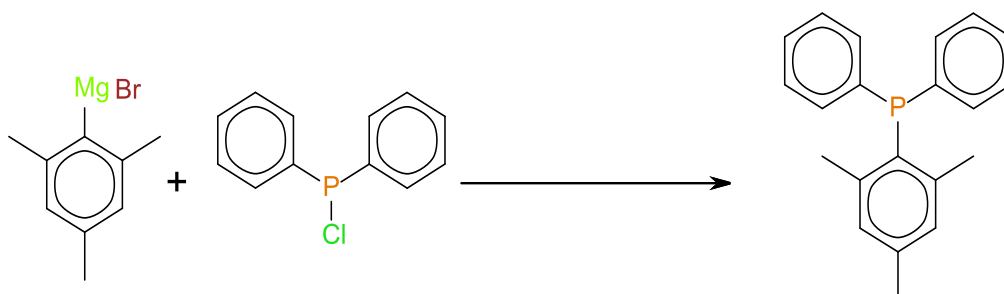
2.20 Synthesis of cyclohexyldiphenylphosphine selenide.



In a typical procedure, to a one-necked round bottomed flask, equipped with magnetic stirrer, was added toluene (40 ml), 0.8 g of the previous product and selenium (0.48 g, 6 mmol). The mixture was heated to reflux for 6 hours. After cooling to room temperature the reaction mixture was filtered and the solvent removed under vacuum to afford a yellow oily solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 82.7 ppm.

2.21 Synthesis of mesityldiphenyl phosphine.

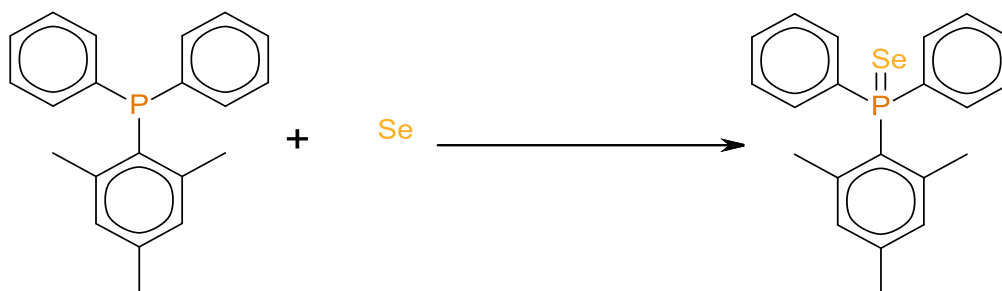


magnesium bromide (3 ml of 1 Molar solution, 3 mmol), and dry tetrahydrofuran (50 ml) were placed in a 250-ml three-necked round-bottomed flask under a nitrogen atmosphere. Then by syringe dichlorodiphenylphosphine (0.4 ml, 3 mmol) was added dropwise over a period of 10 minutes with vigorous stirring. After that the mixture was heated and allowed to maintain a gentle reflux for half hour. The mixture was filtered and concentrated on a rotary evaporator to obtain a yellow oil, yield: 2.21 g.

NMR: $^{31}\text{P}\{^1\text{H}\}$ NMR δ -16.8 ppm ^1H NMR: 2.1(s, 3H, CH_3), 2.2(s, 6H, 2 CH_3),

7-7.8(m, 12H, Ar).

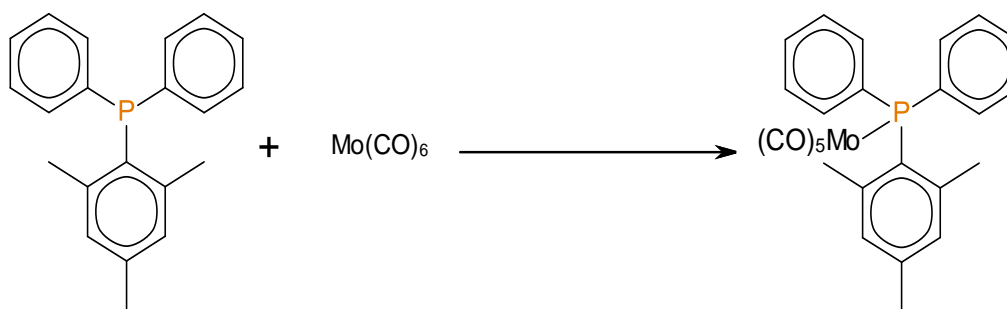
2.22 Synthesis of mesityldiphenylphosphine selenide.



To mesityldiphenylphosphine (2.21 g, 7.266 mmol) was added selenium (1.143 g, 14.47 mmol), and toluene (40 ml). The reaction mixture was stirred and heated to reflux for 6 hours. After that time it was allowed to cool to room temperature, then the reaction mixture was filtered to remove solids, and the filtrate was concentrated to afford an oily yellow solid yield; 1.37 g (49.45 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 27.7 ppm $^1\text{J}(\text{PSe}) = 728$ Hz ^1H NMR: 2.55(s, 6H, $(\text{CH}_3)_2$), 2.5(s, 3H, CH_3), 7.3-7.6(m, 12H, Ar).

2.23 Synthesis of mesityldiphenylphosphine molybdenumpentacarbonyl.

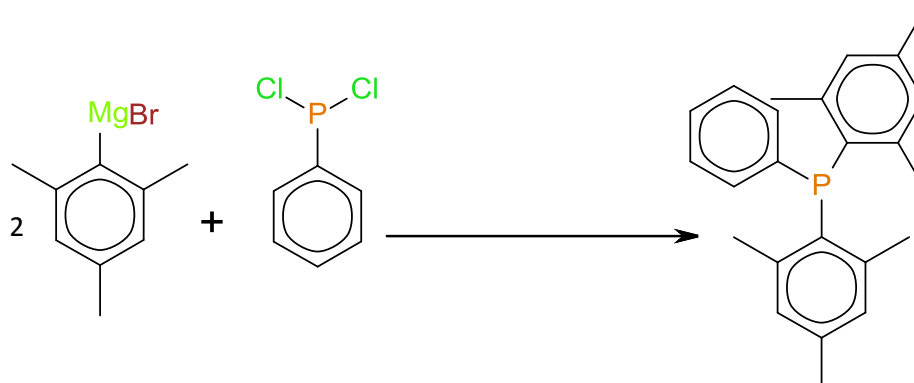


To a round-bottomed flask was added toluene (40 ml) mesityldiphenylphosphine (2.09 g, 6.87 mmol), and molybdenum hexacarbonyl (1.814 g, 6.87 mmol). The reaction mixture was heated to reflux and stirred for a period of 2 hours, after that time the solution was left to cool to room temperature, it was filtered and concentrated to afford to black liquid, yield: 1.64g (44 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 34.1 ppm ^1H NMR: 2.1-2.4(m, $(\text{CH}_3)_3$), 6.8-7.9(m, 12H, Ar).

IR: 3000 (w), 2070.8 (s), 1920.3, 1871 (m), cm^{-1} .

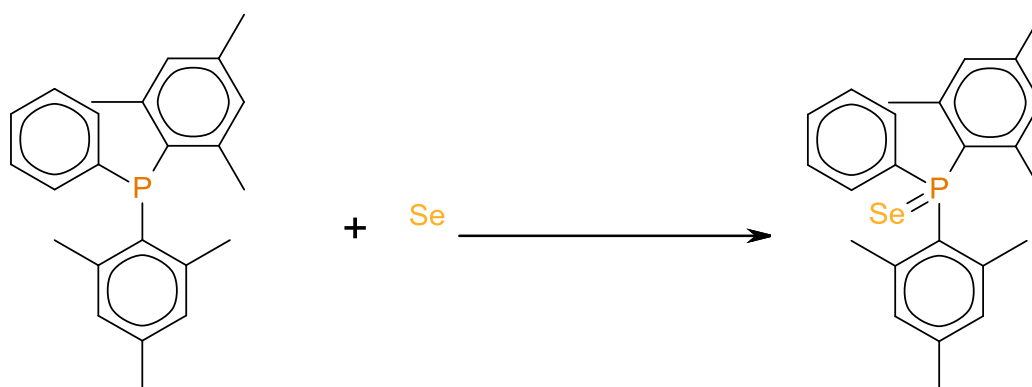
2.24 Synthesis of dimesitylphenylphosphine.



Mesityl magnesium bromide (6 ml, 6 mmol), and dry tetrahydrofuran (50 ml) were placed in a 250-ml three-necked round-bottomed flask under a nitrogen atmosphere. Then by syringe dichlorophenylphosphine (0.4 ml, 3 mmol) was added dropwise over a period of 10 minutes with vigorous stirring. After that time the mixture was allowed to maintain a gentle reflux for 1.5 hours. The mixture was filtered and concentrated on a rotary evaporator to obtain a dark orange oily yield; 4.2g.

$^{31}\text{P}\{^1\text{H}\}$ NMR δ -22.6 ppm ^1H NMR: 2.3(s, 18H, CH_3), 6.7-7.4(m, 9H, Ar)

2.25 Synthesis of dimesitylphenylphosphine selenide.

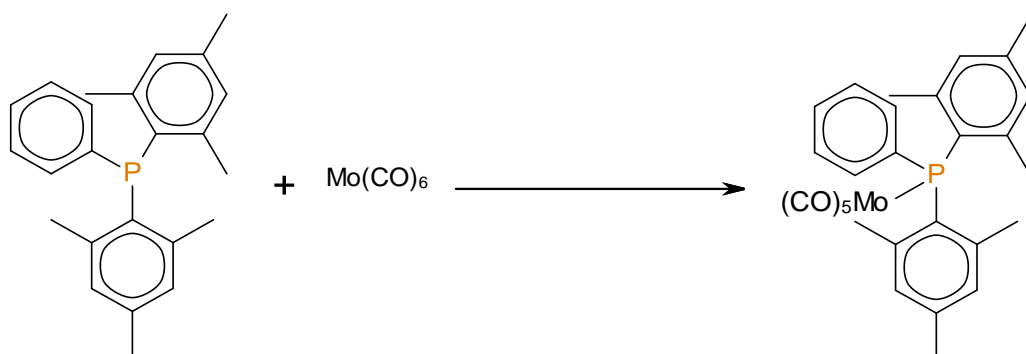


In a typical procedure, to a one-necked round-bottom flask, equipped with magnetic stirrer, was added toluene (40 ml), dimesitylphenylphosphine (4.2 g, 18.3 mmol) and selenium (2.8 g, 36.6 mmol). The mixture was left to stir for 6 hours. After cooling

to room temperature the reaction mixture was filtered and concentrated to afford a black oil, yield: 0.5g.

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 46.1 ppm $^1\text{J}(\text{PSe}) = 818$ Hz. ^1H NMR: 7.0-7.2(m, 9H, Ar), 2.3(s, 18H, CH_3).

2.26 Synthesis of dimesitylphenylphosphine molybdenumpentacarbonyl.



To a round bottomed flask equipped with magnetic stirrer, were dissolved dimesitylphenylphosphine (4.2 g, 3 mmol) and molybdenum hexacarbonyl (0.7 g, 3 mmol) in toluene (40 ml). The reaction mixture was heated and stirred for 2 hours, after which it was left to cool and it was filtered and concentrated to afford a dark red oil yield; 0.43 g (5.14 %)

$^{31}\text{P}\{^1\text{H}\}$ NMR δ 36.6 ppm ^1H NMR: 2.2-2.5(s,18H, CH_3), 7.0-7.2(m, 9H, Ar).

IR: 3356.1 (w), 2918.3 (w) 2857.2 (w), 2071.9 (s), 2020.2 (m), 1605.1 (m) cm^{-1}

Results and discussion section

3. Results and discussion section

3.1 Reaction of triphenyl phosphine with selenium



The reaction between triphenyl phosphine and powdered elemental selenium was the first reaction undertaken. This was carried out over 6 hours at reflux and resulted in a yellow solid product. The phosphorus NMR spectrum showed loss of the peak due to the starting triphenyl phosphine at -5.5 ppm and the rise of a new peak at 35.3 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also shows selenium satellites. These arise from the presence of low-abundance spin-active nuclei of selenium (^{77}Se , $I = 1/2$, 7.6%). Therefore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a phosphine selenide should appear as shown schematically below in figure 1, consisting of a singlet for molecules of $\text{Se}=\text{PR}_3$ and a doublet arising from $^{77}\text{Se}=\text{PR}_3$. The separation between the outer, satellite, peaks is $^1J(\text{PSe})$.

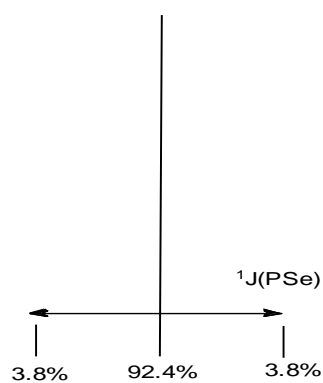


Figure 1. A representation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a phosphine selenide.

An expansion of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product is shown in figure 2 the $^1\text{J}(\text{PSe})$ coupling constant is measured between the two signals marked by *, as 727 Hz. This data is consistent with that previously reported in the literature by Taylor, with $\delta = 35.9$ ppm and $^1\text{J}(\text{PSe})$ 732 ppm⁽²⁴⁾

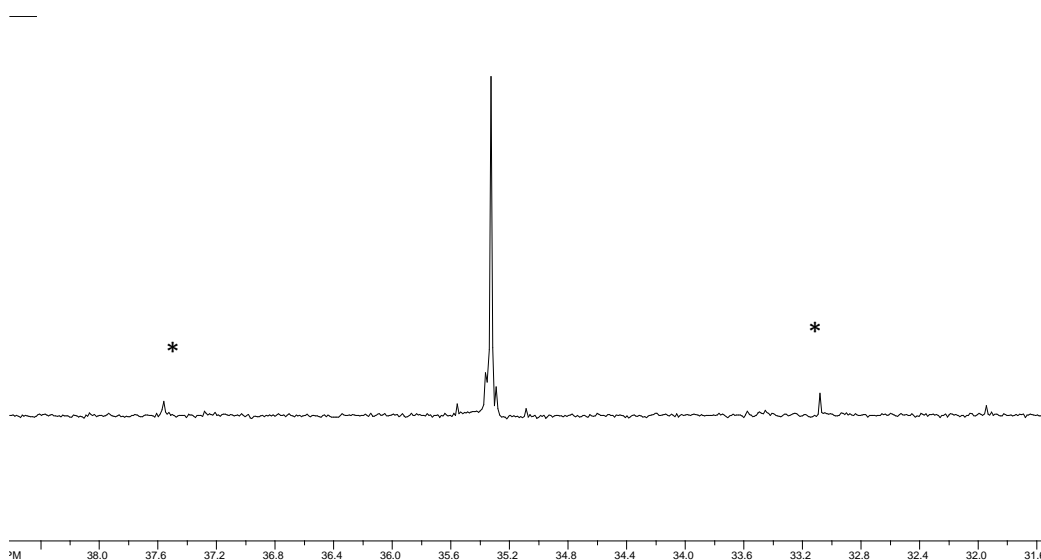


Figure 2: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of triphenyl phosphine selenide.

The proton NMR spectrum shows multiplets within the ranges 7.3-7.7 ppm, consistent with the product, as shown in figure 3. Additionally weak peaks due to CHCl_3 (7.2 ppm) and acetone (2.1 ppm) are visible.

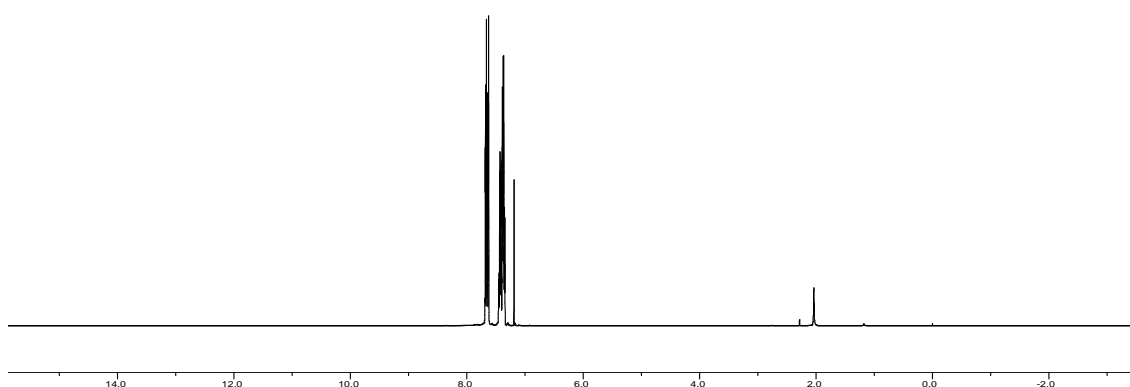
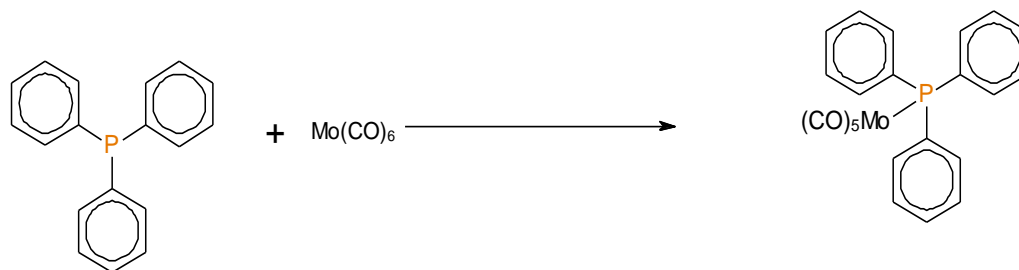


Figure 3: The ^1H NMR spectrum of triphenyl phosphine selenide.

3.2 Reaction of triphenyl phosphine with molybdenum hexacarbonyl.



The reaction between triphenyl phosphine and molybdenum hexacarbonyl in toluene was undertaken for 2 hours after this time the solvent was removed and the sample analysed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a signal at 37.7 ppm, which is shifted from the starting material by 43.3 ppm, indicating that reaction has occurred. The proton NMR spectrum shows multiplets within the range 7.2-7.6 ppm, due to the 15 aromatic protons.

The IR spectrum of the product from the reaction of triphenyl phosphine with molybdenum pentacarbonyl shows CO stretching frequencies at 2071.2 and 1992.0 cm^{-1} .

For a complex of general formula $\text{Mo}(\text{CO})_5\text{L}$, assuming C_{4v} geometry, three CO stretching modes are expected. These are given the symmetry labels of $2\text{A}_1 + \text{E}$.

The most intense, and usually broad, absorption is the E mode and this is assigned as the 1992 cm^{-1} band. The peak at 2071.2 cm^{-1} is assigned to the highest frequency A_1 mode, the other one probably being obscured by the broad E mode. It is the highest frequency A_1 peak that is used when comparing the electronic donating properties of the ligand. ⁽²⁵⁾

3.3 Reaction of meta-tolyldiphenylphosphine with selenium.

The reaction of meta-tolyldiphenylphosphine and selenium in toluene at room temperature was undertaken. After heating for 6 hours the solution was cooled and filtered to give a white solid product. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shown in figure 4 has an intense peak at 35.3 ppm with $^1\text{J}(\text{PSe}) = 727$ Hz. This data can be compared with that of the starting phosphine meta-tolyldiphenylphosphine, which exhibits a signal at -5.4 ppm. This compound does not appear to have been reported before, but tris(m-tolyl)phosphine selenide has, and exhibits $^1\text{J}(\text{PSe})$ of 759 Hz. ⁽²⁶⁾ The proton NMR spectrum shows a singlet of relative intensity 3 at 2.3 ppm and multiplets within the range 7.2-7.7 ppm, of total intensity 14. These data are consistent with the formation of m-tolyldiphenylphosphine selenide.

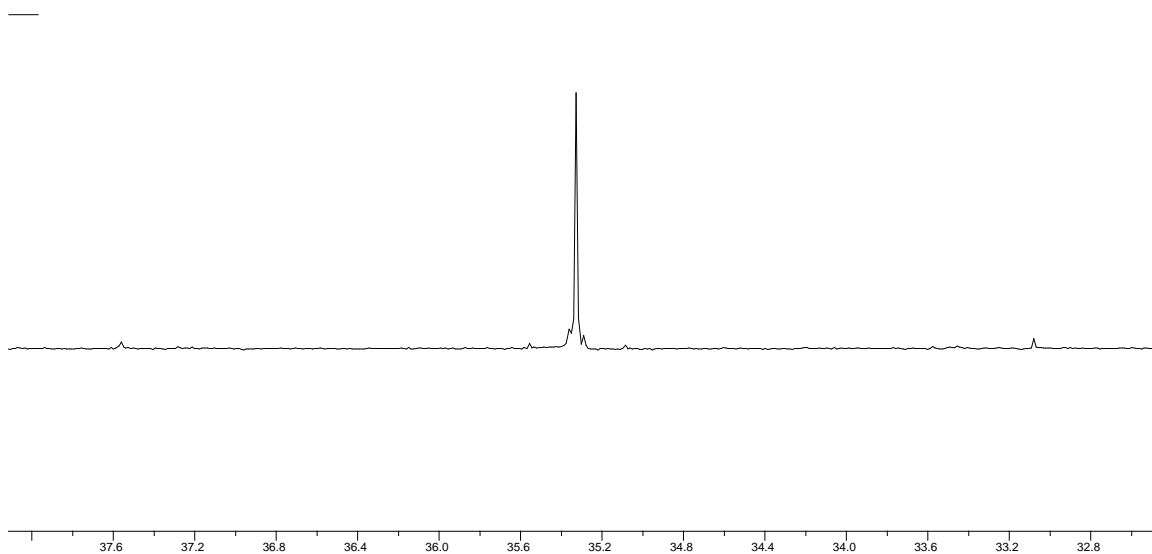


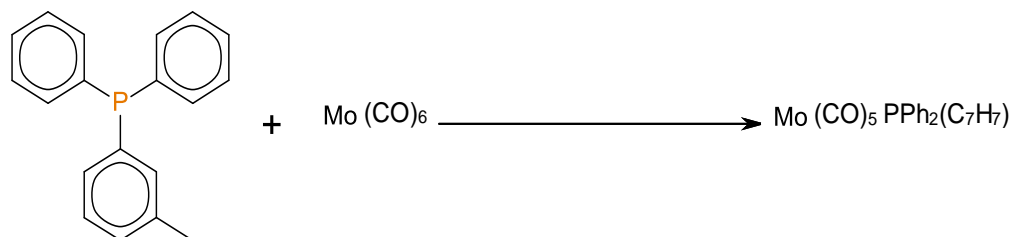
Figure 4: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of meta-tolyldiphenylphosphine selenide.

3.4 Reaction of meta-tolyldiphenylphosphine with molybdenum hexacarbonyl.

A dark green solid product (47%) was obtained from the reaction of meta-tolyldiphenylphosphine with molybdenum hexacarbonyl in toluene, after heating for 2 hours. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a peak at the position 37.4 ppm. This data can be compared with that of starting material meta-tolyldiphenylphosphine, which exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at -5.4 ppm.

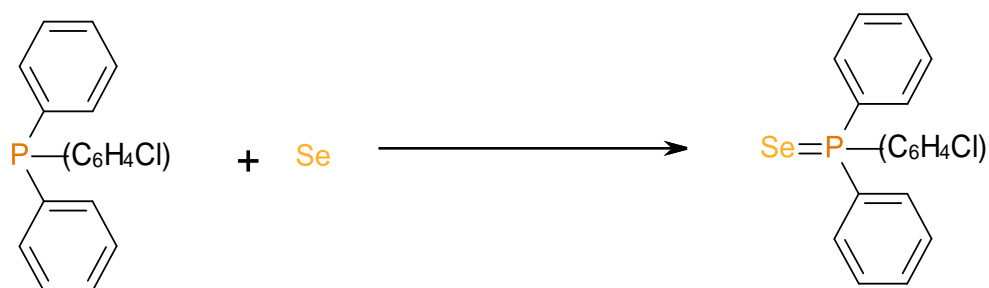
The proton NMR spectrum shows a singlet of relative intensity 3 at 2.3 ppm assigned to the methyl group of the meta-tolyl substituent and multiplets within the range 7.1-7.7 ppm of total intensity 14 due to the aromatic protons.

The reaction is shown in the following equation:



The IR spectrum of meta-tolylbis(diphenyl)phosphine molybdenumpentacarbonyl shows two CO stretching modes at 2071.0 and 1989.6 cm^{-1} . The intense, broad absorption at 1992.02 cm^{-1} is assigned to the E mode, and the peak at 2071.0 cm^{-1} is assigned to the highest frequency A_1 mode, the other one probably being obscured by the broad E mode.

3.5 Reaction of (p-chlorophenyl)diphenylphosphine with selenium.



(p-chlorophenyl)diphenylphosphine selenide was prepared by adding two equivalents of selenium to the phosphine dissolved in toluene. After refluxing the reaction mixture for 6 hours a solid product was obtained after work up.

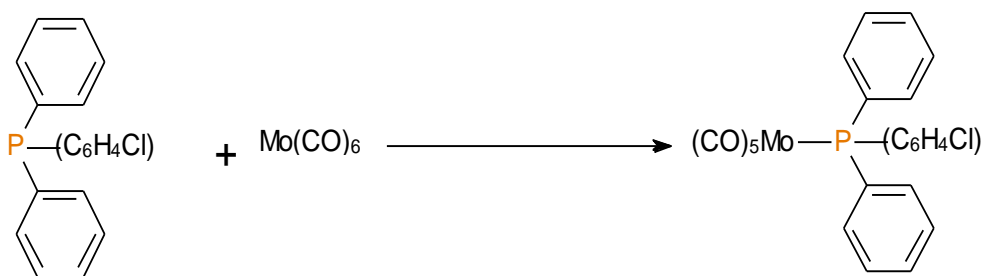
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a peak at 34.6 ppm, which compared with the starting phosphine (p-chlorophenyl)diphenylphosphine, which exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at -6.53 ppm, shows that reaction has occurred. Also the signal from the

product exhibits selenium satellites; the $^1J(\text{PSe})$ coupling constant is measured as 737 Hz.

The proton NMR spectrum is consistent with the product; it shows a complex set of multiplets within the range 7.1-7.8 ppm, due to the aromatic protons.

3.6 Reaction of (p-chlorophenyl)phosphine with molybdenum hexacarbonyl.

(p-Chlorophenyl)diphenylphosphine was reacted with molybdenum hexacarbonyl in toluene to give a dark green solid.

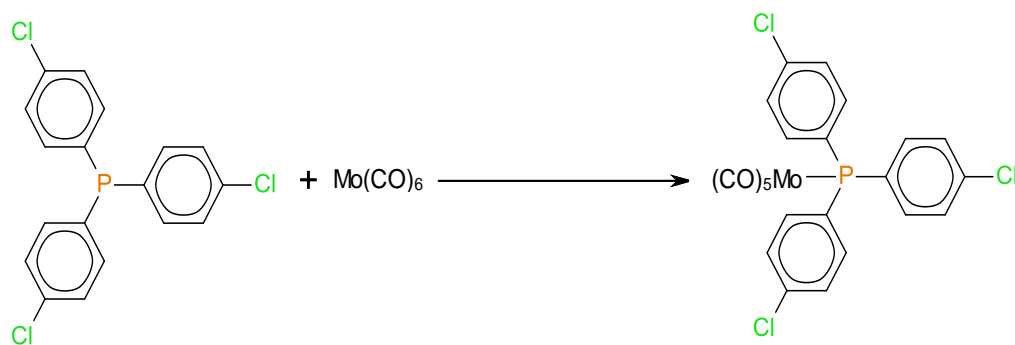


The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product shows a single peak at 37.8 ppm. This can be compared with that of the starting material phosphine (p-chlorophenyl)diphenylphosphine, which exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at -6.53 ppm. This indicates that coordination of the phosphine has occurred. The proton NMR spectrum shows a complex set of multiplets within the range 7.2-7.7 ppm due to the aromatic protons.

The IR spectrum of p-chlorodiphenylphosphine molybdenumpentacarbonyl shows CO stretching modes at 2070.2 and 1797.7 cm^{-1} . These are assigned as previously described to the A₁ and E modes respectively.

3.7 Reaction of tris(p-chlorophenyl)phosphine with molybdenum hexacarbonyl.

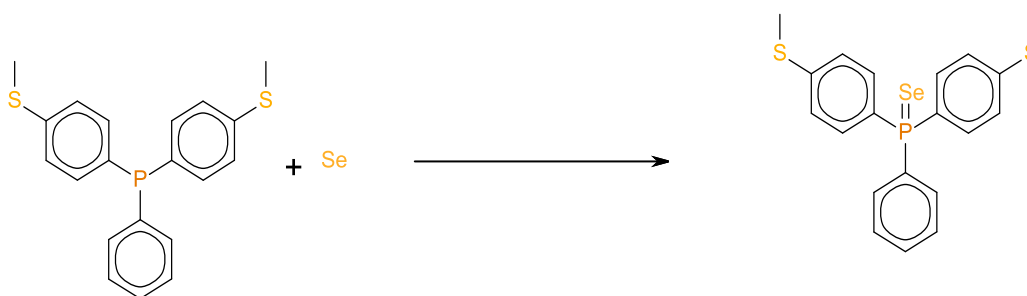
Tris(p-chlorophenyl)phosphine molybdenumpentacarbonyl was prepared according to the following reaction:



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product shows a single peak at 37.7 ppm. This data can be compared with that of the starting phosphine, which exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR signal at -6.5 ppm. Therefore coordination of the phosphine has occurred.

The proton NMR spectrum shows multiplets within the range 7.0-7.4 due to the aromatic protons. The IR spectrum of tris(p-chlorophenyl)phosphine molybdenum pentacarbonyl shows CO stretching modes at 2072.2 (s) and 1920 (m) cm^{-1} .

3.8 Reaction of bis(p-thioanisyl)phenyl phosphine with selenium.



Heating bis(p-thioanisyl)phenyl phosphine and selenium in toluene for 6 hours results in a thick oily yellow product. The NMR spectrum of this oil is shown in figure 5 and shows a single peak at 33.8 ppm with coupling constant $^1\text{J}(\text{PSe}) = 727$

Hz. This can be compared with the starting phosphine which shows a singlet at -7.29 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

The proton NMR spectrum of the product shows a series of multiplets within the range 7.4-7.8 ppm, and a singlet at ca 2.5 ppm due to the methyl protons of the thioanisyl group.

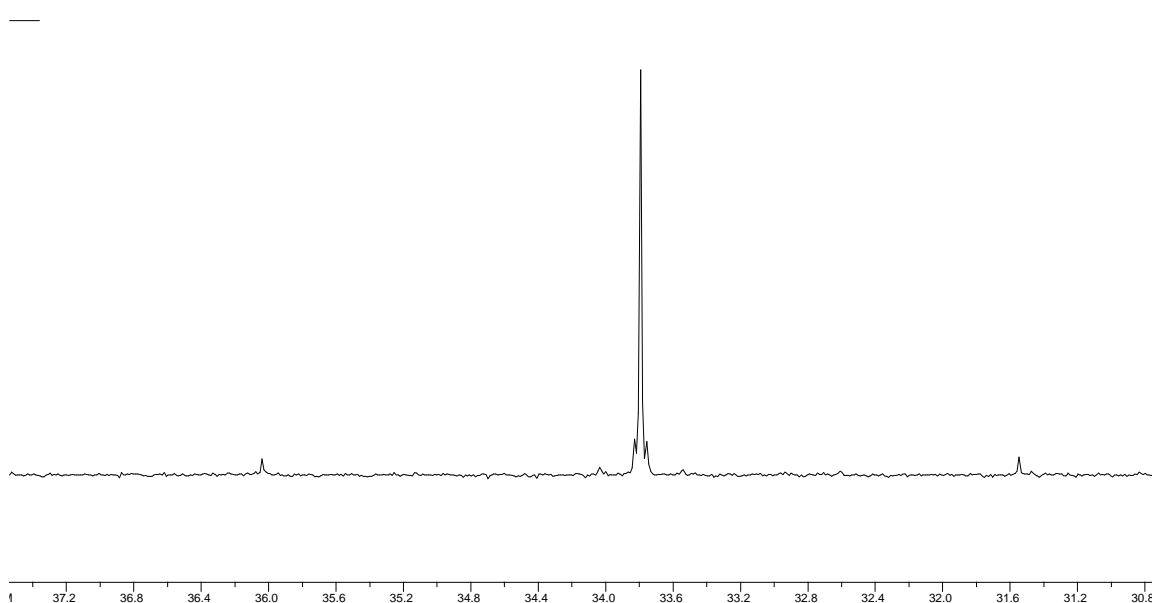


Figure 5: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of bis(p-thioanisyl)phenyl phosphine selenide.

3.9 Reaction of bis(p-thioanisyl)phenyl phosphine with molybdenum hexacarbonyl.

The reaction between bis(p-thioanisyl)phenyl phosphine and molybdenum hexacarbonyl in toluene was conducted for 2 hours, after this time the solvent was removed and the sample analysed the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a signal at 35.97 ppm, which is shifted from the starting material by over 43 ppm (from -7.29 ppm)

The proton NMR spectrum showed in figure 6 displays a singlet at 2.4 ppm and multiplets within the range 7.2-7.4 ppm, of the total intensity of 13, due to the aromatic protons.

The IR spectrum of bis(p-thioanisyl)phenylphosphine molybdenum pentacarbonyl shows CO stretching modes at 2069.7 cm^{-1} and 1910.6 cm^{-1} these are assigned to the A_1 and E modes respectively.

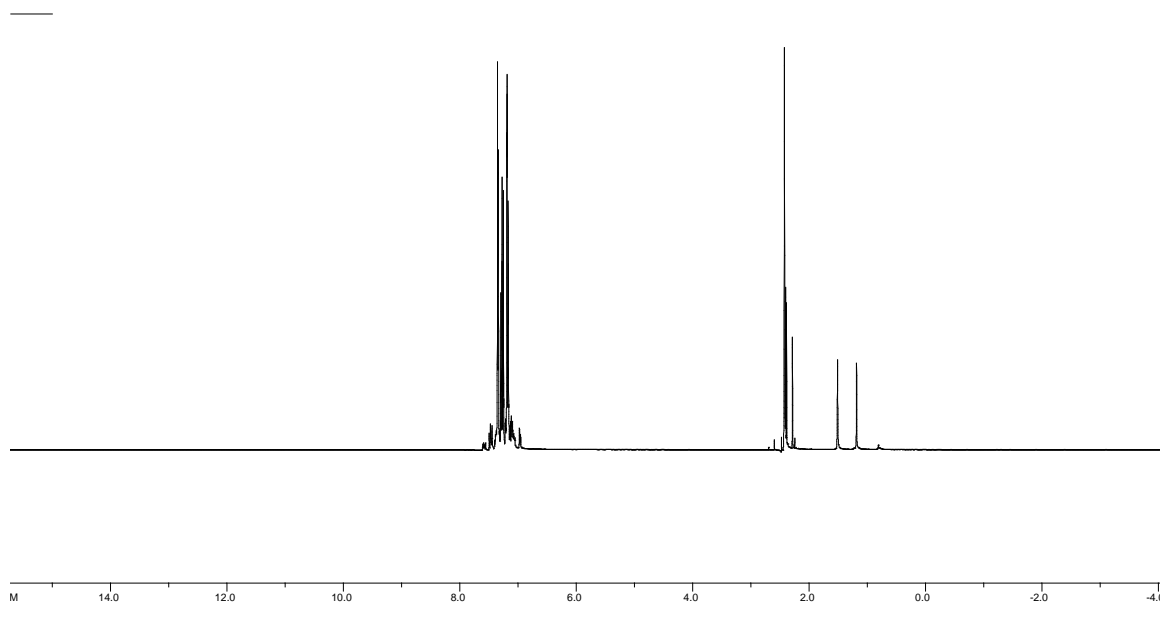
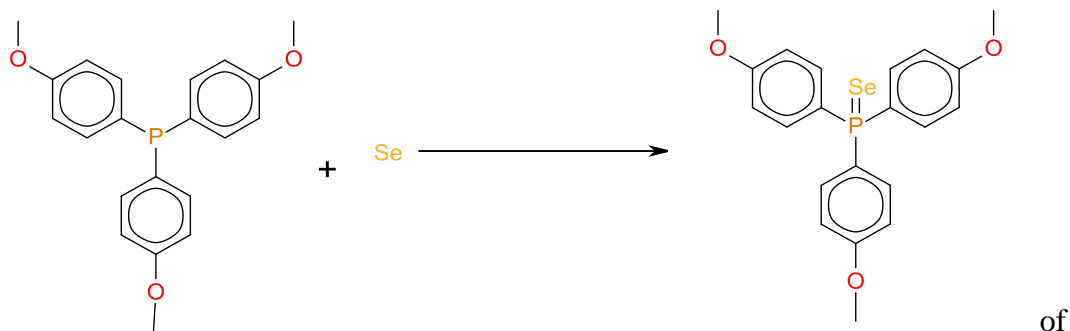


Figure 6: The ^1H NMR spectrum of bis(p-thioanisyl)phenyl phosphine molybdenum pentacarbonyl.

3.10 Reaction of tris(p-anisyl)phosphine with selenium.



tris(p-anisyl)phosphine with selenium in toluene was undertaken. After 6 hours the solution was filtered to give a white oily product. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum, shown in figure 7 exhibits a single peak at 31.6 ppm with coupling constant $^1J(\text{PSe})$ of 714 Hz. When compared with the chemical shift of the starting phosphine at -10.09 ppm this confirms that reaction has occurred to form the selenide.

The proton NMR spectrum shows two sets of multiplets within the range 6.8-6.9 and 7.5-7.7 ppm and a singlet at 3.9 ppm these are in the ratio 2:2:3, consistent with what is expected for the product.

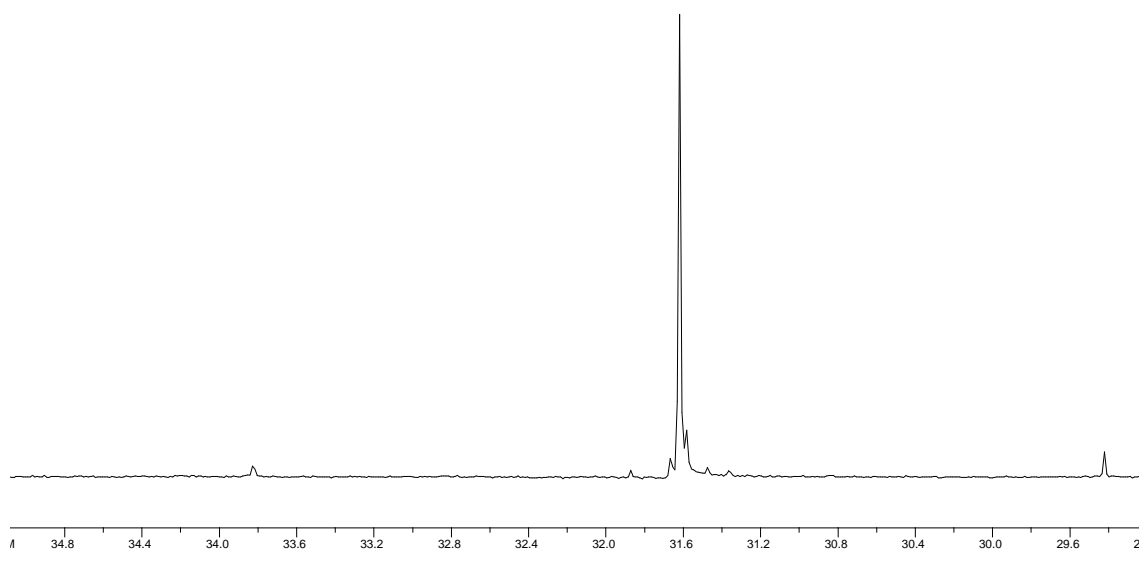
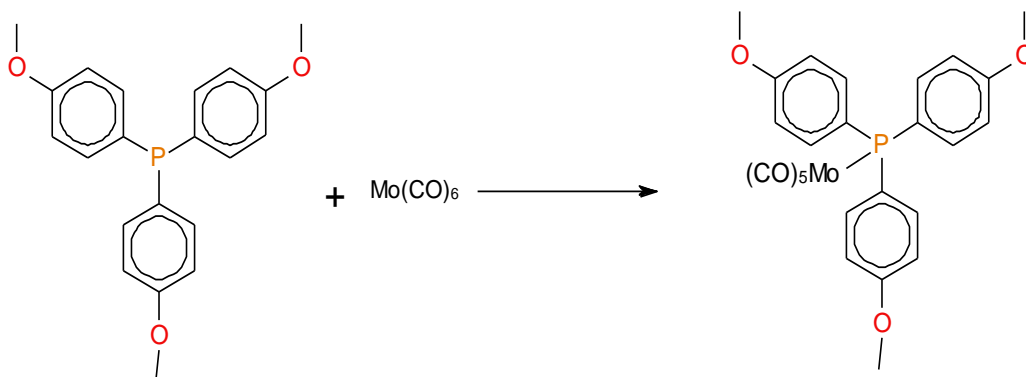


Figure 7: The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of tris(p-anisyl)phosphine selenide.

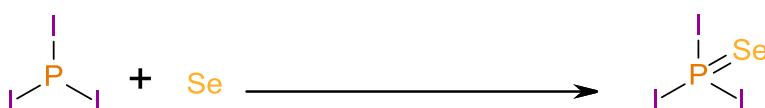
3.11 Reaction of tris(p-anisyl)phosphine with molybdenumhexacarbonyl.



The reaction of tris(p-anisyl)phosphine with molybdenumhexacarbonyl in toluene was undertaken. After 3 hours the coloured solution was filtered to give a white oily product. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum exhibits a peak at 32.2 ppm. This can be compared with the chemical shift of the starting phosphine at -10.09 ppm. The proton NMR shows a singlet at 3.8 ppm and multiplets within the range 6.8-7.6, consistent with the product, although peaks due to some residual toluene were also visible.

The IR spectrum of tris(p-anisyl)phosphine molybdenum pentacarbonyl shows CO stretching modes at 2069.0 cm^{-1} and 1915.3 cm^{-1} these are assigned to the A_1 and E modes respectively.

3.12 Reaction of phosphine triiodine with selenium.



The reaction between PI₃ and selenium in toluene was carried out for 6 hours. However, according to NMR data no product was observed. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum showed a noisy spectrum, with no clear peaks. The reaction was repeated, leaving it longer to react, but the same result was obtained. This reaction does not appear to work; this may be because of the steric effect of three very large iodine atoms around the phosphorus centre.

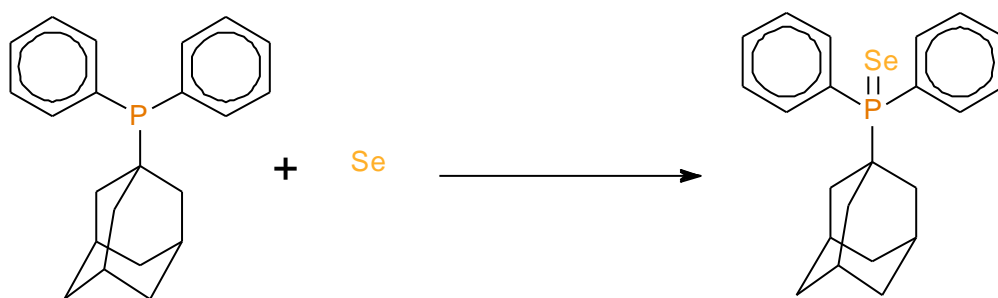
3.13 Reaction of adamantly Grignard reagent with chlorodiphenyl phosphine.

The Grignard reagent was prepared by addition of magnesium to dry diethyl ether followed by addition of 1-bromoadamantane then the mixture being stirred for approximately ½ hour. Chlorodiphenylphosphine was added and the solution was heated for 1 hour. After this time the reaction mixture was filtered to give a yellow oily product. An intense peak is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 29.0 ppm which compared with the starting chlorodiphenyl phosphine (δ 81.01 ppm), indicates that a reaction has occurred.

The ^1H NMR spectrum is complex, with peaks observed in both the aliphatic and aromatic regions; the assignment of these signals was made based on the ^1H NMR spectrum of 1-bromoadamantane.

3.14 Reaction of adamantyldiphenylphosphine with selenium.

Adamantyldiphenyl phosphine selenide was prepared from adamantyldiphenyl phosphine and powdered elemental selenium in toluene with the reaction mixture being heated and stirred 6 hours. The reaction can be described by the following equation:

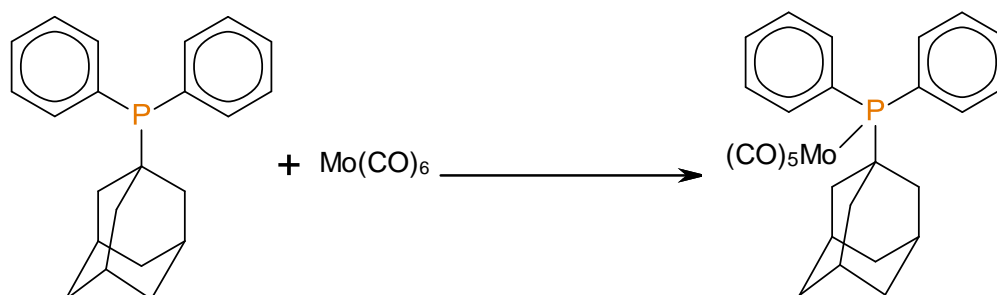


The $^{31}\text{P}\{^1\text{H}\}$ NMR data for the product dissolved in CDCl_3 showed a single peak at 852.3 ppm with selenium satellites $^1\text{J}(\text{PSe}) = 833 \text{ Hz}$.

The ^1H NMR spectrum of the product prepared in this way displays and confirms the presence of the aromatic protons on the phenyl rings, and adamantly group.

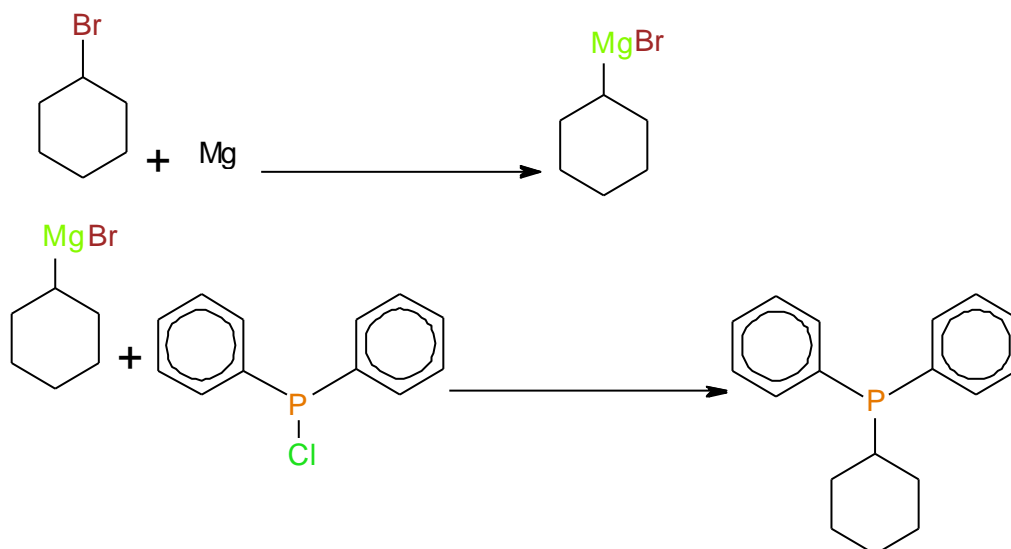
3.15 Reaction of adamantyldiphenyl phosphine with molybdenum hexacarbonyl.

The reaction between adamantyldiphenyl phosphine and molybdenum hexacarbonyl was carried out in toluene, as illustrated in the following scheme:



After heating for 2 hours the solution was cooled and filtered to give a dark green solid product. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum however, did not show any peaks consistent with reaction. It may be that the ligand is too big to allow it to coordinate to the metal centre.

3.16 Reaction of bromocyclohexyl-Grignard reagent with chlorodiphenyl phosphine.



The Grignard reagent was prepared by addition of magnesium to dry diethyl ether followed by addition of bromocyclohexane, after which the mixture was stirred for approximately $\frac{1}{2}$ hour. Chlorodiphenylphosphine was added slowly, and then the

solution was heated for 1 hour. After this time the mixture was filtered to give an oily yellow product. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows that the starting chlorodiphenyl phosphine (δ 81.01 ppm) has been completely used up, this indicates that a reaction has occurred. However, no signal is seen at -3 ppm, where the peak has been reported before. Instead, four peaks are observed at 41.1, 32.8, 22.4 and -40.5 ppm. Of these the peak at -40.5 ppm could be due to Ph_2PH which has been reported at -41 ppm.⁽²⁷⁾ The identity of the other peaks are unknown, but are in the region for P(V) or P-OH containing by-products.

It is likely that the Ph_2PH has been formed by reaction between Ph_2PCl and unreacted magnesium.

3.17 Reaction of cyclohexyldiphenylphosphine with selenium.

The selenide of Ph_2PH has been reported before,⁽²⁷⁾ as δ 6.9 ppm and $J = 758$ Hz so the reaction of the product of the previous reaction with selenium was undertaken in order to obtain further support for the proposed identity of the product.

After reaction the product was dissolved in CDCl_3 and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded, as shown in figure 8. The spectrum shows peaks in the P(V) and P-OH region, however the peak at -40.5 ppm is no longer present and the major phosphorus-containing compound gives rise to a peak with apparent selenium satellites at 82.7 ppm.

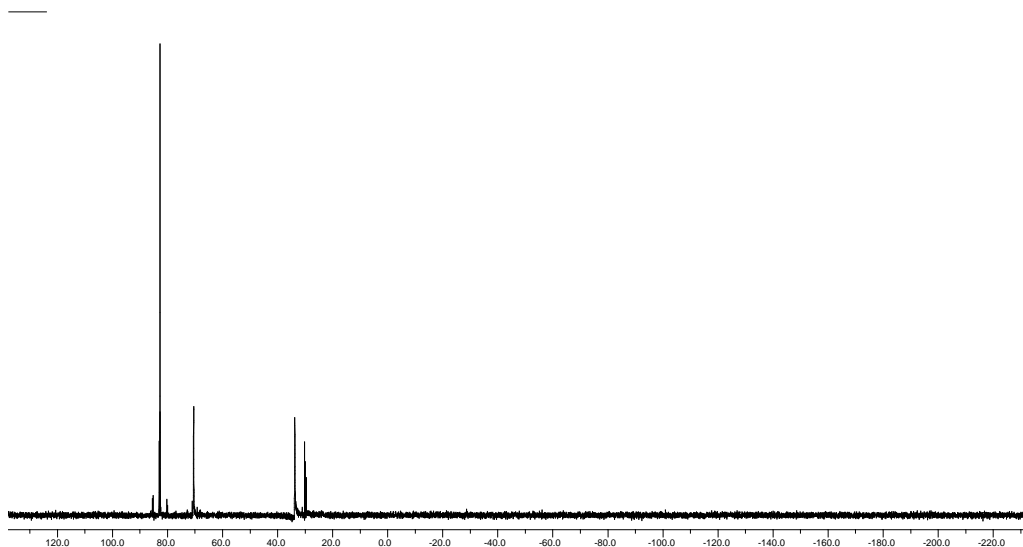


Figure 8: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after the reaction of Ph_2PH with selenium.

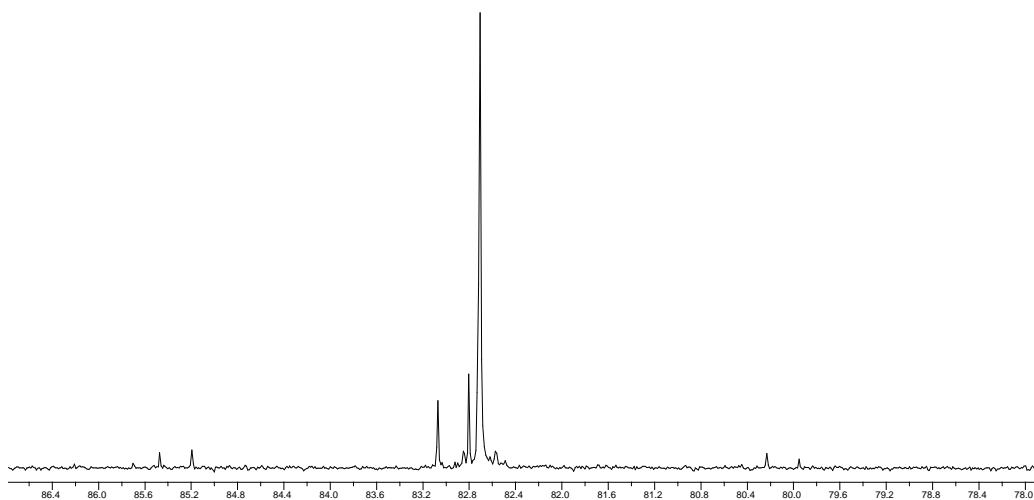


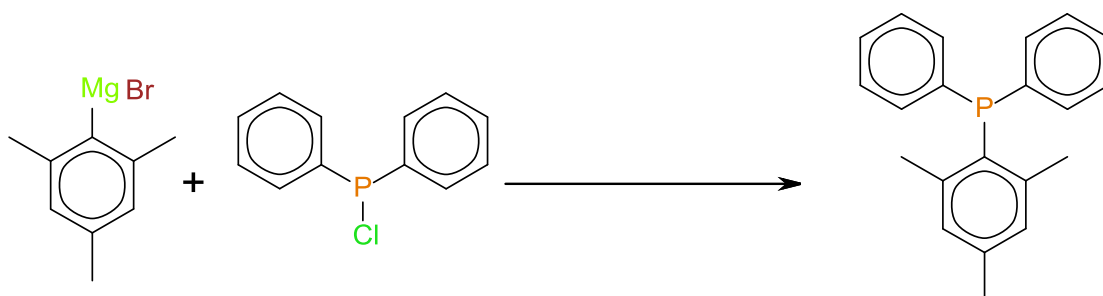
Figure 9: An expansion of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shown in figure 8.

An expansion of this signal is shown in figure 9. It is clear that the spectrum consists of two sets of selenium satellites rather than one (as was observed for all the previous phosphine-selenides). The appearance of this signal is similar to that which has been reported for bis-phosphines, for example of the type $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe). However, the identity of this species remains currently unclear. This reaction should be investigated further.

3.18 Reaction of mesityl magnesium bromide with chlorodiphenyl phosphine.

Mesityl diphenylphosphine was prepared from the reaction of mesityl magnesium bromide with chlorodiphenyl phosphine in dry tetrahydrofuran.

The reaction can be described according to the following equation:



$^{31}\text{P}\{^1\text{H}\}$ NMR data observed for the product dissolved in CDCl_3 shows a resonance at -16.8 ppm. This data can be compared with that of the starting phosphine chlorodiphenyl phosphine, which exhibits a $^{31}\text{P}\{^1\text{H}\}$ NMR single at 82 ppm.

The proton NMR spectrum shows the appropriate peaks due to the CH_3 groups at 2.2 ppm and multiplets due to the aromatic protons between 7.0 and 7.8 ppm.

3.19 Reaction of mesityldiphenylphosphine with selenium.



The reaction of mesityldiphenylphosphine with selenium was undertaken with heating for 6 hours. After that time the solution was filtered to give an oily yellow product which showed an intense peak in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 27.7 ppm as shown in figure 10. Selenium satellites were also observed, $^1\text{J}(\text{PSe}) = 728$ Hz. The ^1H NMR spectrum shows peaks due to the CH_3 groups at 2.55 and 2.5 ppm and multiplets due to the aromatic protons between 7.3 and 7.6 ppm.

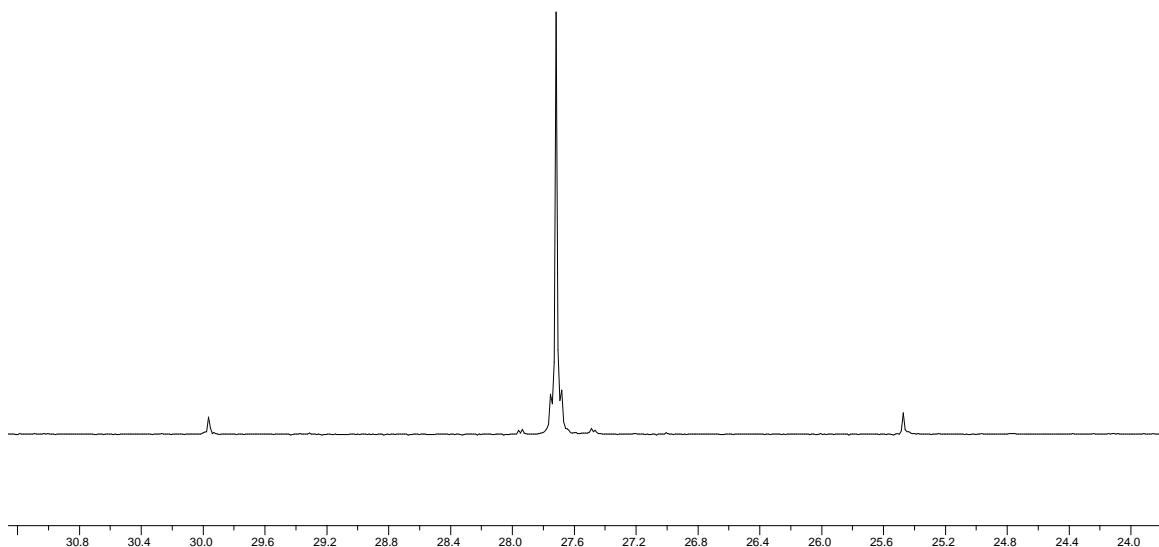
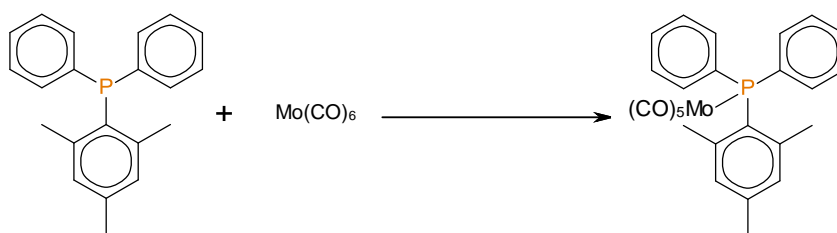


Figure 10: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of mesityldiphenylphosphine selenide.

3.20 Reaction of mesityldiphenylphosphine with molybdenum hexacarbonyl.

The reaction between mesityldiphenyl phosphine and molybdenum hexacarbonyl was carried out over 2 hours at reflux in toluene.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum obtained after work up from this reaction shows a peak at 34.1 ppm as shown in figure 11 the proton spectrum of mesityldiphenylphosphine molybdenumpentacarbonyl shows multiplets at 2.1 and 2.4 ppm. The IR spectrum of mesityldiphenylphosphine molybdenumpentacarbonyl shows the CO stretching modes at 2070.8 cm^{-1} , and 1920.3 cm^{-1} these are assigned as previously described to the A_1 and E vibrational modes.

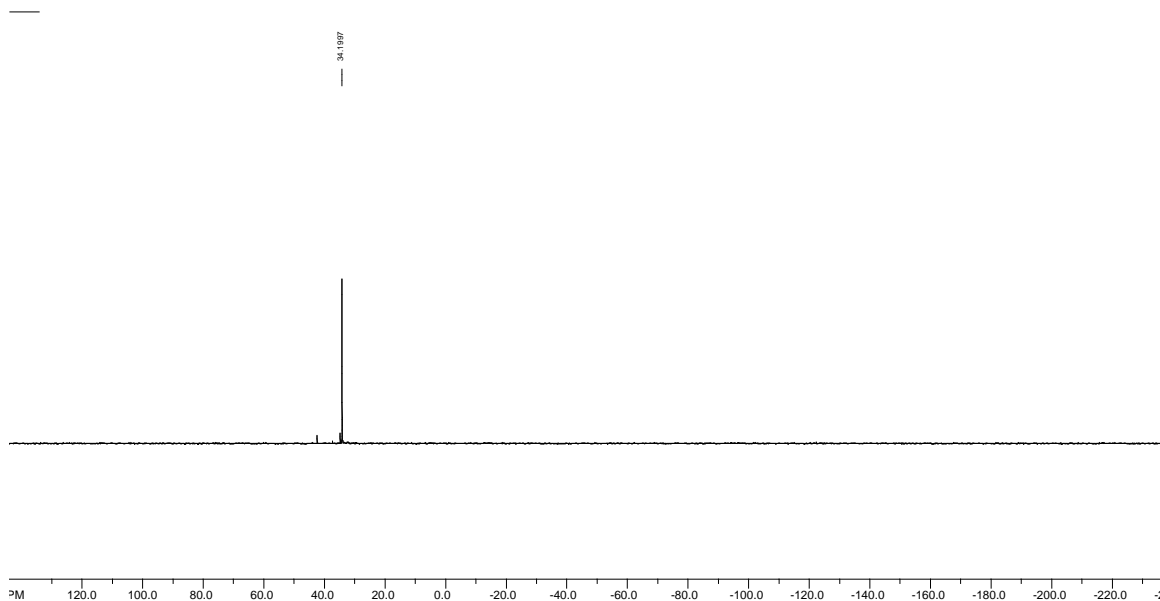
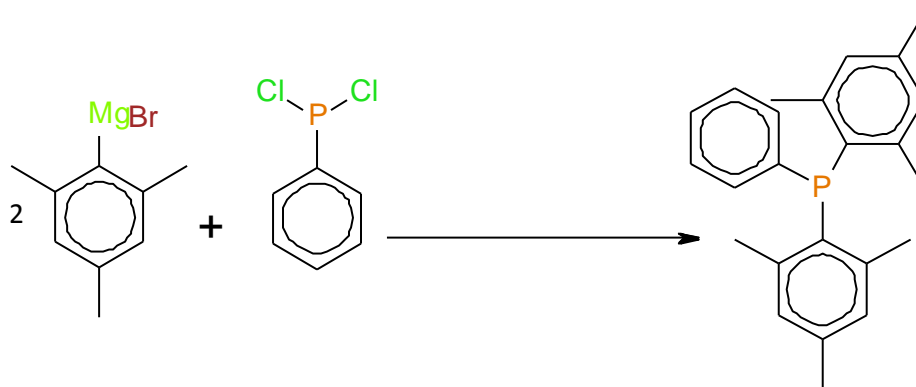


Figure 11: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of mesityldiphenylphosphine molybdenumpentacarbonyl.

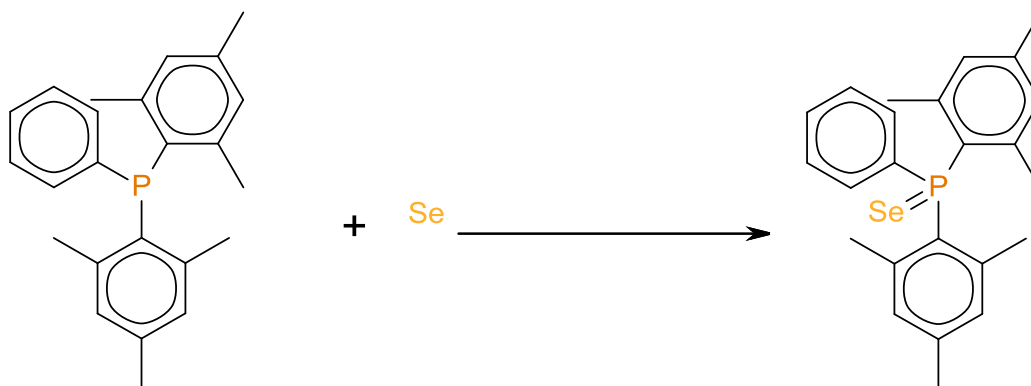
3.21 Reaction of mesityl magnesium bromide with dichlorophenyl phosphine.

Dimesitylphenylphosphine was prepared according to the reaction:



After work up the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction shows a singlet peak at -22.6 ppm. The ^1H NMR spectrum which confirms the inclusion of the mesityl groups with resonances being observed between 6.7-7.4 ppm and a CH_3 signals at ca. 2.3 ppm.

3.22 Reaction of dimesitylphenyl phosphine with selenium.



The reaction between dimesitylphenyl phosphine and powdered elemental selenium was carried out over 8 hours at reflux in toluene. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this shows a very clear singlet at 46.1 ppm with selenium satellites with $^1J(\text{PSe}) = 818$ Hz, as illustrated in figure 12.

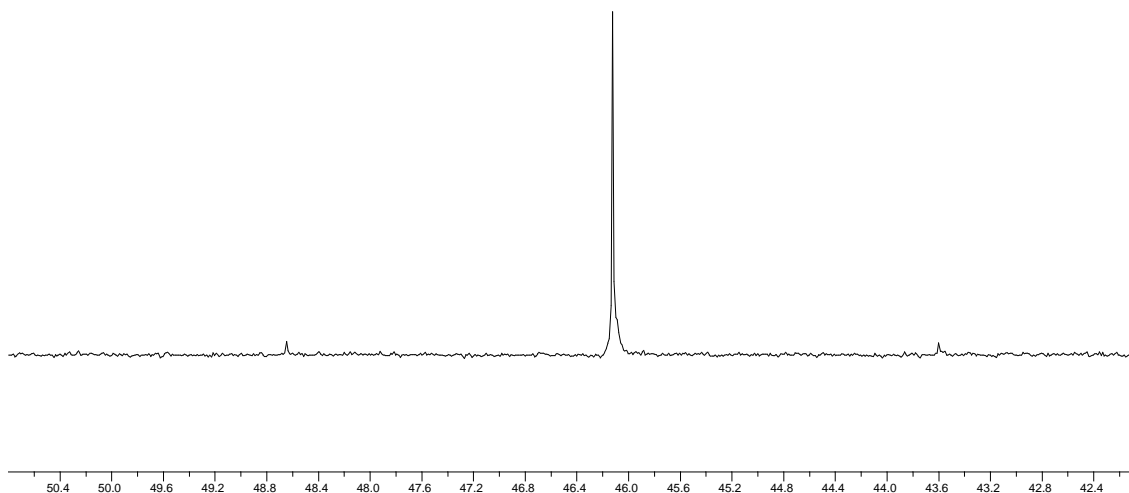


Figure12: The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of dimesitylphenyl phosphine selenide

Moreover, the ^1H NMR spectrum confirms the presence of this product as shown in figure 13. The two CH_3 groups are observed as singlets at ca. 2.3 ppm of relative intensity 18. This spectrum also confirms the presence of the aromatic group with resonances being observed between 7.0-7.2 ppm which integrate to 9 protons.

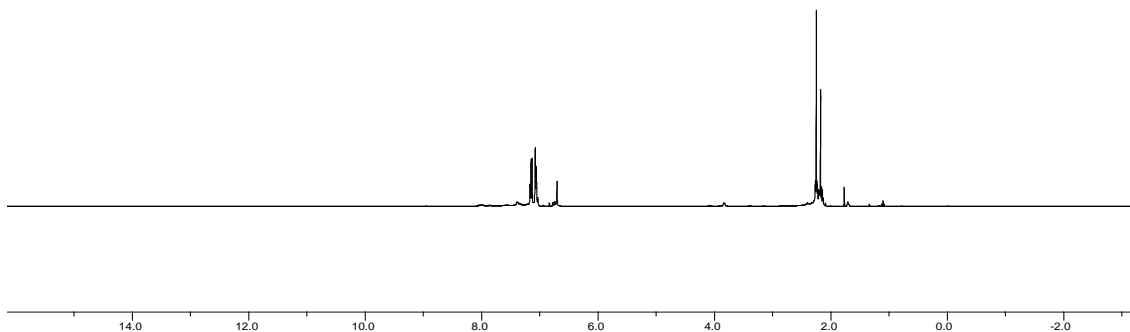
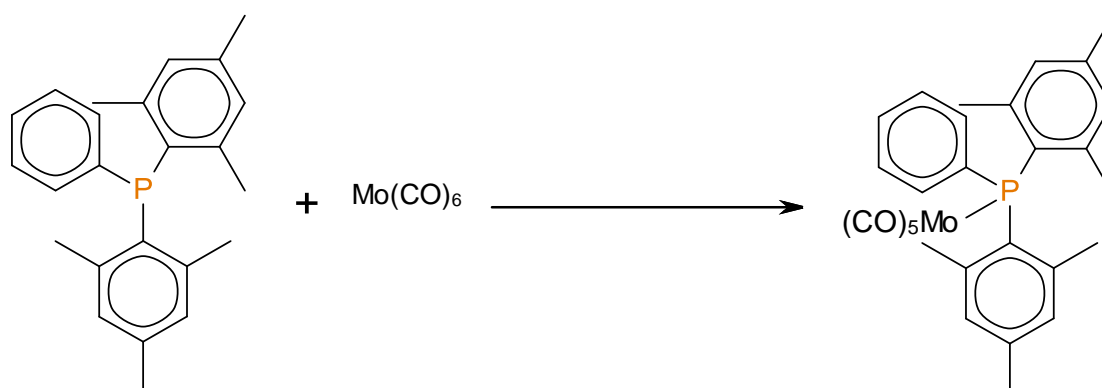


Figure 13: the ^1H NMR spectrum of dimesitylphenylphosphineselenide.

3.23 Reaction of dimesitylphenylphosphine with molybdenumhexacarbonyl.



The reaction between dimesitylphenyl phosphine and molybdenum hexacarbonyl in toluene was undertaken for 2 hours, after this time the solvent was removed and the sample analysed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a weak singlet at 36.6 ppm. This is shifted from the starting material by approximately 58.85 ppm, an incomplete reaction has therefore occurred. The proton NMR spectrum shows multiplets within the range 7.0-7.2 ppm of relative intensity 9 due to the aromatic protons, and 2 signals for the methyl protons. It also showed peaks due to remaining solvent or a by-product. A CO stretching peak is observed at 2071.9 cm^{-1} which is tentatively assigned to the product, but needs further confirmation.

A summary of the data obtained during this project is shown below (Table 2):

Phosphines	$^{31}\text{P}\{^1\text{H}\}$	$\nu(\text{CO})$	$^1\text{J}(\text{PSe})$
meta-tolyldiphenylphosphine selenide.	35.3		727
meta-tolyldiphenylphosphine molybdenumpentacarbonyl	37.4	2071	
(p-chlorophenyl)diphenylphosphine selenide	34.6		737
(p-chlorophenyl)diphenylphosphine molybdenumpentacarbonyl	37.8	2070.2	
tris(p-chlorophenyl)phosphine molybdenumpentacarbonyl	37.7	2072.2	
bis(p-thioanisyl)phenyl phosphine selenide	33.8		727
bis(p-thioanisyl)phenylphosphine molybdenumpentacarbonyl	35.97	2069.7	
tris(p-anisyl)phosphine selenide	31.6		714
tris(p-anisyl)phosphine molybdenumpentacarbonyl	32.2	2069.0	
triphenylphosphine selenide	35.3		728
triphenylphosphine molybdenumpentacarbonyl	37.7	2071.2	
adamantyldiphenylphosphine	29.0		
adamantyldiphenyl phosphine selenide	52.3		833
mesityldiphenylphosphine	-16.8		
mesityldiphenylphosphine selenide	27.7		728
mesityldiphenylphosphine molybdenumpentacarbonyl	34.1	2070.8	
dimesitylphenylphosphine	-22.6		
dimesitylphenylphosphine selenide	46.1		818
dimesitylphenylphosphine molybdenumpentacarbonyl	36.6	2071.9	

Having made a number of phosphine selenides and molybdenumpentacarbonyl complexes the next stage of the project was to compare these numbers with the $\nu(\text{CO})$ values for the nickel complexes $[\text{Ni}(\text{CO})_3\text{P}]$.

As shown previously it is possible to convert the $\nu(\text{CO})$ values of the $[\text{Mo}(\text{CO})_5\text{P}]$ complexes to values for the $[\text{Ni}(\text{CO})_3\text{P}]$ complex. The formula used to achieve this is given by:

$$\nu(\text{CO})_{\text{Ni}} = 1.116 \nu(\text{CO})_{\text{Mo}} - 243 \text{ cm}^{-1}$$

Using this there is a good correlation for complexes of known phosphines. For example for PPh_3 the $\nu(\text{CO})$ for the molybdenum pentacarbonyl complex is 2071.2 cm^{-1} , using the above formula this converts to a $\nu(\text{CO})_{\text{Ni}}$ value of 2068.5 cm^{-1} . Which is very close to the value reported of 2068.9 cm^{-1} .

The value of $^1\text{J}(\text{PSe})$ coupling constants has also been used before. However, there are only a small number of phosphines known for which the $\nu(\text{CO})$ values for the nickel complexes $[\text{Ni}(\text{CO})_3\text{P}]$ and the $^1\text{J}(\text{PSe})$ coupling constants are known. However, from these the following formula was obtained:

$$\nu(\text{CO})_{\text{Ni}} = 0.159 \text{ J}(\text{PSe}) + 1952.3 \text{ cm}^{-1}$$

Again, for the known complexes good agreement is seen; for PPh_3 , $^1\text{J}(\text{PSe})$ is 728 Hz , which gives a $\nu(\text{CO})_{\text{Ni}}$ value of 2068.1 cm^{-1} , just 0.8 cm^{-1} away from the observed peak.

We can also work out values for phosphines which were not included in Tolman's original work. For example, mesityldiphenylphosphine. Based on the stretching frequency of the molybdenum pentacarbonyl complex the $[\text{Ni}(\text{CO})_3\{\text{PPh}_2\text{Mes}\}]$ CO stretch should be at 2068.0 cm^{-1} . Based on the $^1\text{J}(\text{PSe})$ coupling constant this CO stretch should be at 2068.1 cm^{-1} .

This process has been carried out for all of the phosphines studied here, and the results of this are shown in Table 3.

Phosphines	$\nu(\text{CO})_{\text{Mo}}$	$^1\text{J}(\text{PSe})$	TEP from $\nu(\text{CO})_{\text{Mo}}$	TEP from $^1\text{J}(\text{PSe})$	Δ / cm^{-1}
meta-tolyldiphenylphosphine selenide.		727		2067.9	0.3
meta-tolyldiphenylphosphine molybdenumpentacarbonyl	2071		2068.2		
(p-chlorophenyl)diphenylphosphine selenide		737		2069.5	1.8
(p-chlorophenyl)diphenylphosphine molybdenumpentacarbonyl	2070.2		2067.3		
bis(p-thioanisyl)phenyl phosphine selenide		727		2067.9	0.9
bis(p-thioanisyl)phenylphosphine molybdenumpentacarbonyl	2069.7		2066.8		
tris(p-anisyl)phosphine selenide		714		2065.8	0.2
tris(p-anisyl)phosphine molybdenumpentacarbonyl	2069.0		2066.0		
triphenylphosphine selenide		728		2068.1	0.4
triphenylphosphine molybdenumpentacarbonyl	2071.2		2068.5		
mesityldiphenylphosphine selenide		728		2068.1	0.1
mesityldiphenylphosphine molybdenumpentacarbonyl	2070.8		2068.0		
dimesitylphenylphosphine selenide		818		2082.4	13.2
dimesitylphenylphosphine molybdenumpentacarbonyl	2071.9*		2069.2		

* = tentative assignment

The last column shows the difference between the TEP value calculated from the molybdenum pentacarbonyl complex and from the selenium-phosphorus coupling constant. Apart from the last values, the agreement is very good. The poor value for the dimesitylphenyl phosphine may be due the CO-stretching value being uncertain.

Therefore, using a combination of CO-stretching frequencies and $^1J(\text{PSe})$ coupling constants it is possible to estimate the TEP values for phosphines on Tolman's original scale. Both of these compounds are easier to prepare than the nickel tricarbonyl complexes, because of the toxicity of the starting material $\text{Ni}(\text{CO})_4$.

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