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Phosphine – Porphyrin Conjugates

A Thesis Presented in Partial Fulfilment of The Requirements For The Degree
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David James Lun

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Abstract

The research carried out in this thesis comprises an investigation into the synthesis and characterisation of a variety of complexed phosphine-aldehydes, complexed phosphinoporphyrins, and phosphinoferrocene conjugates. The porphyrin and phosphine moieties are linked together *via* the vinyl group, a product of Wittig chemistry. In general, functionalisation occurs at the β -pyrrolic position of the porphyrin and at the *para* position of a phenyl group on the phosphine.

Chapter One introduces the properties of porphyrins and the triphenylphosphine ligand, as well as a brief review on the types of functionalised triphenylphosphines. A brief review of existing phosphinoporphyrins is also discussed. The proposal for using the vinylic linking group (and hence Wittig chemistry) to connect the porphyrin and the phosphine moieties is also described.

Chapter Two outlines the synthesis of the 4-(diphenylphosphino)benzaldehyde (**5**) ligand, which is a necessary precursor for the Wittig reaction with *meso*-tetraphenylporphyrin (TPP) phosphonium salt (**1**). It was discovered that the Wittig reaction of (**1**) with (**5**) led to the synthesis of the product of oxidation, phosphinoporphyrin oxide (**7**), instead of the desired phosphinoporphyrin (**6**). Therefore an alternative scheme was pursued – complexation before the Wittig reaction. Hence the remainder of the chapter describes both the synthesis and characterisation aspects of five transition metal complexes of (**5**). These include complexes of gold, ruthenium, tungsten, and platinum.

Chapter Three describes the synthesis and characterisation of a variety of novel complexed phosphinoporphyrins, including two bis-phosphinoporphyrin complexes. This was achieved by utilising Wittig chemistry of TPP phosphonium salt (**1**) with the appropriate complexed phosphine-aldehyde. In each case, optimisation of the Wittig conditions was required in order to obtain the sterically and thermodynamically favoured *trans* isomer.

Chapter Four extends the phosphinoporphyrin chemistry by investigating the synthesis of a novel phosphinoporphyrin trimer. In order to achieve this, a phosphine tris-aldehyde was synthesised. This chapter focuses on the synthesis and characterisation of tris(4-formylphenyl)phosphine oxide (**20**). The results of the Wittig reaction of (**20**) with TPP phosphonium salt (**1**) are also described.

Chapter Five demonstrates the versatility of both the Wittig and phosphine chemistry. In this chapter, the synthesis of phosphinoferrocenes *via* Wittig chemistry is investigated. The ferrocene and phosphine moieties are linked *via* the vinyl group, in a similar manner as the phosphinoporphyrins. In this case, functionalisation occurs at the *para* position of a phenyl group of the phosphine to the cyclopentadienyl ring of the ferrocene. A phosphinoferrocene monomer, (**24**), was synthesised by Wittig reaction of a ferrocene phosphonium salt (**22**) with (**5**). Both the synthesis and characterisation of this compound is reported. Also described is the attempted synthesis of a phosphinotrisferrocene *via* Wittig reaction of (**22**) with (**20**).

Chapter Six contains a brief summary of the results obtained during this study, and also mentions future research to be pursued in this field of study.

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Abbreviations

4-PCHO	4-(diphenylphosphino)benzaldehyde
Ar	Aryl
Au(4-PCHO)	Gold phosphine-aldehyde
C _p	Cyclopentadienyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
FAB	Fast Atom Bombardment
HRMS	High-resolution Mass Spectrometry
NMR	Nuclear Magnetic Resonance
O=P(4-CHO) ₃	Tris(4-formylphenyl)phosphine oxide
P(4-CHO) ₃	Tris(4-formylphenyl)phosphine
Ph	Phenyl
PPh ₃	Triphenylphosphine
Pt(4-PCHO) ₂	Platinum bis(phosphine-aldehyde) complex
Ru(4-PCHO)	Ruthenium phosphine-aldehyde
Ru(4-PCHO) ₂	Ruthenium bis(phosphine-aldehyde) complex
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TPP	<i>meso</i> -Tetraphenylporphyrin
UV-Vis	Ultraviolet-Visible
W(4-PCHO)	Tungsten phosphine-aldehyde

Chapter One

Introduction

1.1 The porphyrin molecule.

Tetrapyrrolic macrocycles are utilised in a number of important biological roles including the harvesting of light, transport of small molecules, and the transfer of energy. The most common structural type in the tetrapyrrolic family is the porphin molecule, and this porphin skeleton is present in all other porphyrin derivatives. Functionalities can be added at the *meso* and/or β -pyrrolic positions, to give different properties and solubilities.

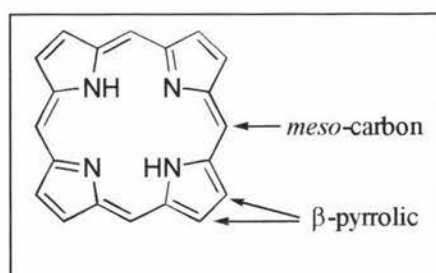


Figure 1.1

The porphin molecule.

Porphyrins all possess a large, flat aromatic core and in solution exist predominantly as a pair of tautomers. Although the conjugated system contains 22 π -electrons in total, each tautomer contains an [18]-annulene type aromatic delocalisation pathway with two isolated double bonds at the β -pyrrolic positions (figure 1.2).¹ Other aromatic tautomeric forms can be drawn, however they are of higher energy and have never been directly observed.

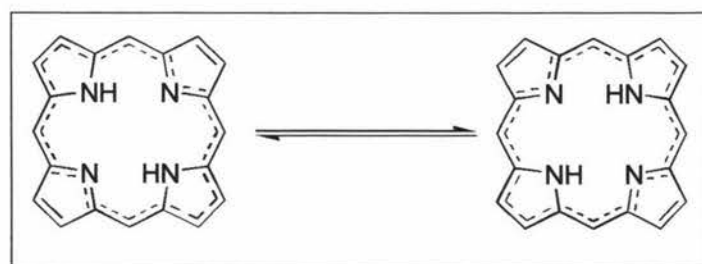


Figure 1.2

Equilibrium of tautomers of the porphin molecule.

The tautomers in the above diagram are examples of what are termed free base porphyrins; that is they have two protons bound to the inner nitrogens. Free base porphyrins can either donate two protons or accept two protons, to form the 2^- dianion, or the 2^+ dication respectively. It is in the dianion form that the porphyrin becomes a tetra-dentate chelating-ligand capable of binding to almost every metal in the periodic table, forming metalloporphyrins.

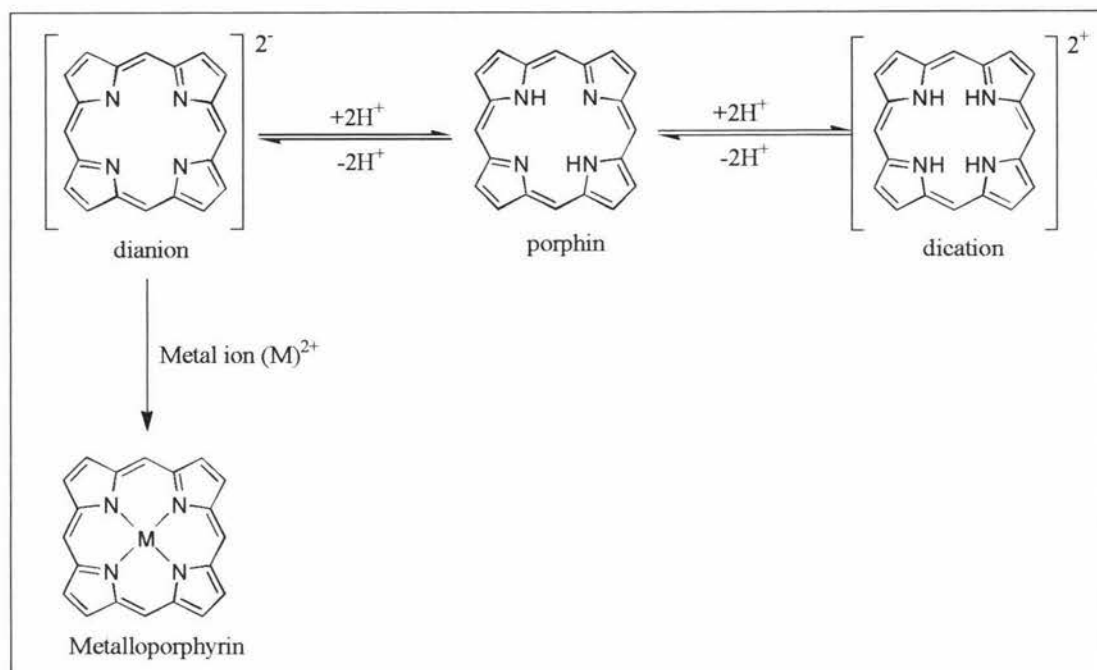


Figure 1.3

The acid-base chemistry of the porphyrin molecule.

Porphyrins also have very characteristic spectroscopic properties. In solution, porphyrins are intensely coloured due to the high amount of conjugation. The UV-vis spectra is dominated by $\pi-\pi^*$ and $n-\pi^*$ transitions, with the Soret band appearing between 400-500 nm with a corresponding molar extinction coefficient (ϵ) well over one hundred thousand. In addition to this, a number of smaller Q bands exist, appearing at a longer wavelength between 500-650 nm with ϵ generally between a thousand and ten thousand. Because porphyrins are aromatic macrocycles, the resulting anisotropic ring current causes distinct features in their ^1H NMR spectra. The interior protons (i.e. pyrrolic N-H protons) become shielded, and the protons on the outside (i.e. *meso* and β -pyrrolic protons) become deshielded, so it is common for the chemical shifts for free base porphyrins to be spread over 13 ppm or more.

The types of substituents attached to the porphyrin ring can influence all of these properties. The coupling of a porphyrin with a substituent capable of functions such as: redox chemistry, polymerisation, or chelation/complexation, could give rise to an entity that may possess unique physical and chemical properties that can be exploited.

1.2 Triphenylphosphine and its complexes.

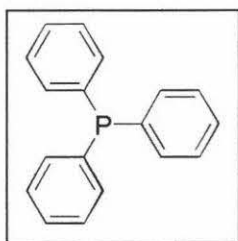


Figure 1.4

The triphenylphosphine molecule.

Triphenylphosphine (PPh₃) has been described by some authors as one of the most important ligands in transition metal chemistry² and one of the most widely used ligands in coordination chemistry.³ PPh₃ is a trivalent phosphorus molecule with three aromatic groups attached capable of complexing to a variety of transition metals *via* the lone pair of electrons on the phosphorus. On its own, PPh₃ is a white crystalline powder, which is soluble in polar solvents. In solution it is basic and acts as a relatively strong nucleophile. However, the key properties of this ligand are the steric demands of the phenyl rings, its σ donor ability, and its π acidity. These properties all define the stability of its resulting complexes. The steric demands of the phenyl groups can be explained or represented by what is defined as the cone angle.⁴ Using the angle of a cone swept out by the van der Waals radii of the phenyl groups with a nickel atom at the top of the cone, the angle is approximately 145° (see figure 1.5). This large cone angle tends to lengthen the M-P bond and may reduce the π component of bonding,⁴ but it also assists in protecting the metal centre.

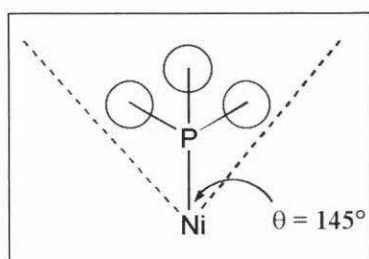


Figure 1.5

The cone angle of PPh_3 .

The transition metal chemistry of PPh_3 is well established. The metal ion is bound through interaction with the lone pair of electrons of the phosphorus atom, but there is still some debate over the type of bonding involved, especially the degree of π -bonding. However, the general theory is that M-PPh_3 complexes form primarily by donor σ -bonds (P to metal), but then use empty orbitals to accept back electron density from the metal *via* a π back-bonding system.

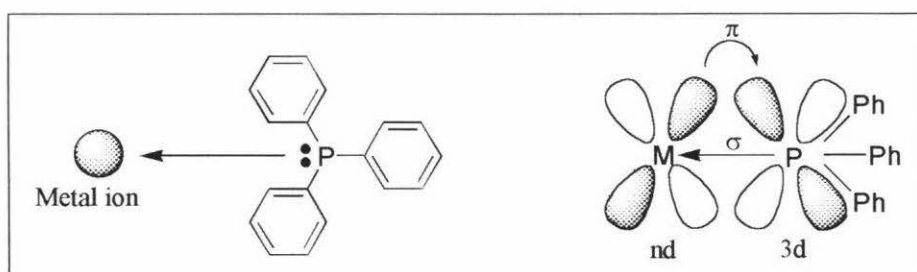


Figure 1.6

Complexation and bonding.

Despite the knowledge gained on the bonding of M-PPh_3 type complexes, the bonding aspect in such complexes is considered not as important as it once was. Instead, the focus of interest is mainly on the properties of the complexes, in particular, their catalytic ability.

1.2.1 PPh_3 in catalysis: Wilkinson's catalysts.

Since the mid sixties, transition metal complexes containing PPh_3 ligands, especially those of Rh(I) , have played a fundamental role in the development of transition metal catalysis. In particular, the homogenous catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ or Wilkinson's catalyst has been the focus of many studies, and to date is probably still one of the

most widely studied catalytic systems. $[\text{RhCl}(\text{PPh}_3)_3]$ has been used as a catalyst to hydrogenate a wide variety of alkenes and was first developed and reported by Wilkinson and co-workers in 1965.⁵⁻⁷ There is some debate over the exact mechanism, however the first step in a simplified mechanism is believed to be ligand substitution of a labile PPh_3 with a solvent molecule, S (see figure 1.7).

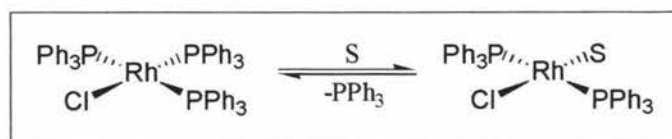


Figure 1.7

The formation of the solvated $[\text{RhCl}(\text{PPh}_3)_2\text{S}]$ complex.

The catalytic cycle is then initiated by the oxidative addition of H_2 to $[\text{RhCl}(\text{PPh}_3)_2\text{S}]$, forming a reactive six coordinate species. Ligand substitution of an alkene with the coordinated solvent, followed by two successive hydrogen transfers then completes the catalytic cycle. The first migratory insertion generates a rhodium-alkyl; the second hydrogen transfer results in the reductive elimination of the alkane product. This simplified catalytic cycle is represented in figure 1.8.

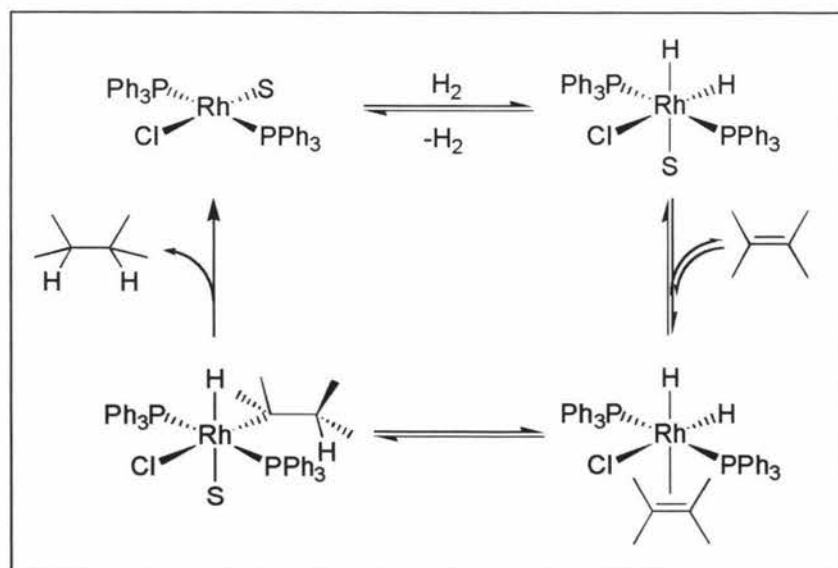


Figure 1.8

Simplified catalytic cycle of the hydrogenation of an alkene by species derived from $[\text{RhCl}(\text{PPh}_3)_3]$.

The size of the R groups on the alkene used in the above catalytic cycle is also important. For the $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst, the rates of hydrogenation decrease with increasing alkene substitution, as generally, terminal alkenes have a higher rate than internal alkenes. Hindered internal alkenes may not get hydrogenated at all as it is assumed that they are too sterically crowded to coordinate to the catalyst.

The nature of the phosphine is also of great importance. It was found that replacing PPh_3 with alkylphosphines gave rise to virtually no hydrogenation at all. These ligands are more basic and sterically less demanding than PPh_3 , and the lack of activity is attributed to the fact that alkylphosphine ligands are strongly bound to the metal and hence do not readily dissociate.² It is also suggested that hydrido-species with alkylphosphine ligands do not readily lose or transfer hydrogen to the alkene when compared with aryl phosphine ligands.⁸

The success of the $[\text{RhCl}(\text{PPh}_3)_3]$ catalyst sparked tremendous interest into transitional metal- PPh_3 type catalysts. There are numerous examples of such compounds in the literature, and a selection is listed in the table below.

<u>Reaction Type.</u>	<u>Catalyst</u>
Hydrogenation	$[\text{RhCl}(\text{PPh}_3)_3]$, $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$, $[\text{RuCl}_2(\text{PPh}_3)_2]$
Hydroformylation	$[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$, $[\text{CoH}(\text{CO})_3\text{PPh}_3]$, $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$
Hydrosilation	$[\text{NiCl}_2(\text{PPh}_3)_2]$, $[\text{Pd}(\text{PPh}_3)_4]$
Oxidation	$[\text{Pt}(\text{PPh}_3)_4]$, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$
Polymerisation	$[(\pi\text{-C}_3\text{H}_6)\text{Ni}(\text{PPh}_3)]$

Table 1.

Examples of M- PPh_3 type catalysts.

1.3 Functionalised triphenylphosphines.

The synthesis of tertiary phosphines can be separated into four main categories: Friedel-Crafts reactions, reaction of halophosphines with organometallic reagents, and the reaction of phosphides or diarylphosphine compounds in the presence of a transition metal catalyst with aryl halides or sulphonate esters.⁹ This provides a wide variety of compounds, of which the type of functional group is dependent on the type of research being undertaken.

Apart from complexation to a metal ion, triphenylphosphine derivatives can have substituents on one or both the *ortho* positions,¹⁰⁻¹² *meta* positions,¹³⁻¹⁵ or *para* positions.^{10, 16, 17} The literature provides a vast variety of functional groups, with the most common types including: halogen,^{10, 16, 18, 19} alkyl,²⁰⁻²² alkoxy,^{21, 23, 24} aldehyde,^{15, 16, 25, 18} nitro,²⁷⁻²⁹ carboxyl,^{16, 26, 30} cyano,^{16, 31} and amine.³² Moreover, the aromatic ring may be bi-,^{20, 23} tri-,^{21, 33} or even tetra²¹ substituted, and one,^{10, 11, 27} two,^{12, 13, 19} or even all three^{18, 25, 34} of the aromatic rings may be substituted.

In the past 10 years or so, interest in binuclear and polynuclear tertiary aryl phosphines has seen the development of some new, novel compounds. The literature contains a moderate number of examples of such compounds, with the attached functionalities ranging from: ferrocenes,^{35, 36} crown ethers,^{37, 38} to porphyrins.^{39, 40} In addition to this, there are also cases where one of the aryl rings of the phosphine is swapped with a ring from another aryl system such as naphthalene,^{41, 42} quinoline,⁴³⁻⁴⁵ anthracene,⁴² bipyridine,⁴⁶ or metallocenes.⁴⁷⁻⁵⁰ These polynuclear compounds can be joined or linked in two general ways; either directly linked or by a bridging ligand. An important feature of the latter is the type of bridge between the tertiary aryl phosphine and its other functionality. This is because the length, orientation, relative steric size and chemical nature of the bridge will ultimately affect the physical properties of the polynuclear compound and its resulting complex.

1.3.1 Types of connections.

Whether the bridge serves as a spacer for steric reasons only, or its function is to provide a link for communication between two centres, the type of bridge is

important. Many different types of bridges or linking groups have been employed with the functionalisation of tertiary aryl phosphines, and a selection of some commonly found in the literature are summarised in the figure below.

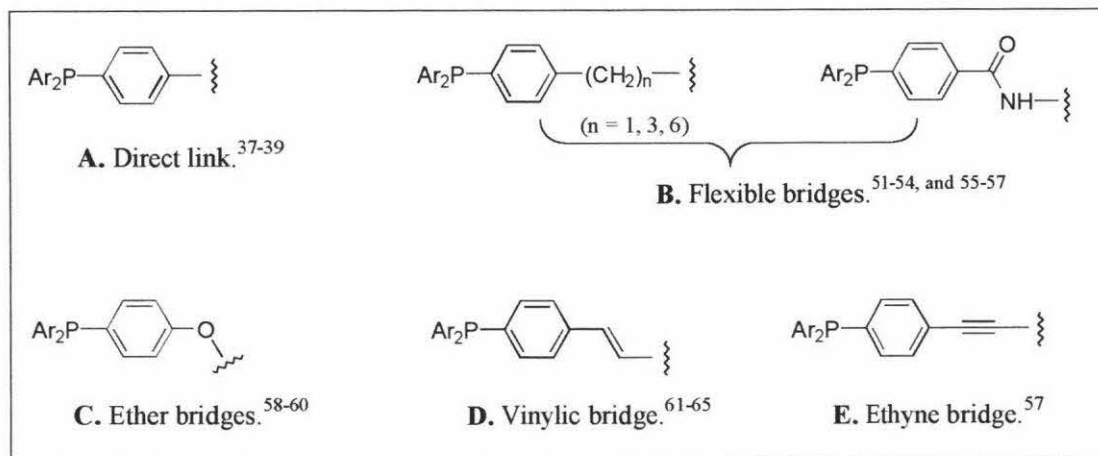


Figure 1.9

Commonly used linkages for the functionalisation of tertiary aryl phosphines.

Each of these bridges will of course have their own advantages and disadvantages, so again the type of linkage used will depend on the type of research being pursued.

1.3.2 The Vinylic Bridge.

When connecting a tertiary aryl phosphine to a second conjugated compound, it may be advantageous to use a bridge that itself will become part of the conjugated system, thereby ensuring the conjugation extends from the tertiary aryl phosphine to the other functionality. Such a binuclear or polynuclear compound may then be able to facilitate energy or electron flow through the system, which is essential for photo or redox communication between the two centres. Hence a vinylic bridge is a three bond couple between two centres creating a fully conjugated entity. For this reason, and the ease of synthesis in comparison to alkyne linkers, the vinylic bridge is chosen for this research project.

A convenient procedure for connecting a tertiary aryl phosphine and another functionality *via* the vinylic bridge is by the classical Wittig reaction. The Wittig reaction firstly involves the treatment of a phosphonium salt in basic conditions to

phosphinoporphyrin (see figure 1.12) was synthesised by utilising the Adler reaction conditions for the condensation of pyrrole and 4-(diphenylphosphino)benzaldehyde, resulting in *meso*-tetrakis[4-(diphenylphosphino)-phenyl] porphyrin. This phosphinoporphyrin was then reacted with $W(CO)_5$ THF, giving the first such reported porphyrin containing a bound transition metal complex fragment.

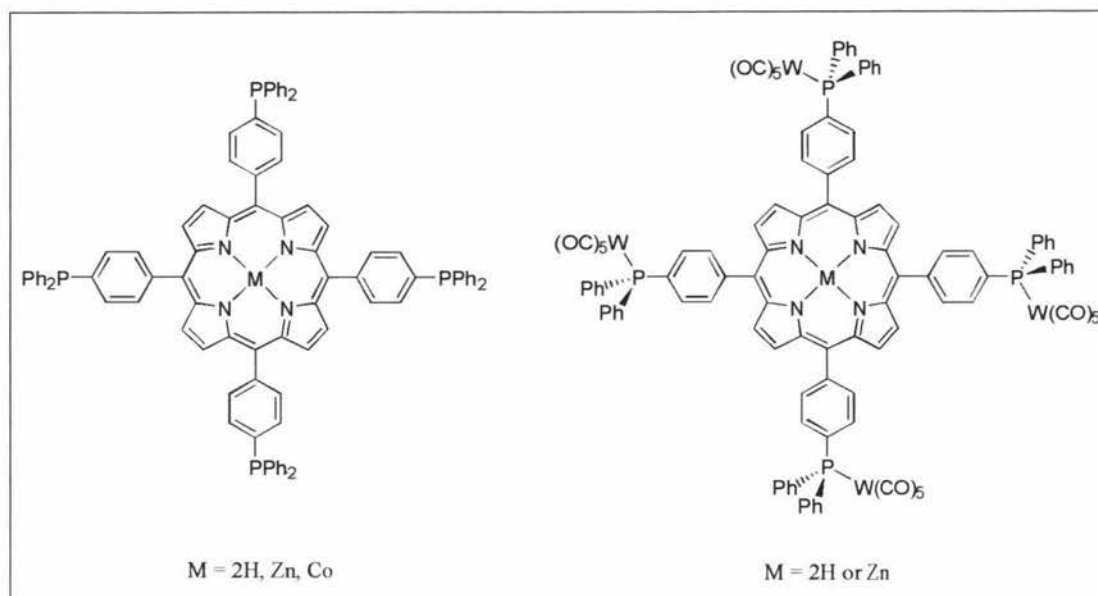


Figure 1.12

meso-tetrakis[4-(diphenylphosphino)-phenyl] porphyrin (left) and its tungsten derivative (right).

The paper also went on to discuss the synthesis of a water-soluble porphyrin. These types of porphyrins are of interest because of their potential interaction with biological systems. In this case, *meso*-tetrakis[4-(diphenylphosphino)-phenyl] porphyrin was treated with *p*-xylylene dibromide to give the water-soluble octakis(phosphonium salt) porphyrin double-decker. This compound is the first example of an ionic, vertically stacked porphyrin and has been described having a cage type structure. It was also suggested that by altering the length of the xylylene spacers, the height of the porphyrin cage would change, hence different guest molecules could be accommodated.

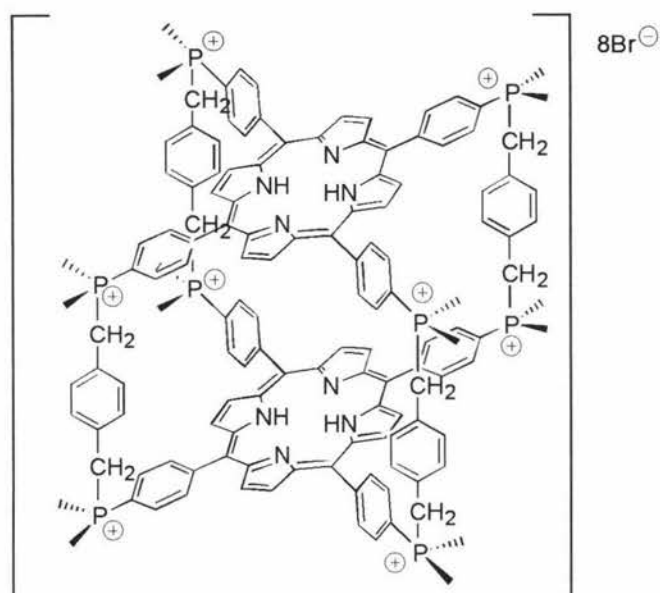


Figure 1.13

The water-soluble porphyrin double-decker.

1.4 Research proposal.

The research carried out for this thesis includes an investigation into the joining of the photoactive porphyrin moiety to triphenylphosphine type complexes *via* the conjugated vinylic linker. To the best of our knowledge, no one else has linked a tertiary aryl phosphine to a porphyrin *via* the vinylic bridge, so the first task was to formulate an efficient methodology for synthesising such phosphinoporphyrins, and eventually the complexed phosphinoporphyrins. Moreover, the phosphine will be connected to the porphyrin at the β -pyrrolic position, in contrast to Märkl *et al.*, whose porphyrin is functionalised at the *meso* position. Because there are very few phosphinoporphyrins in the literature, little is known about their properties, so any new phosphinoporphyrin compounds may have attributes worthy of further investigation. The following chapters will present results of investigations into the synthetic and characterisation aspects of such compounds.

- Chapter Two will investigate the strategy involved in the synthesis of the desired phosphinoporphyrins. It will also introduce one of the key starting materials for this project, 4-(diphenylphosphino)benzaldehyde, and its resulting complexes.

- Chapter Three will investigate the synthesis of phosphinoporphyrins *via* the Wittig reaction using the porphyrin phosphonium salt and the appropriate complex of 4-(diphenylphosphino)benzaldehyde as starting materials.
- Chapter Four will investigate the synthesis of the trialdehyde species tris(4-formylphenyl)phosphine, and the attempted attachment of porphyrins *via* the Wittig reaction.
- Chapter Five will explore the synthesis of phosphinoferrocenes *via* the Wittig reaction, with 4-(diphenylphosphino)benzaldehyde and ferrocene phosphonium salt as starting materials.

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Chapter Two

4-(diphenylphosphino)benzaldehyde and its complexes.

As described earlier in Chapter One, the porphyrin and the phosphine are to be linked *via* the vinylic bridge, a product from the Wittig reaction. Depending on the starting materials, the desired phosphinoporphyrins can be achieved by two methods; using a 2-porphyrinylmethylphosphonium salt developed by Bonfantini and Officer¹ with a phosphine-aldehyde, or conversely, a phosphinomethylphosphonium salt with 2-formylporphyrin. For this research project, the first method has been chosen primarily because the research group has successfully synthesised the appropriate porphyrin phosphonium salts. Moreover, the versatility of these phosphonium salts has been demonstrated by the successful Wittig reactions with a wide range of different carbonyl compounds.^{1,2}

The porphyrin phosphonium salt of choice is the tetraphenylporphyrin (TPP) methyl phosphonium salt (**1**), which is made by a six-step synthesis from two commercially available precursors, pyrrole and benzaldehyde. The use of this TPP phosphonium salt is further strengthened given that some tertiary aryl phosphine-aldehydes are commercially available or can be readily synthesised. In this case, the desired phosphine-aldehyde, 4-(diphenylphosphino)benzaldehyde (**5**), had to be synthesised in our laboratory.

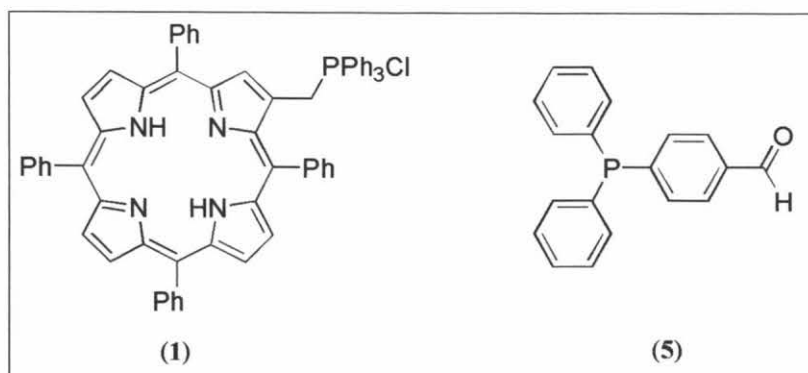


Figure 2.1

Tetraphenylporphyrin (TPP) phosphonium salt (left), and 4-(diphenylphosphino)benzaldehyde (right).

2.1. Synthesis of 4-(diphenylphosphino)benzaldehyde.

4-(diphenylphosphino)benzaldehyde (4-PCHO) was first synthesised by Schiemenz³ in 1966 by a two-step derivatisation of 4-Ph₂PC₆H₄CO₂H, which itself was synthesised in two steps. However, it wasn't until 1973 when Schiemenz and Kaack^{4, 5} devised a reliable, relatively straightforward methodology for compounds such as 4-PCHO. This firstly involves the cyclic protection of the *ortho*, *meta*, or *para* bromo-benzaldehyde followed by the reaction of the resulting dioxolane with Mg to form the Grignard reagent. Reaction of this Grignard with Ph₂PCl, followed by a deprotection step gives the desired compound.

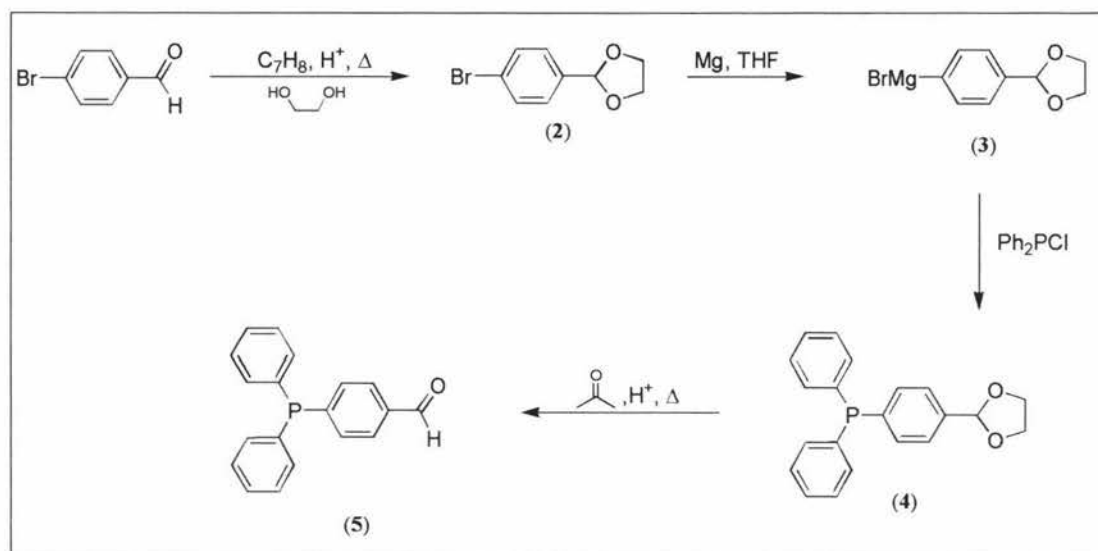


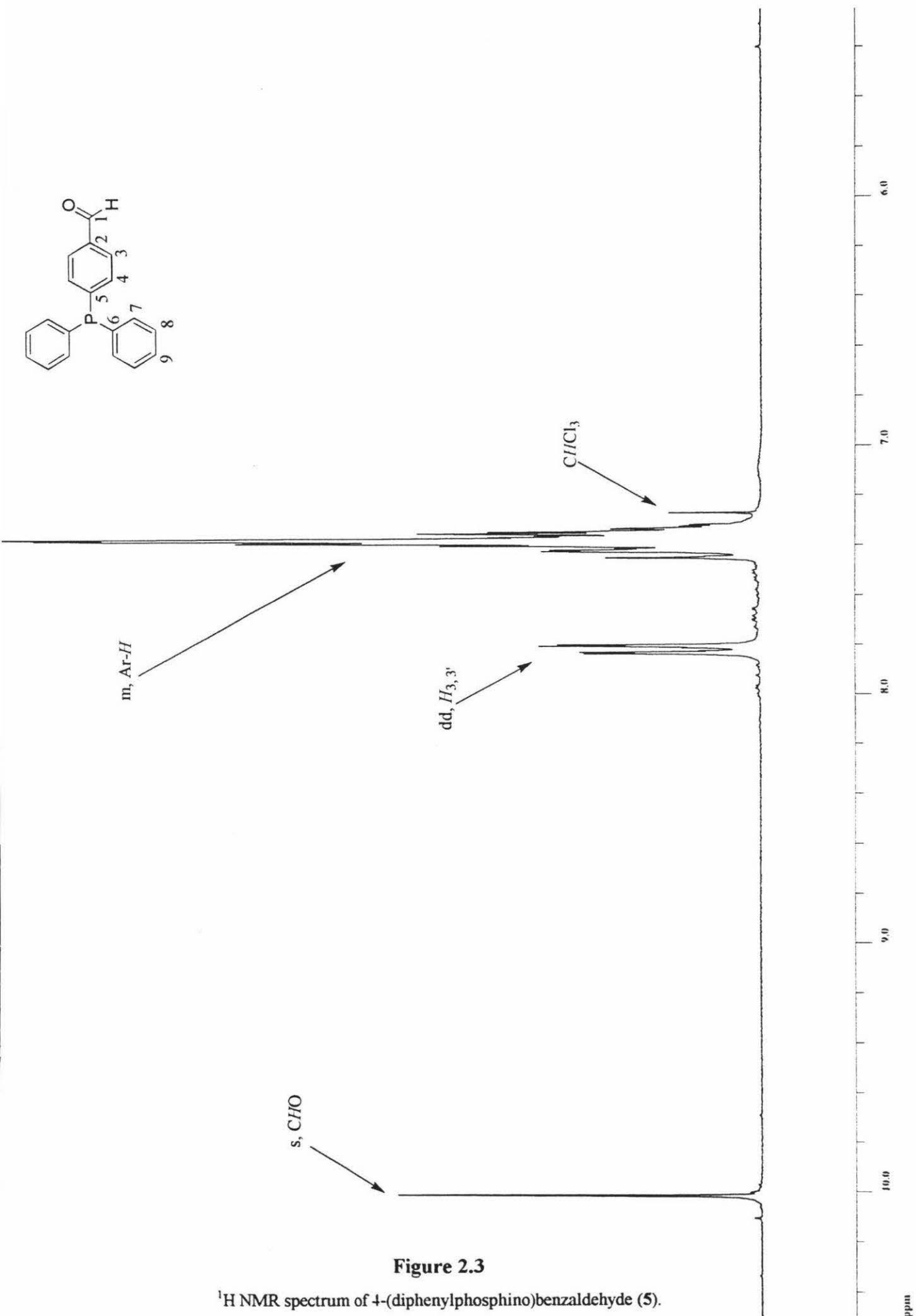
Figure 2.2

The synthesis of 4-(diphenylphosphino)benzaldehyde.

This scheme (figure 2.2) is more or less a standard procedure for synthesising these types of phosphine-aldehydes. Typically, these reactions can be scaled up to yield ~100 grams of product in >50% overall yield.⁶

2.1.1. Compound characterisation.

All samples were characterised by ¹H NMR spectroscopy with (4) and (5) requiring additional ³¹P NMR, and (5) was also characterised by ¹³C NMR and infrared spectroscopy. The ¹H NMR spectrum of 4-PCHO (5) is shown in figure 2.3.



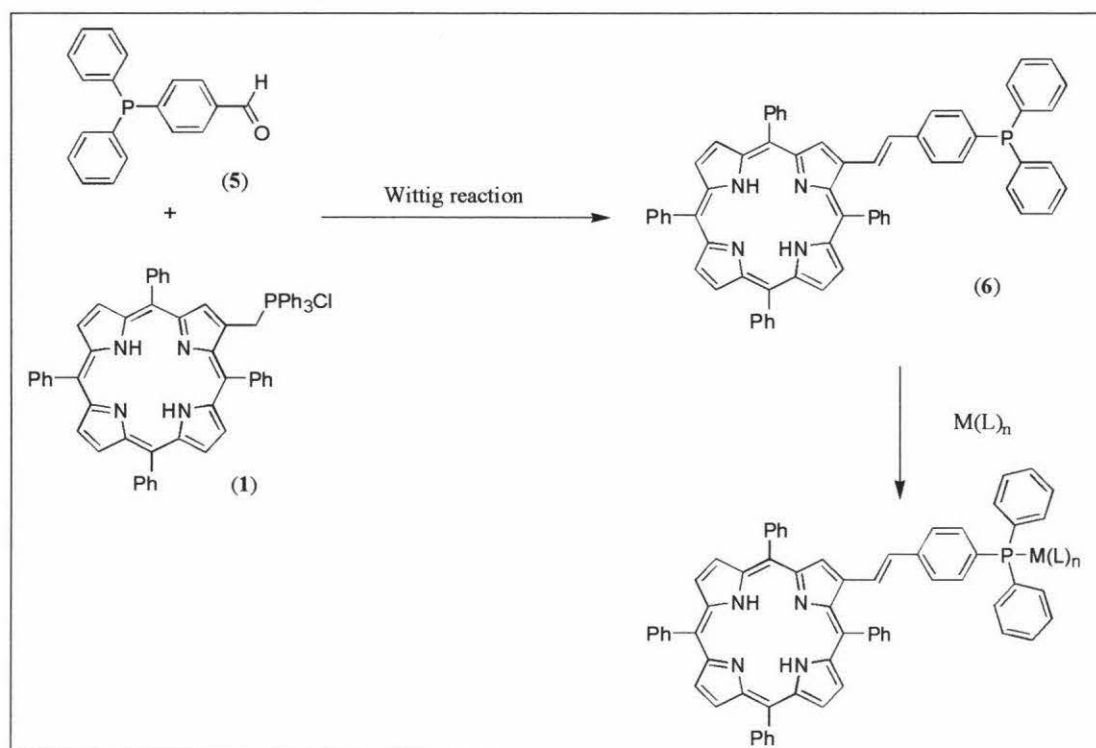
The ^1H NMR spectrum of (**5**) has the distinctive peak at 10.01 ppm corresponding to the aldehyde proton, and this aldehyde group has an effect on the nearest neighbouring phenyl protons. Compared to PPh_3 , which consists of a multiplet signal spanning from 7.08-7.88 ppm, the signal in (**5**) belonging to the $\text{H}_{3,3'}$ protons is shifted downfield due to the influence of the aldehyde group. This signal is split into a doublet of doublets due to the strong three bond coupling to the adjacent $\text{H}_{4,4'}$ protons ($J = 8.24$ Hz), and a smaller four bond coupling to the aldehyde proton ($J = 1.53$ Hz). The signal for the $\text{H}_{4,4'}$ protons is obscured by the signal of the remaining phenyl protons, which appear as a multiplet signal spanning from 7.31 to 7.45 ppm.

The ^{13}C NMR spectrum of (**5**) becomes slightly more complicated than PPh_3 because of the reduction in symmetry due to the introduction of the aldehyde group. In general, the spectrum of (**5**) is fairly similar to that of PPh_3 . However, the most significant differences are the single peak at 191.76 ppm belonging to the aldehyde carbon, and the downfield shift of the C_5 doublet signal to 146.37 ppm ($J = 16.01$ Hz), and the C_2 singlet to 135.86 ppm. These peaks compare to 137.20 ppm ($J = 12.00$ Hz) and 128.53 ppm for the same carbon atoms in PPh_3 .

The ^{31}P NMR spectrum of (**5**) has a single peak at -4.21 ppm, a chemical shift that is consistent with P(III) type compounds. Infrared spectroscopy was also employed to confirm the presence of the aldehyde carbonyl group, which gave a characteristic $\nu(\text{C}=\text{O})$ peak at 1707 cm^{-1} .

2.2 Schemes for the synthesis of phosphinoporphyryns.

Now that the desired starting materials are available, utilisation of the Wittig reaction should yield the desired phosphinoporphyryn linked *via* the vinylic bridge, and eventually the complexed phosphinoporphyryn (see scheme 2.1).



Scheme 2.1

The synthesis of a phosphinoporphyrin.

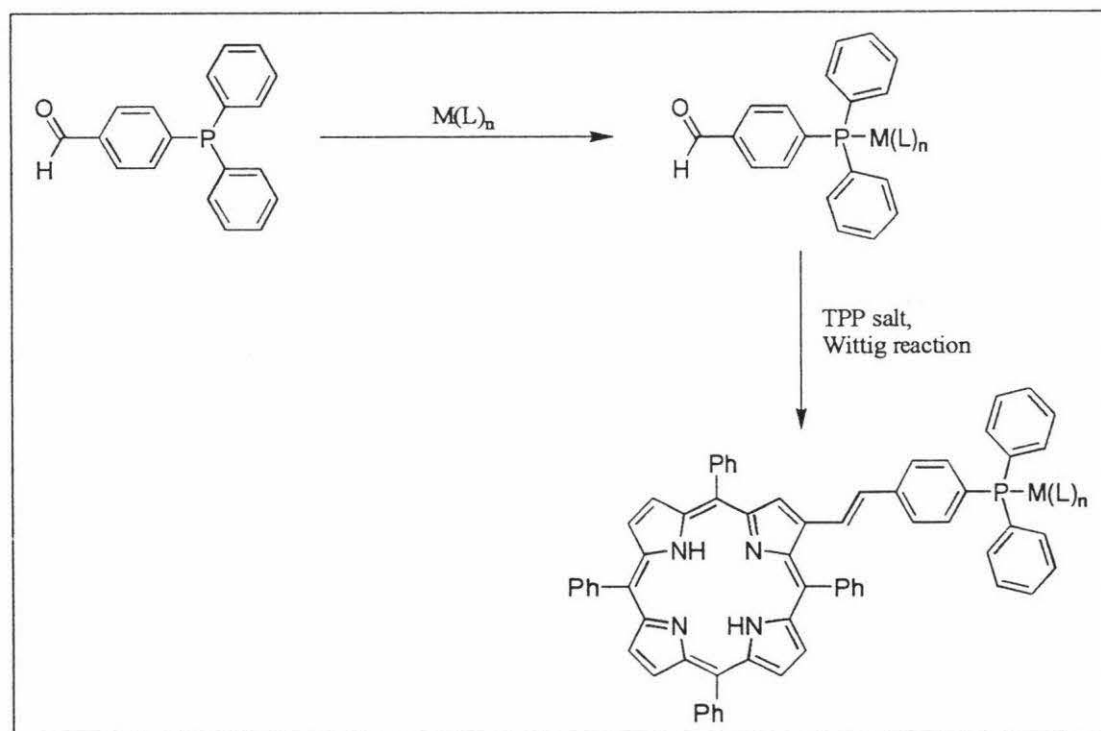
This phosphinoporphyrin (6) is an important target molecule because it will provide the perfect starting material or precursor for the complexation reaction.

Phosphinoporphyrin (6) was synthesised by the reaction of TPP phosphonium salt (1) with an excess of 4-PCHO (5) under standard Wittig conditions. Analysis of the crude product by ^1H NMR indicated a *cis/trans* mixture of (6), in a ratio of $\sim 1:15$. TLC analysis (1:1 $\text{CH}_2\text{Cl}_2/n$ -hexane) showed the appearance of a streaky spot ($R_f = 0.69$) plus some remaining starting material. Purification by column chromatography using 1:1 CH_2Cl_2 /hexane as the eluent resulted in the elution and isolation of the product of oxidation, (7). This was confirmed by ^{31}P NMR with a resonance at a chemical shift characteristic for P(V) being observed ($\delta = 29.60$ ppm). Changing the reaction solvent from CH_2Cl_2 to toluene allowed temperatures of $\sim 110^\circ\text{C}$ to be reached, resulting in the exclusive formation of the thermodynamically favoured *trans* product. Purification by column chromatography was avoided in an effort to minimise oxidation of the product, so recrystallisation from CHCl_3 /ethanol was employed instead. However, analysis of the ^{31}P NMR indicated that partial oxidation had

occurred with only $\frac{1}{4}$ of the isolated material being (6). The remainder was identified as the product of oxidation, (7).

Oxidation in phosphinoporphyrins at the phosphorus centre has been reported previously. Märkl *et al.*⁷ found that their phosphinoporphyrin (see Chapter One figure 1.12, left) underwent autooxidation in solution under atmospheric conditions. Märkl *et al.* suggested this autocatalysed oxidation by the porphyrin system could be due to intramolecular or intermolecular photoinduced activation of oxygen in air, as triphenylphosphine has been shown to rapidly oxidise in air by the presence of catalytic amounts of *meso*-TPP under the same conditions.

The air oxidation of phosphinoporphyrin (6) was problematic and therefore an alternative route was pursued. Reactions of transition metal complexes of (5) were investigated. Complexing (5) before the Wittig reaction will prevent reactions with oxygen, resulting in the desired complexed phosphinoporphyrin (see scheme 2.2).



Scheme 2.2

Modified scheme for the synthesis of a phosphinoporphyrin.

By using this method, a wide variety of metal complexes and their corresponding complexed phosphinoporphyryns will be synthesised. The following section will give details of the types of complexes synthesised during this project.

2.3 Complexes of 4-(diphenylphosphino)benzaldehyde.

A brief review of the literature revealed very few complexes of 2, 3 or 4-(diphenylphosphino)benzaldehyde have been reported. In fact, only two complexes of 4-(diphenylphosphino)benzaldehyde have been described in the literature. These two compounds by Ainscough *et al.*⁸ include molybdenum pentacarbonyl and tungsten pentacarbonyl derivatives.

2.3.1 Gold phosphine-aldehyde.

For simplicity, gold was chosen for the first attempt at complexing 4-PCHO (**5**) (see figure 2.4). Chloro(tetrahydrothiophene)gold(I) (**8**) was synthesised from $\text{H}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ and SC_4H_8 according to the method of Uson *et al.*⁹ Equal mole equivalents of (**8**) and (**5**) were stirred in CH_2Cl_2 at room temperature under an inert atmosphere, followed by purification by flash column chromatography to yield the desired complex, (**9**), as a relatively soluble white solid in 58% yield.

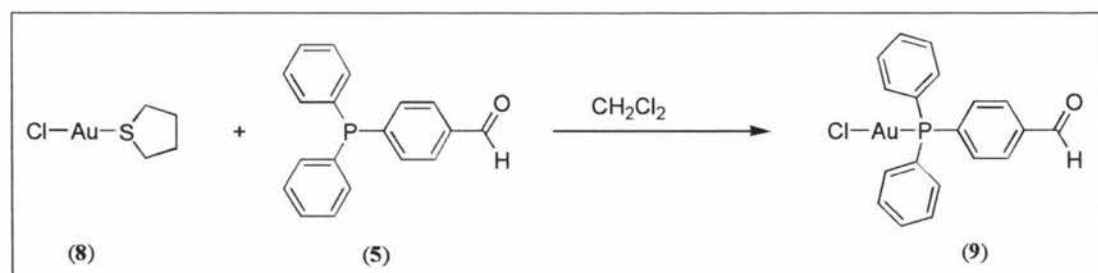


Figure 2.4

Synthesis of a gold phosphine-aldehyde.

The ^1H NMR spectrum of (**9**) (see figure 2.5) has a similar pattern to the free ligand (**5**). However, there are some subtle changes. For example, the aldehyde resonance for (**9**) has shifted downfield slightly to 10.09 ppm (10.01 ppm for (**5**)).

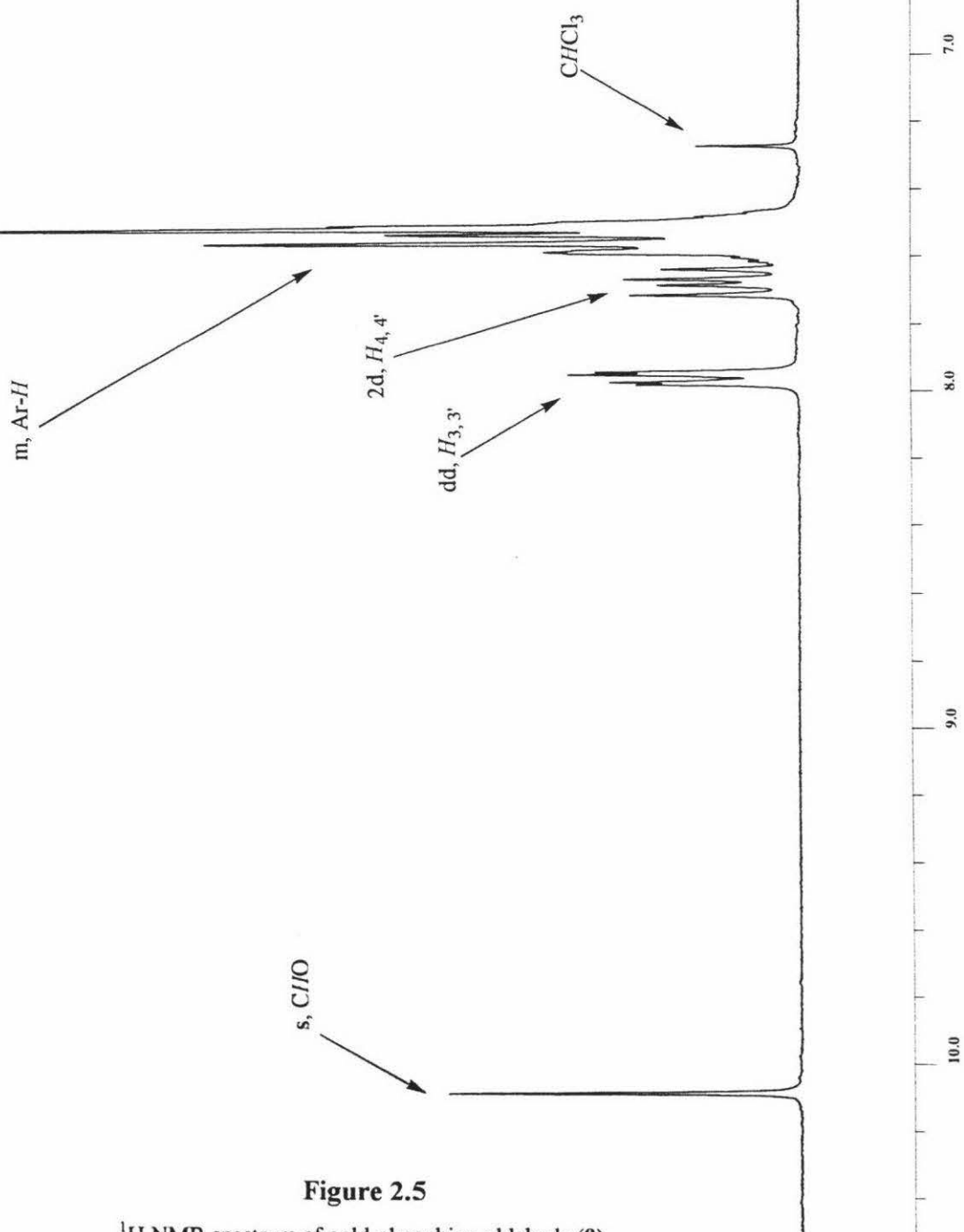
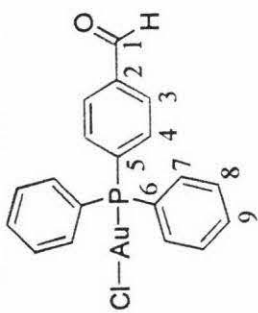


Figure 2.5

^1H NMR spectrum of gold phosphine-aldehyde (9).

The doublet of doublets belonging to the H_{3,3'} protons have also shifted downfield, from 7.82 ppm to 7.96 ppm, however the magnitude of the coupling constants remains more or less the same. A new feature is the appearance of a two partially overlapping doublet signals at 7.66 ppm ($J = 12.75$ Hz), and 7.69 ppm ($J = 12.75$ Hz). These two signals integrate for two protons and are assigned to the H_{4,4'} protons, which have shifted downfield on coordination of the gold. Previously, these resonances were obscured by the signal of the remaining phenyl protons, which have now shifted slightly downfield by 0.15 ppm, and appear as multiplet signal at 7.48-7.58 ppm.

The ¹³C NMR spectrum of (9) is also more or less the same as that of (5). Generally, most of the peaks have shifted by only 1-2 ppm on coordination of the gold, however there are two notable exceptions. The resonances for the carbons closest to the phosphorus atom, C₅ and C₆, experience quite large changes, as upon coordination, the C₅ signal shifts from 146.37 ppm to 135.93 ppm with an increase in coupling constant from 16.00 Hz to 58.03 Hz. Similarly, the C₆ carbon signal shifts upfield from 135.65 ppm to 127.50 ppm with an increase in coupling constant from 10.00 Hz to 63.04 Hz.

The phosphorus signal in the ³¹P NMR spectrum also changes upon coordination of the gold, with an expected downfield shift occurring from -4.21 ppm to 33.46 ppm. Infrared spectroscopy was also acquired to confirm the presence of the aldehyde functional group, and high-resolution mass spectrometry was used to support the identity of the product.

2.3.2 Ruthenium phosphine-aldehyde.

The second transition metal to be coordinated to 4-PCHO was ruthenium. Benzeneruthenium(II) chloride dimer was prepared from RuCl₃·3H₂O according to the procedure of Bennett.¹⁰ This precursor was then mixed in CH₂Cl₂ with two equivalents of (5) and stirred at room temperature under an inert atmosphere. Recrystallisation from CH₂Cl₂/ethanol afforded the desired complex, (10), as a rust coloured powder in 96% yield (see figure 2.6). This compound is soluble in chlorinated solvents, and is air stable.

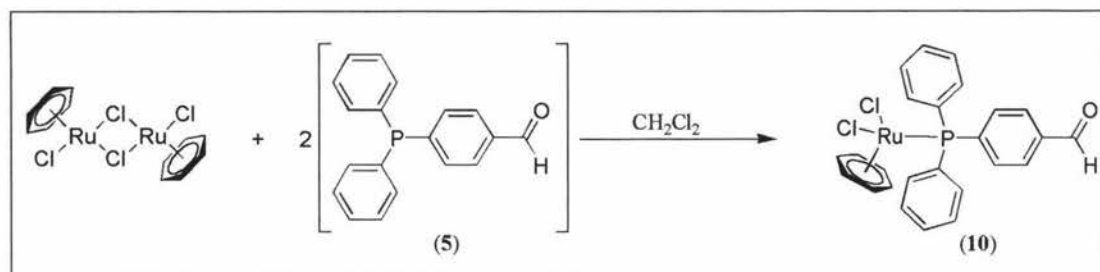


Figure 2.6.

Synthesis of ruthenium phosphine-aldehyde.

The ¹H NMR spectrum of (10) follows the same general pattern to that of the gold complex (9). Major differences include the signals belonging to the H_{3,3'} and H_{4,4'} protons both appearing as multiplets rather than as clear doublet of doublets. Also, a new singlet peak at 5.45 ppm appears, and is assigned to the equivalent η⁶-C₆H₆ protons. The ¹³C NMR of (10) is also more or less the same as (9), but the shifts are of smaller magnitude. Again, the carbons closest to the phosphorus, C₅ and C₆, are affected the most on coordination of the metal. The C₅ doublet signal appears at 139.66 ppm (*J* = 44.02 Hz) and the C₆ signal at 132.62 ppm (*J* = 47.03 Hz). The appearance of a new upfield signal at 89.30 ppm (*J* = 4.00 Hz) is observed, and is assigned to the equivalent η⁶-C₆H₆ carbons.

The ³¹P NMR shows a downfield shift similar to that of (9), with the new signal shifting from -4.21 ppm to 27.96 ppm. Infrared spectroscopy was also acquired to confirm the presence of the aldehyde functional group, and high-resolution mass spectrometry was used to support the identity of the product, giving a very accurate mass reading for the M⁺ ion.

2.3.3 Tungsten phosphine-aldehyde.

Ainscough *et al.*⁸ have published the synthesis of [W(CO)₅(4-PCHO)] (11), and this methodology was utilised to prepare (11). Irradiation of W(CO)₆ in THF by a mercury lamp followed by addition of (5) yielded the crude product. Purification by flash column chromatography followed by recrystallisation from CH₂Cl₂/*n*-hexane then afforded (11) as a pale yellow solid in 49% yield. This compound is most soluble in benzene and chlorinated solvents, and displays decomposition in acidic conditions.

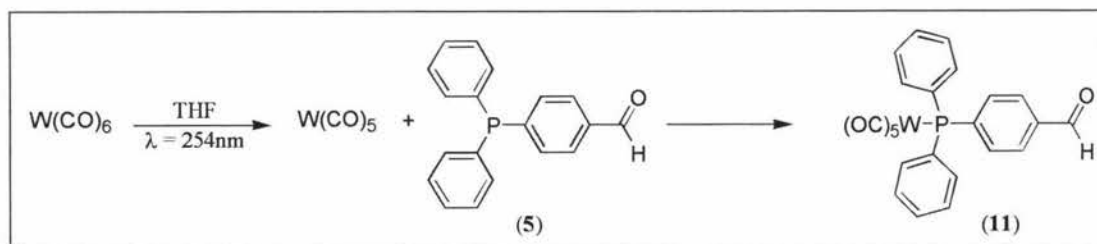


Figure 2.7.

Synthesis of tungsten phosphine-aldehyde.

As expected, the ^1H NMR of (11) followed the same general pattern as the previous phosphine complexes; hence characterisation was relatively straightforward. The ^{13}C NMR spectrum was similar to that of (9), however, the C_5 and C_6 signals appear downfield by approximately 4.00 and 7.00 ppm respectively. The coupling constants are also smaller, both by about 20.00 Hz. Two new downfield doublet signals appear at 197.32 ppm ($J = 7.01$ Hz) and 198.84 ppm ($J = 22.01$ Hz) respectively, and are assigned to the four equivalent *cis* carbonyls and the single *trans* carbonyl.

The ^{31}P NMR differs from the previous phosphine complexes as ^{183}W - ^{31}P coupling is observed. This triplet signal appears at 22.26 ppm ($J = 123.05$ Hz), and is upfield from the resonances of the ruthenium complex (27.96 ppm) and the gold complex (33.46 ppm). Infrared spectroscopy was used to confirm the presence of the aldehyde and carbon monoxide functional groups, and high-resolution mass spectrometry was used to support the identity of the product, giving a very accurate mass reading.

2.3.4 Ruthenium bis(phosphine-aldehyde) complex.

A publication by Anderson *et al.*¹¹ outlines the synthesis and complexation of the polymeric $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ compound. Complexation of this polymer with a variety of functionalised bipyridine ligands proved successful. Therefore coordination of 4-PCHO should also be successful. Once $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ was obtained, reaction with two equivalents of 4-PCHO (5) in refluxing methanol afforded the methoxy-protected product. Acid catalysed deprotection followed by recrystallisation from CH_2Cl_2 /ethanol yielded $\text{Ru}(4\text{-PCHO})_2$, (12), as a pale yellow solid in 59% overall yield (see figure 2.8).

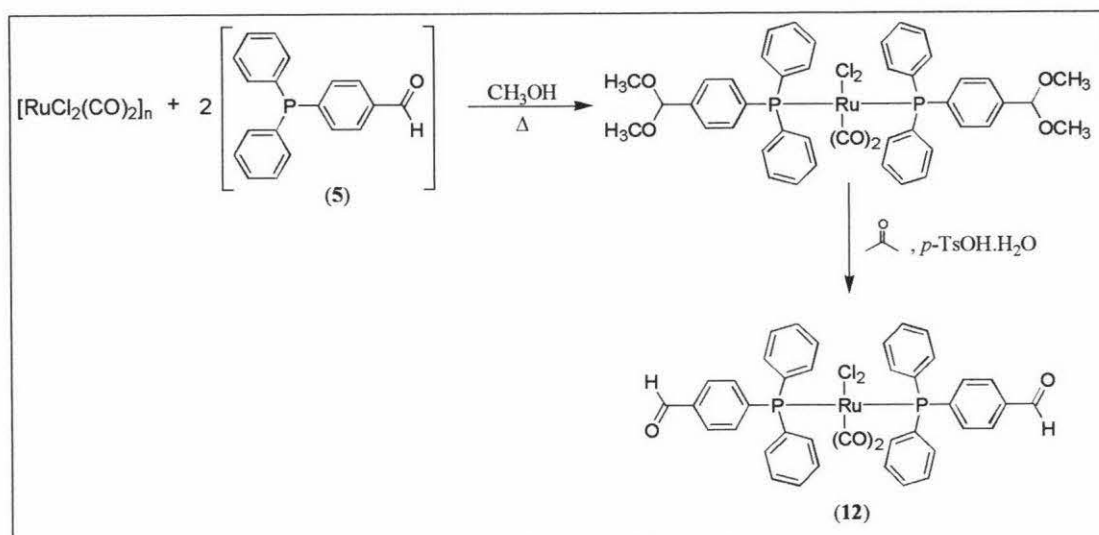


Figure 2.8

Synthesis of ruthenium bis(phosphine-aldehyde) complex.

The ^1H NMR spectrum of (12) was of similar pattern to that of the $\text{Ru}(4\text{-PCHO})$ (10), but the signals for the aromatic protons have shifted downfield by approximately 0.20 ppm. Similarly, the ^{13}C NMR spectrum of (12) was also comparable to that of (10). The main difference for (12) is that due to the *trans* arrangement of the phosphines around the ruthenium centre, the signals for the ipso carbons (C_5 and C_6) are split into “virtual triplets” at 138.09 ppm ($J = 23.01$ Hz) and 130.83 ppm ($J = 24.01$ Hz) respectively.

The ^{31}P NMR spectrum shows a single peak at 18.40 ppm, which is approximately 10 ppm upfield from the signal observed from the $\text{Au}(4\text{-PCHO})$ and $\text{Ru}(4\text{-PCHO})$ complexes. Infrared spectroscopy was utilised to confirm the presence of the aldehyde and metal coordinated carbonyl groups, and high-resolution mass spectrometry also supported the proposed characterisation, with an accurate mass reading.

2.3.5 Platinum bis(phosphine-aldehyde) complex.

A platinum complex, bis(benzonitrile)dichloroplatinum (II), was chosen to coordinate to 4-PCHO, which should also yield a bis-phosphine product similar to that of (12). A *cis/trans* mixture of the platinum complex was stirred in CH_2Cl_2 with two equivalents of 4-PCHO to yield a *cis/trans* mixture of $\text{PtCl}_2(4\text{-PCHO})_2$. Separation of the isomers was achieved *via* column chromatography, affording *cis*- $\text{PtCl}_2(4\text{-PCHO})_2$ (13a) as a

cream coloured powder (17%), and *trans*-PtCl₂(4-PCHO)₂ (**13b**) as a white powder (39%) (see figure 2.9). Both compounds are air stable, and soluble in chlorinated solvents, however, (**13b**) is sparingly soluble in deuterated chlorinated solvents.

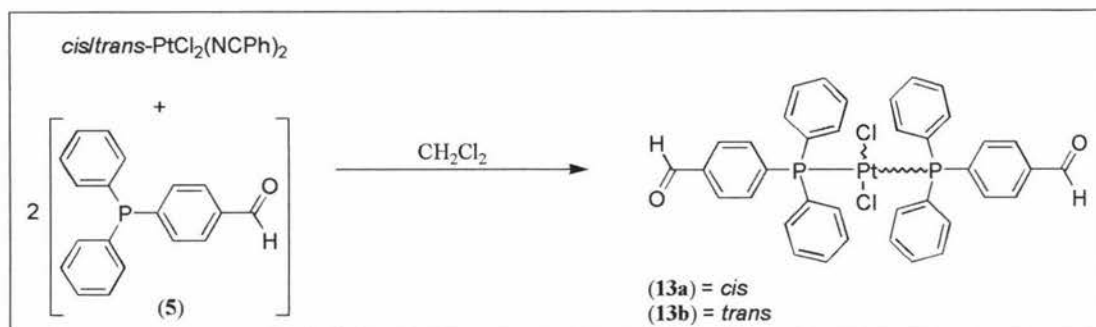


Figure 2.9

Synthesis of platinum bis(phosphine-aldehyde) complex.

Confirmation of the identities of the *cis* and *trans* isomers was provided by analysis of the ¹³C NMR and ³¹P NMR spectra. For the ¹³C NMR of (**13b**), the *trans* arrangement of the phosphines around the platinum splits the signals for carbons closest to the phosphorus into “virtual triplets” in a similar manner to Ru(CO)₂Cl₂(4-PCHO)₂. In the ³¹P NMR, the *trans*-isomer was easily recognised by the large ³¹P-¹⁹⁵Pt splitting observed for the phosphorus signal. For (**13b**), a triplet signal at 13.85 ppm with a coupling constant of 1836 Hz was observed.

2.4 Summary.

The synthesis of 4-PCHO (**5**) was first published by Schiemenz in 1966,³ then revised and optimised in 1973 by Schiemenz and Kaack.⁴ The synthesis of a novel phosphinoporphyrin (**6**) *via* the Wittig reaction of 4-PCHO with TPP phosphonium salt (**1**) was severely limited due to oxidation. To avoid this problem, complexation of 4-PCHO was employed. By using this new method, a wide variety of complexed 4-PCHO compounds were successfully prepared, including gold, ruthenium, tungsten, and platinum complexes. In all these examples, coordination of the metal has a definite influence on the environment of the phenyl protons. The ¹H NMR shows that the signals of these protons have shifted downfield by at least 0.15 ppm, with the H_{4,4'}

signal shifting by at least 0.30 ppm. In contrast, coordination of the metal has little affect on the carbon environment. Only the *ipso* carbons are significantly affected, as their signals are shifted downfield by 5-10 ppm with a dramatic increase in ^{13}C - ^{31}P coupling of 20-40 Hz.

The development of this new procedure has led to the simple and efficient synthesis of key starting materials for the Wittig reaction, which is the next stage for this research project; the synthesis of complexed phosphinoporphyrins.

2.5 Experimental procedures.

2.5.1 General methods

When required, solvents and reagents were dried according to the methods of Perrin and Amerego.¹²

Column chromatography was carried out using distilled lab grade solvents on columns packed with silica gel (0.032-0.063 mm, Merck Kieselgel 60). Thin layer chromatography (TLC) was performed using pre-coated, aluminium backed silica plates (Riedel de-Haën, Kieselgel 60F₂₅₄).

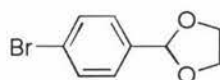
^1H nuclear magnetic resonance spectroscopy was performed at 270.20 MHz using a JEOL JMN-GX270 FT-NMR spectrometer. The data is expressed in parts per million (ppm) downfield from an internal standard, tetramethylsilane (TMS), and referenced to CHCl_3 ($\delta = 7.270$ ppm). ^{13}C nuclear magnetic resonance spectroscopy was performed at 68.06 MHz using a JEOL JMN-GX270 FT-NMR spectrometer with proton decoupling. The data is expressed in ppm and referenced to CDCl_3 ($\delta = 77.00$ ppm), except for compound (**11**), which is referenced to C_6D_6 ($\delta = 128.00$ ppm). ^{31}P nuclear magnetic resonance spectroscopy was performed at 109.38 MHz using a JEOL JMN-GX270 FT-NMR spectrometer with proton decoupling. The data is expressed in ppm downfield from an external standard, 85% H_3PO_4 .

Infrared spectroscopy was run on a Perkin-Elmer PARAGON 1000 FT-IR spectrometer with the samples as Nujol mulls. The data is reported in wavenumbers (cm^{-1}).

Mass spectra were recorded using a Varian VG70-250S double focusing magnetic sector mass spectrometer. Samples were analysed by fast atom bombardment in the positive mode (FAB^+) for high-resolution mass spectra (HRMS), and were supported in a *p*-nitrobenzyl alcohol matrix.

Electronic absorption spectra were obtained using a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer. Band positions are expressed in wavelength (nm), with the corresponding log molar absorptivity coefficient (ϵ).

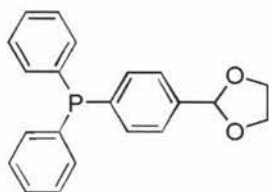
2.5.2 Experimental section



(2) *2-(4-bromophenyl)-1,3-dioxolane*

4-bromobenzaldehyde (25 g, 135 mmol) was reacted with ethylene glycol (12.50 g, 206 mmol) under the conditions described by Hoots *et al.*⁶ Compound (2) was isolated as colourless crystals in 92% yield (literature yield⁶ 93%).

¹H NMR (270 MHz, CDCl_3) δ /ppm: 4.00-4.05 (m, 2H, $-\text{CH}_2-$), 4.08-4.15 (m, 2H, $-\text{CH}_2-$), 5.77 (s, 1H, $-\text{CH}-$), 7.34-7.38 (m, 2H, Ar-H), 7.51-7.54 (m, 2H, Ar-H).



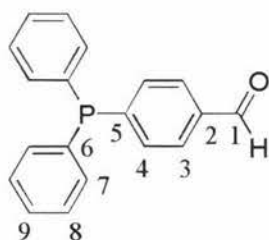
(4) *[4-(1,3-Dioxolan-2-yl)phenyl]diphenylphosphine*

Compound (4) was synthesised using a modified procedure of Hoots *et al.*⁶ Mg turnings (1.07 g, 44 mmol) and dry THF (100 mL) were stirred under and inert

atmosphere before the drop-wise addition of (2) (10 g, 43.7 mmol) in 5 mL THF. A single crystal of I₂ was added, and then the solution heated at reflux temperature until all the Mg had dissolved, forming (3) *in vitro*. Once cooled in an ice bath, a solution of freshly distilled Ph₂PCl (8.10 mL, 45 mmol) in 10 mL THF was added drop-wise to the stirred Grignard solution. After the addition was complete, the reaction was heated at reflux temperature overnight. After cooling to room temperature, the reaction was quenched with 10% NH₄Cl (50 mL), then the organic phase was extracted with saturated NaCl. The organic phase was then dried over MgSO₄, and then reduced in volume on a rotary evaporator. Purification by column chromatography eluting with CH₂Cl₂ removed the oxide impurity, and the solution was then reduced in volume to a yellow oil after removing the solvent. Recrystallisation from 95% ethanol then afforded (4) as a white solid, in 60% yield.

¹H NMR (270 MHz, CDCl₃) δ/ppm: 3.97-4.02 (m, 2H, -CH₂-), 4.08-4.11 (m, 2H, -CH₂-), 5.83 (s, 1H, -CH-), 7.36-7.44 (m, 12H, Ar-H), 7.51-7.54 (m, 2H, Ar-H).

³¹P NMR (109MHz, CH₂Cl₂) δ/ppm: -5.57 (s, 1P, Ar₃P), 29.65 (s, 1P, Ar₃P=O).



(5) 4-(diphenylphosphino)benzaldehyde

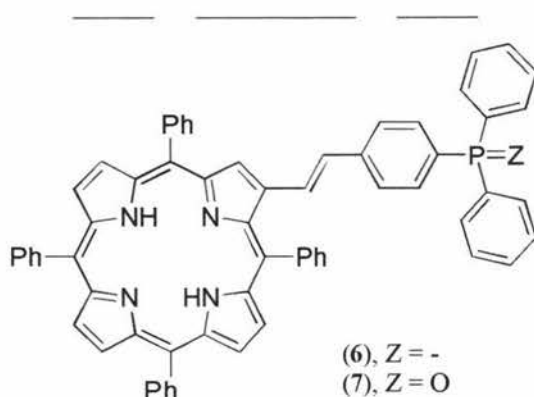
Compound (5) was synthesised using a modified procedure of Hoots *et al.*⁶ Compound (4) (8.76 g, 26.2 mmol) was dissolved in dry acetone (100 mL) under an inert atmosphere before the addition of *p*-toluenesulphonic acid monohydrate (250 mg, 1.31 mmol). After refluxing overnight, the solution was diluted with H₂O (25 mL) and the product extracted with CH₂Cl₂. After drying over MgSO₄, the solvent was removed *via* rotary evaporator and the resulting yellow oil was recrystallised from 95% ethanol to afford (5), as a pale yellow solid in 51% yield.

$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : 7.31-7.45 (m, 12H, Ar-*H*), 7.82 (dd, $^3J = 8.24$ Hz, $^4J = 1.53$ Hz, 2H, Ar- $H_{3,3'}$), 10.01 (s, 1H, -CHO).

$^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ/ppm : 128.66 (d, $^3J_{\text{C-P}} = 7.00$ Hz, C_8), 129.21 (s, C_9), 131.93 (d, $^3J_{\text{C-P}} = 10.01$ Hz, C_3), 133.40 (d, $^2J_{\text{C-P}} = 18.07$ Hz, C_7), 133.93 (d, $^2J_{\text{C-P}} = 20.01$ Hz, C_4), 135.65 (d, $^1J_{\text{C-P}} = 10.00$ Hz, C_6), 135.86 (s, C_2), 146.37 (d, $^1J_{\text{C-P}} = 16.01$ Hz, C_5), 191.76 (s, C_1).

$^{31}\text{P NMR}$ (109 MHz, CDCl_3) δ/ppm : -4.21 (s, 1P, Ar_3P).

IR (Nujol mull) cm^{-1} : 1707 (m) $\nu(\text{C}=\text{O})$.



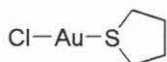
(6) and (7) Phosphinoporphyrin.

4-PCHO (**5**) (47.5 mg, 163.6 μmol) and TPP salt (**1**) (100 mg, 108 μmol) were heated at reflux temperature in dry toluene (10mL) for 10 minutes before the addition of DBU (80 μL , 535 μmol). After 30 minutes, the reaction was stopped, the solvent removed *via* a rotary evaporator, and the resulting residue recrystallised from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, giving a purple powder (76.5 mg, 84.9 μmol , 79%). This powder was found to be a mixture of both the desired product (**6**), and the phosphine oxide product (**7**) in approximately a 1:3 ratio.

$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : -2.52 (br s, 2H, N-*H*), 7.15 (d, $^3J = 16.17$ Hz, 1H, H_{vinyllic}), 7.36-7.39 (m, 3H, phosphine Ar-*H* + H_{vinyllic}), 7.52-7.67 (m, 10H, phosphine Ar-*H*), 7.70-7.84 (m, 14H, porphyrin Ar- $H_{\text{meta, para}}$ + phosphine Ar-*H*), 8.21-8.31 (m, 8H, porphyrin Ar- H_{ortho}), 8.78-8.89 (m, 6H, $H_{\beta\text{-pyrrolic}}$), 9.08 (s, 1H, $H_{\beta\text{-pyrrolic}}$).

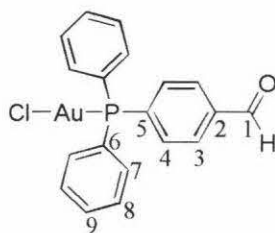
$^{31}\text{P NMR}$ (109 MHz, CHCl_3) δ/ppm : -5.36 (s, TPPAr_3P), 29.60 (s, $\text{TPPAr}_3\text{P}=\text{O}$).

HRMS (positive FAB) m/z : M^+ for $\text{C}_{64}\text{H}_{45}\text{N}_4\text{OP}$: calculated $\text{M}^+ = 916.3331$, observed $\text{M}^+ = 916.3328$.



(8) chloro(tetrahydrothiophene) gold(I).

AuCl(SC₄H₈) was prepared by the reaction of hydrogen tetrachloroaurate(III) (980.8 mg, 2.38 mmol) with tetrahydrothiophene (500 mg, 5.67 mmol) following the procedure of Uson *et al.*⁹ The yield for this reaction was 657 mg, 86% (lit. 95%).



(9) Gold phosphine-aldehyde.

AuCl(SC₄H₈) (**8**) (63.9 mg, 199.3 μ mol) and 4-PCHO (55.8 mg, 192.2 μ mol) were dissolved in CH₂Cl₂ (10 mL) and stirred at room temperature. The reaction was monitored by TLC (CH₂Cl₂, R_f = 0.50) and after 90 minutes the reaction mixture was purified by normal phase flash column chromatography eluting with CH₂Cl₂. After removing the solvent from this fraction *via* a rotary evaporator, the resulting residue was then recrystallised from CH₂Cl₂/ethanol, forming (**9**) as a white precipitate (58 mg, 58%).

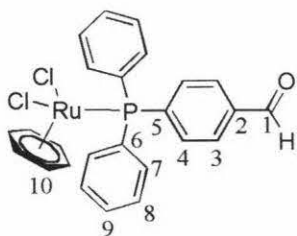
¹H NMR (270MHz, CDCl₃) δ /ppm: 7.48-7.58 (m, 10H, Ar-H), 7.66 (d, ³J = 12.75 Hz, 1H, Ar-H_{4 or 4'}), 7.69 (d, ³J = 12.75 Hz, 1H, Ar-H_{4 or 4'}), 7.94-7.98 (dd, ³J = 8.24 Hz, ⁴J = 1.98 Hz, 2H, Ar-H_{3,3'}), 10.09 (s, 1H, -CHO).

¹³C NMR (68 MHz, CDCl₃) δ /ppm: 127.50 (d, ¹J_{C-P} = 63.04 Hz, C₆), 129.40 (d, ³J_{C-P} = 12.01 Hz, C₃/C₈), 129.71 (d, ³J_{C-P} = 12.01 Hz, C₃/C₈), 132.36 (d, ⁴J_{C-P} = 3.00 Hz, C₉), 134.14 (d, ²J_{C-P} = 14.01 Hz, C₄/C₇), 134.39 (d, ²J_{C-P} = 14.01 Hz, C₄/C₇), 135.93 (d, ¹J_{C-P} = 58.03 Hz, C₅), 138.21 (d, ⁴J_{C-P} = 2.00 Hz, C₂), 190.92 (s, C₁).

³¹P NMR (109 MHz, CHCl₃) δ /ppm: 33.46 (s, Ar₃P-Au)

IR (Nujol mull) cm⁻¹: 1703 (s) ν (C=O).

HRMS (positive FAB) m/z : M^+ for $C_{19}H_{15}AuClOP$: calculated $M^+ = 522.0214$, observed $M^+ = 522.0252$.



(10) Ruthenium phosphine-aldehyde.

Benzeneruthenium(II) chloride dimer (75 mg, 149.9 μmol), and 4-PCHO (99 mg, 341 μmol) were mixed in dry CH_2Cl_2 (20 mL) and stirred at room temperature. The initial rust coloured solution gradually changed to a dark crimson colour, and after 90 minutes the reaction was stopped. The solvent was then removed *via* rotary evaporator, and the residue recrystallised in CH_2Cl_2 /ethanol to give (11) as a dark rust coloured powder (155 mg, 96%).

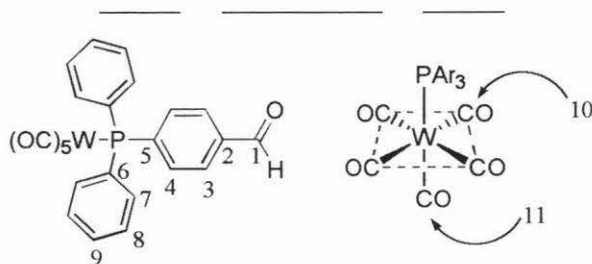
$^1\text{H NMR}$ (270MHz, CDCl_3) δ/ppm : 5.45 (s, 6H, $\eta^6\text{-C}_6\text{H}_6$), 7.42-7.54 (m, 7H, Ar-H), 7.71-7.82 (m, 5H, Ar-H), 7.92-7.99 (m, 2H, Ar- $H_{3,3'}$), 10.00 (s, 1H, -CHO).

$^{13}\text{C NMR}$ (68MHz, CDCl_3) δ/ppm : 89.30 (d, $^2J_{\text{C-P}} = 4.00$ Hz, C_{10}), 128.47 (d, $^3J_{\text{C-P}} = 10.00$ Hz, C_3 and C_8), 130.91 (s, C_9), 132.62 (d, $^1J_{\text{C-P}} = 47.03$ Hz, C_6), 134.01 (d, $^2J_{\text{C-P}} = 10.00$ Hz, C_4/C_7), 134.68 (d, $^2J_{\text{C-P}} = 9.01$ Hz, C_4/C_7), 136.81 (s, C_2), 139.66 (d, $^1J_{\text{C-P}} = 44.02$ Hz, C_5), 191.70 (s, C_1).

$^{31}\text{P NMR}$ (109MHz, CHCl_3) δ/ppm : 27.96 (s, $\text{Ar}_3\text{P-Ru}$).

IR (Nujol mull) cm^{-1} : 1698 (s) $\nu(\text{C=O})$.

HRMS (positive FAB) m/z : M^+ for $\text{C}_{25}\text{H}_{21}\text{Cl}_2\text{OPRu}$: calculated $M^+ = 539.9751$, observed $M^+ = 539.9754$.



(11) *Tungsten phosphine-aldehyde.*

$W(CO)_6$ (110 mg, 313 μmol) was dissolved in THF (25 mL) and the resulting clear solution irradiated with a mercury lamp (254nm) for approximately 30 minutes. After ceasing irradiation, 4-PCHO (**5**) (100 mg, 344 μmol) was added to the resulting yellow solution and stirred for 30 minutes. After removing the solvent *via* a rotary evaporator, the residue was purified by normal phase flash chromatography eluting with CH_2Cl_2 . The product (**11**) was recrystallised from CH_2Cl_2/n -hexane, resulting in a pale yellow solid (overall yield 94 mg, 49%).

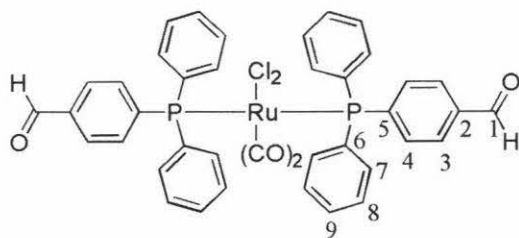
1H NMR (270 MHz, $CDCl_3$) δ /ppm: 7.46-7.50 (m, 10H, Ar-*H*), 7.59 (d, $^3J = 10.10$ Hz, 1H, Ar-*H*_{4 or 4'}), 7.62 (d, $^3J = 10.10$ Hz, 1H, Ar-*H*_{4 or 4'}), 7.94 (dd, $^3J = 8.57$ Hz, $^4J = 1.98$ Hz, 2H, Ar-*H*_{3,3'}), 10.07 (s, 1H, -CHO).

^{13}C NMR (68 MHz, C_6D_6) δ /ppm: 129.00 (d, $^3J_{C-P} = 10.01$ Hz, C₃/C₈), 129.37 (d, $^3J_{C-P} = 10.00$ Hz, C₃/C₈), 130.79 (s, C₉), 133.15 (d, $^2J_{C-P} = 6.01$ Hz, C₄/C₇), 133.29 (d, $^2J_{C-P} = 10.00$ Hz, C₄/C₇), 134.68 (d, $^1J_{C-P} = 42.02$ Hz, C₆), 137.54 (s, C₂), 142.22 (d, $^1J_{C-P} = 38.02$ Hz, C₅), 190.28 (s, C₁), 197.32 (d, $^2J_{C-P} = 7.01$ Hz, C₁₀), 198.84 (d, $^2J_{C-P} = 22.01$ Hz, C₁₁).

^{31}P NMR (109 MHz, C_6H_6) δ /ppm: 22.26 (t, $J_{P-W} = 123.05$ Hz, 1P, Ar₃P-W).

IR (Nujol mull) cm^{-1} : 2071 (m), 1939 (s), and 1915 (s) $\nu(C\equiv O)$, 1709 (m) $\nu(C=O)$.

HRMS (positive FAB) m/z : M^+ for $C_{24}H_{15}O_6PW$: calculated $M^+ = 614.0116$, observed $M^+ = 614.0121$.



(12) *Ruthenium bis(phosphine-aldehyde)*.

[Ru(CO)₂Cl₂]_n (29 mg, 127.2 μmol) and 4-PCHO (**5**) (106 mg, 365.1 μmol) were heated at reflux temperature in CH₃OH for approximately 20 minutes. During this time, the solution changed from a murky yellow to a transparent yellow colour. The solvent was then removed *via* rotary evaporator and the pale yellow residue recrystallised from CH₂Cl₂/ethanol, giving a mixture of (**12**) (minor product) and the methoxy-protected product as a sticky light yellow solid. This mixture was then dissolved in acetone (~15 mL) before *p*-TsOH.H₂O (~5 equivalents) was added. The reaction mixture was then heated at reflux temperature under N₂ and monitored by TLC (1 drop of CH₃OH + 8 mL CH₂Cl₂, R_f = 0.75), and after 60 minutes the reaction was deemed complete. After cooling to room temperature, the reaction was quenched by the addition of NEt₃ (~5 equivalents), then the solvent removed *via* rotary evaporator. The residue was then dissolved in CH₂Cl₂, filtered, and then recrystallised from CH₂Cl₂/ethanol, giving product (**12**) as a pale yellow solid (56.1 mg, 59%).

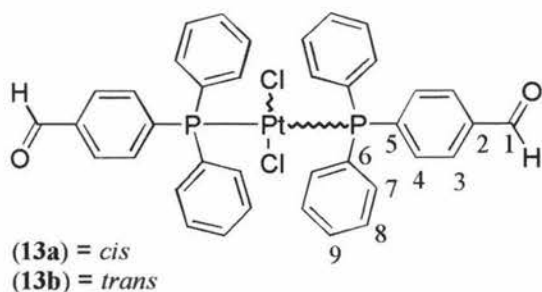
¹H NMR (270 MHz, CDCl₃) δ/ppm: 7.41-7.46 (m, ~14H, Ar-*H*), 7.87-7.94 (m, ~10H, Ar-*H*), 8.16-8.23 (m, 4H, Ar-*H*_{3,3'}), 10.04 (s, 2H, -CHO).

¹³C NMR (68 MHz, CDCl₃) δ/ppm: 128.51 (t, ³*J* = 5.01 Hz, C₃/C₈), 128.84 (t, ³*J* = 5.01 Hz, C₃/C₈), 130.83 (t, ¹*J* = 24.01 Hz, C₆), 130.99 (s, C₉), 133.96 (t, ²*J* = 6.01 Hz, C₄/C₇), 135.06 (t, ²*J* = 6.01 Hz, C₄/C₇), 137.12 (s, C₂), 138.09 (t, ¹*J* = 23.01 Hz, C₅), 191.57 (s, C₁).

³¹P NMR (109 MHz, CH₂Cl₂) δ/ppm: 18.40 (s, 2P, Ar₃P-Ru-PAr₃).

IR (Nujol mull) cm⁻¹: 1704 (m) ν(C=O), 1992 (m), 2056 (m) ν(C≡O).

HRMS (positive FAB) *m/z*: M⁺ for C₄₀H₃₀Cl₂O₄P₂Ru: calculated M⁺ = 808.0040, observed M⁺ = 800.0045.



(13) *Platinum bis(phosphine-aldehyde).*

A mixture of *cis* and *trans* bis(benzonitrile)dichloroplatinum (II) (100 mg, 211.8 μmol) and 4-PCHO (5) (129 mg, 444.4 μmol) were mixed in CH_2Cl_2 and stirred for 120 minutes. TLC analysis (CH_2Cl_2) indicated two products, $R_f = 0.43$, and $R_f = 0.00$, and these two products (13a) and (13b) were isolated by flash chromatography eluting with CH_2Cl_2 , then with 5% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$. The respective fractions were then reduced to dryness *via* a rotary evaporator, then the residue recrystallised from CH_2Cl_2 /ethanol, giving (13a) as a cream coloured powder (30.6 mg, 36.1 μmol , 17%) and (13b) as a white powder (70 mg, 82.7 μmol , 39%).

(13a)

$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : 7.45-7.60 (m, Ar-H)*, 7.72-7.86 (m, Ar-H)*, 10.03 (s, 2H, -CHO). * The optimum integrated value could not be determined due the presence of an inseparable phosphine impurity.

$^{13}\text{C NMR}$ (68MHz, CDCl_3) δ/ppm : 127.40 (d, $^1J_{\text{C-P}} = 29.02$ Hz, C_6), 128.49 (br s, C_3/C_8), 129.43 (br s, C_3/C_8), 131.06 (s, C_9), 132.36 (d, $^1J_{\text{C-P}} = 42.02$ Hz, C_5), 133.54 (app d, $J = 6.00$ Hz, C_4/C_7), 135.11 (app d, $J = 6.00$ Hz, C_4/C_7), 137.06 (s, C_2), 191.52 (s, C_1).

IR (Nujol mull) cm^{-1} : 1707 (m) $\nu(\text{C}=\text{O})$.

(13b)

$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : 7.20-7.26 (m, Ar-H)*, 7.39-7.68 (m, Ar-H)*, 9.98 (s, 2H, -CHO). * The optimum integrated value could not be determined due the presence of an inseparable phosphine impurity.

^{13}C NMR (68MHz, CDCl_3) δ/ppm : 128.26 (t, $J = 5.00$ Hz, C_3/C_8 and C_6^*), 131.43 (s, C_9), 134.53 (t, $J = 6.00$ Hz, C_4/C_7), 134.90 (t, $J = 6.00$ Hz, C_4/C_7 and C_5^*), 136.92 (s, C_2), 191.27 (s, C_1). * Peaks appear to be coincident.

^{31}P NMR (109MHz, CHCl_3) δ/ppm : 13.85 (t, $^1J_{\text{P-C}} = 1836$ Hz, 2P, $\text{Ar}_3\text{P-Pt-PAr}_3$).

IR (Nujol mull) cm^{-1} : 1702 (m) $\nu(\text{C=O})$.

2.6 References.

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Chapter Three

Metal complexes of phosphinoporphyrin conjugates

This chapter describes the synthesis and characterisation of novel complexed phosphine ligands functionalised *via* the vinylic linker group to the porphyrin moiety. The methodology developed utilises Wittig chemistry to react complexed phosphine-aldehydes synthesised in the previous chapter, with the TPP phosphonium salt (see scheme 2.2, page 21). Following this scheme should ensure the successful synthesis of the desired complexed phosphinoporphyrin conjugates.

To the best of the author's knowledge, the compounds described in this chapter are the first of their kind to be synthesised, especially since the porphyrin is functionalised *via* the vinylic bridge at the β -pyrrolic position. Similar compounds have been synthesised by Märkl *et al.*¹ (see figure 1.12, left), but their phosphinoporphyrin is functionalised directly at the *meso* position.

3.1 Synthesis of complexed phosphinoporphyrin conjugates.

3.1.1 Gold-phosphinoporphyrin.

Given that Au(4-PCHO) (**9**) was the first complexed phosphine-aldehyde synthesised in this project, it was also the first aldehyde to be used in the Wittig reaction with the TPP phosphonium salt (**1**). Equal mole equivalents of (**1**) and (**9**) were reacted under standard Wittig conditions with DBU as the base and CH₂Cl₂ as the solvent. Column chromatography using CH₂Cl₂ as the eluent gave (**14**) as an inseparable *cis/trans* mixture in a ratio of 1:4. Attempted thermal isomerisation by refluxing in CHCl₃ overnight improved the *cis/trans* ratio to 1:10. However, given that (**14**) appeared to be thermodynamically stable, the Wittig reaction was repeated using refluxing toluene as the solvent instead of CH₂Cl₂ (see figure 3.1). This change to a higher boiling point solvent resulted in the exclusive formation of the *trans* product.

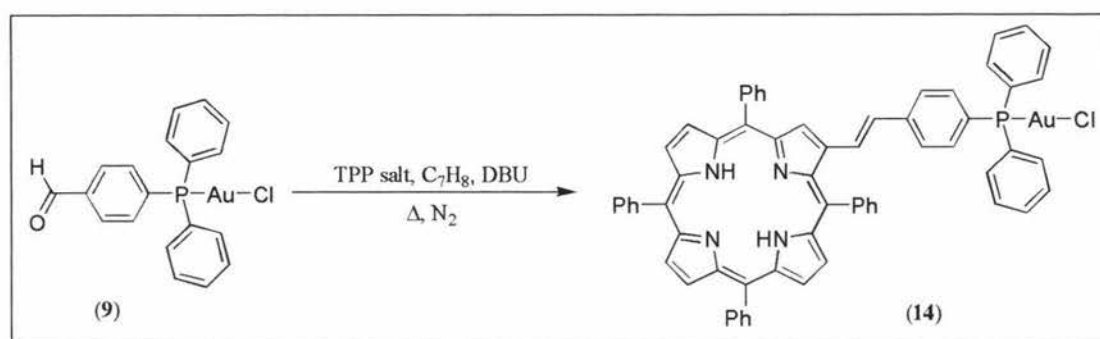


Figure 3.1

Synthesis of gold-phosphinoporphyrin.

Compound (14) was characterised by ^1H NMR (see figure 3.2), and was supported by ^{31}P NMR, high-resolution mass spectrometry, and UV-Vis spectrometry results. The ^1H NMR spectrum contains a distinctive broad singlet signal at -2.57 ppm corresponding to the two-shielded *N-H* protons in the porphyrin core. A doublet signal centred at 7.11 ppm corresponds to one of the protons of the *trans*-vinylic linker group. This peak is split into a doublet due to the strong three-bond coupling to its neighbouring vinylic proton. The coupling constant of this doublet is 16.18 Hz, which is indicative of a strong *trans*-vinylic couple. A doublet of doublets centred at 7.33 ppm ($^3J = 8.24$ Hz, $^4J = 2.14$ Hz) is assigned to the $\text{H}_{3,3'}$ protons, which have shifted upfield by 0.60 ppm when compared to the spectrum of the gold phosphine-aldehyde. A multiplet signal at 7.48 – 7.64 ppm integrating for 13 protons is assigned to the remaining vinylic proton, which itself is hidden by the multiplet signal of the remaining 12 phosphine protons. A new multiplet signal at 7.74 – 7.86 ppm integrating for 12 protons is assigned to the *meta* and *para* protons from the phenyl groups at the *meso*-position of the porphyrin. The remaining 8 *ortho* protons appear as a multiplet signal further downfield at 8.19 – 8.28 ppm, as these protons experience increased deshielding due to their proximity to the porphyrin core. A multiplet signal at 8.79 – 8.84 ppm corresponds to the six β -pyrrolic protons isolated from the vinylic substitution. The remaining β -pyrrolic proton directly beside the vinylic linker gives a single peak slightly further downfield at 9.03 ppm.

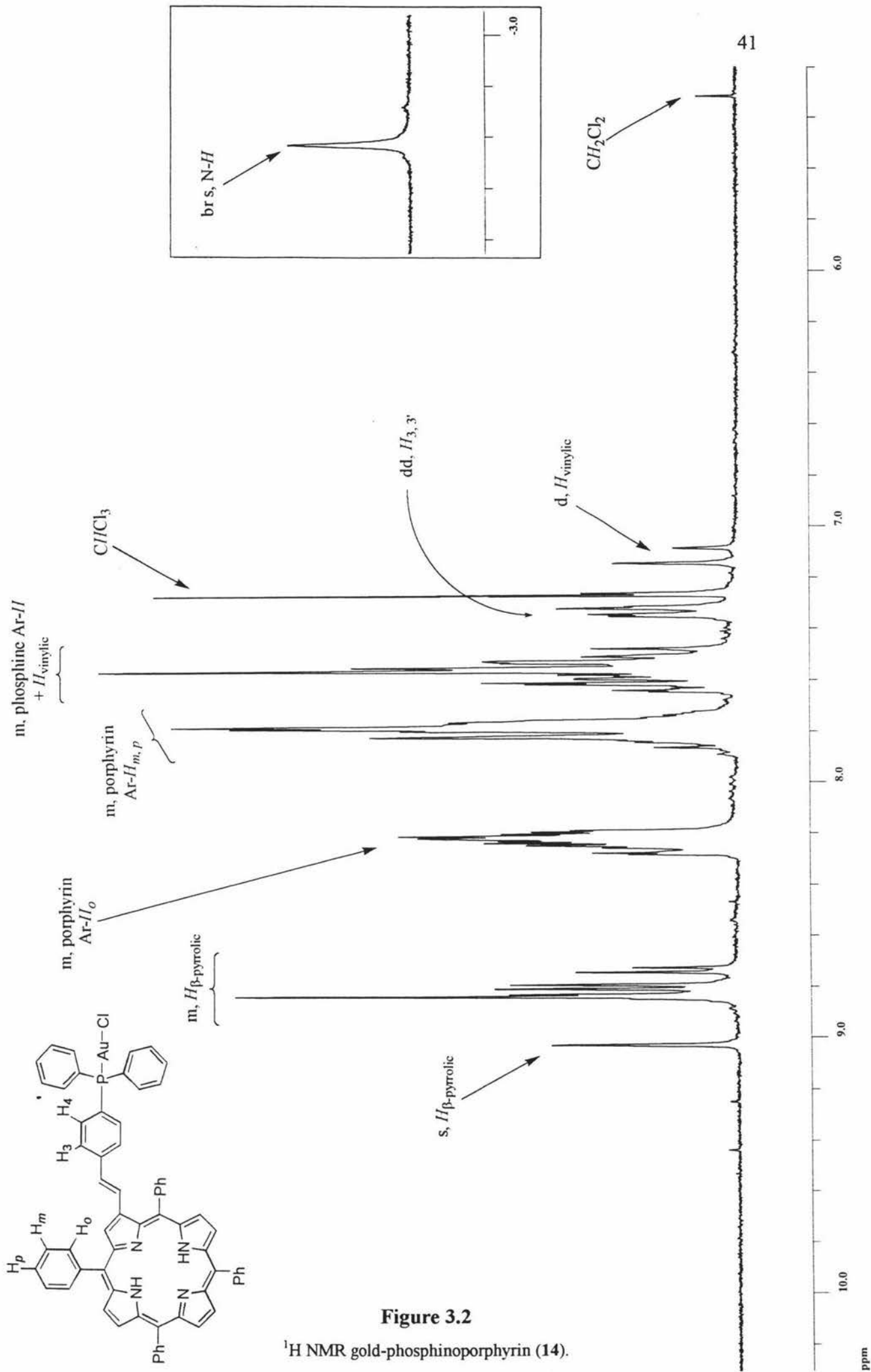


Figure 3.2

^1H NMR gold-phosphinoporphyrin (14).

As expected, the porphyrin has little effect on the environment of the phosphorus. The ^{31}P NMR spectrum of (14) gave a single peak at 32.68 ppm, which is consistent in comparison with the gold phosphine-aldehyde (33.46 ppm). The UV-Vis spectroscopy produced a spectrum typical of a free base porphyrin, with a large Soret band at 429 nm accompanied with four weaker Q bands at longer wavelengths. The Soret band recorded a molar extinction coefficient (ϵ) of over 180000. High-resolution mass spectrometry was also used to support the characterisation (as compound (14)) with an accurate mass reading.

3.1.2 Ruthenium-phosphinoporphyrin.

The second complexed phosphinoporphyrin to be synthesised was that of the ruthenium derivative (10). A slight excess of TPP phosphonium salt (1) and Ru(4-PCHO) (10) were reacted under standard Wittig conditions with DBU as the base and CH_2Cl_2 as the solvent. Column chromatography using 3% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ gave a *cis/trans* mixture of the desired product, (15), in a ratio of 1:10. Attempted thermal isomerisation by refluxing overnight in CHCl_3 failed, as the product decomposed under these conditions. However, optimised Wittig conditions were eventually achieved, using DBU as the base and refluxing CH_2Cl_2 as the solvent (see figure 3.3). Under these conditions the *trans* isomer predominates, and compound (15) was afforded as a purple powder in 36% yield.

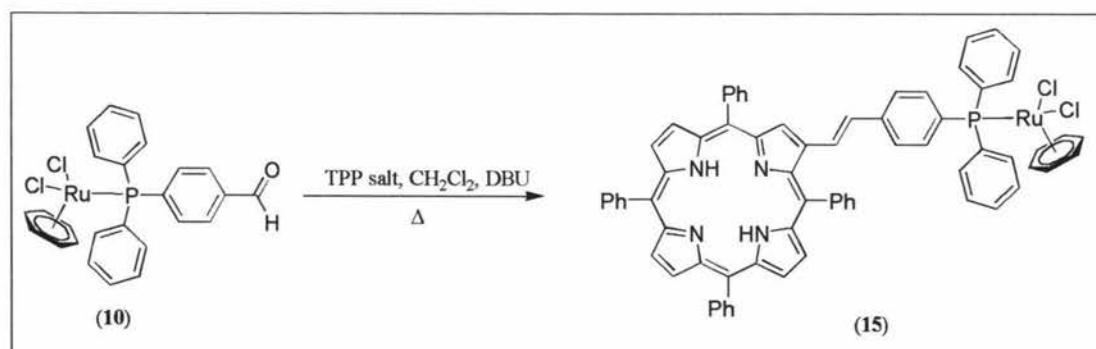


Figure 3.3

The synthesis of ruthenium-phosphinoporphyrin.

The ^1H NMR spectrum of (**15**) followed the same general pattern observed for the gold-phosphinoporphyrin (see figure 3.2). The main feature is the doublet signal at 7.11 ppm ($^3J = 16.48$ Hz), which belongs to one of the vinylic protons and provides proof of the *trans* vinylic bridge. A new singlet peak integrating for six protons appears at 5.39 ppm, and is assigned to the equivalent $\eta^6\text{-C}_6\text{H}_6$ protons. The ^{31}P NMR spectrum gave a single peak at 29.71 ppm, which compares well with the ruthenium phosphine-aldehyde (27.96 ppm). The UV-Vis spectrum, as expected, was similar to that of (**14**). The Soret band at 427 nm has a molar extinction coefficient (ϵ) of over 230000, and four weaker Q bands are also observed at longer wavelengths. High-resolution mass spectrometry was also used to support the identity of the product, giving a very accurate mass reading for the MH^+ ion.

3.1.3 Tungsten phosphinoporphyrin.

The tungsten phosphinoporphyrin was synthesised by reaction of TPP phosphonium salt (**1**) with W(4-PCHO) (**11**) under optimised Wittig conditions. These conditions include the use of DBU as the base and benzene heated to 60°C as the solvent (see figure 3.4). Purification by column chromatography using 4:1 CH_2Cl_2 :*n*-hexane as the eluent, afforded the *trans*-isomer of the desired product, (**16**), as a dark purple powder. This compound was readily soluble in CH_2Cl_2 and CHCl_3 , and was characterised according to the usual spectroscopic techniques.

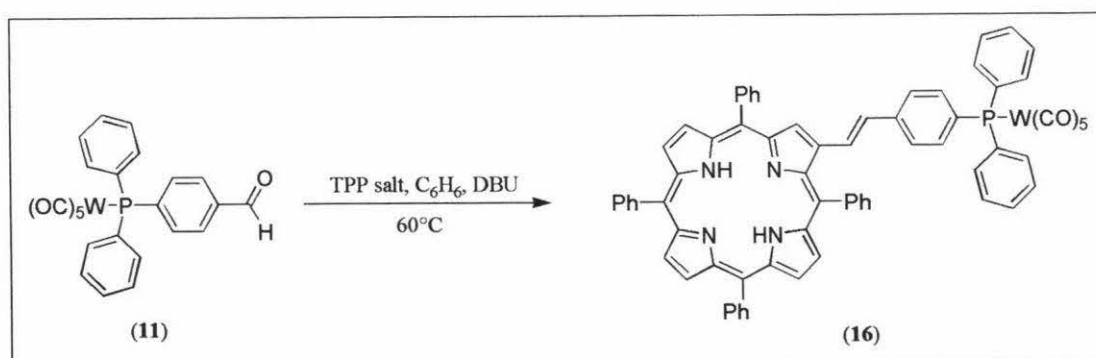


Figure 3.4

The synthesis of tungsten phosphinoporphyrin.

As expected, the ^1H NMR spectrum of (**16**) followed the same general pattern observed for the previous complexed phosphinoporphyrins; hence characterisation was relatively straightforward. The most important feature is the doublet resonance centred at 7.07 ppm ($^3J = 16.18$ Hz), which belongs to one of the *trans*-vinylic protons. The ^{31}P NMR spectrum gave a triplet signal centred at 20.38 ppm ($^1J = 121.58$ Hz), which is similar to that of W(4-PCHO) (22.26 ppm, $^1J = 123.05$ Hz).

The UV-Vis spectrum of (**16**) was similar to that of the previous gold and ruthenium phosphinoporphyrins. The distinctive Soret band at 428 nm has a molar extinction coefficient of over 229000, which is similar to that of (**15**). High-resolution mass spectrometry also supported the proposed characterisation, with an accurate mass reading for the MH^+ ion.

3.1.4 Ruthenium bis-phosphinoporphyrin.

The use of the $\text{Ru}(4\text{-PCHO})_2$ (**12**) should lead to the synthesis of a bis-phosphinoporphyrin complex. 2.1 equivalents of TPP phosphonium salt (**1**) and (**12**) were reacted under optimised Wittig conditions, using CH_2Cl_2 at reflux temperature and DBU as the base (see figure 3.5). Under these conditions, the *trans* isomer predominates, with a *cis/trans* ratio of approximately 1:10. Unfortunately, these conditions could not be optimised any further. Purification by column chromatography afforded (**17**) as a dark purple solid in 45% yield. This compound was most soluble in CH_2Cl_2 and CHCl_3 .

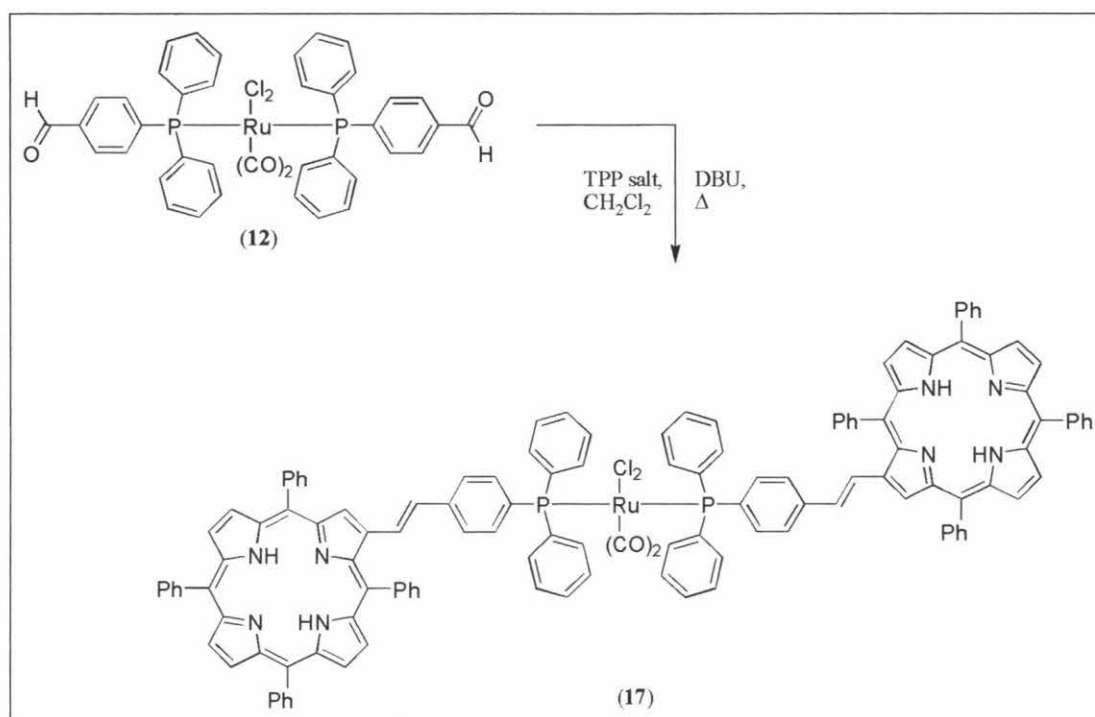


Figure 3.5

The synthesis of ruthenium bis-phosphinoporphyrin complex.

The ¹H NMR spectrum of (17) displays slight line broadening, which is probably caused by lower solubility or intermolecular aggregation. Despite this, the main feature of the spectrum is the doublet signal centred at 7.05 ppm (³J = 16.02 Hz), which is indicative of the *trans*-vinylic link. The ³¹P NMR spectrum of (17) gives a singlet peak at 17.25 ppm, which is similar to that of the Ru(4-PCHO)₂ (18.40 ppm). The UV-Vis, as expected, follows the same pattern observed for the previous complexed phosphinoporphyrins. However, the Soret band at 429 nm recorded a molar extinction coefficient of over 500000, which is considerably higher than the other complexed phosphinoporphyrins (approximately 200000). This increase was expected, given that (17) contains two porphyrins. High-resolution mass spectrometry confirmed the proposed characterisation as (17), with a very accurate mass reading.

3.1.5 Attempted synthesis of platinum bis-phosphinoporphyrin.

The Wittig reaction of Pt(4-PCHO)₂ (13b) with TPP phosphonium salt (1) should lead to a compound similar to (17) (see figure 3.6). Compounds (1) and (13b) were reacted under the same modified Wittig conditions as for the synthesis of (17). Purification by

column chromatography afforded (**18**) as a purple solid in 48% yield. Unfortunately, this compound could not be purified to spectroscopic quality due to an inseparable phosphine impurity; hence very limited data could be obtained and interpreted.

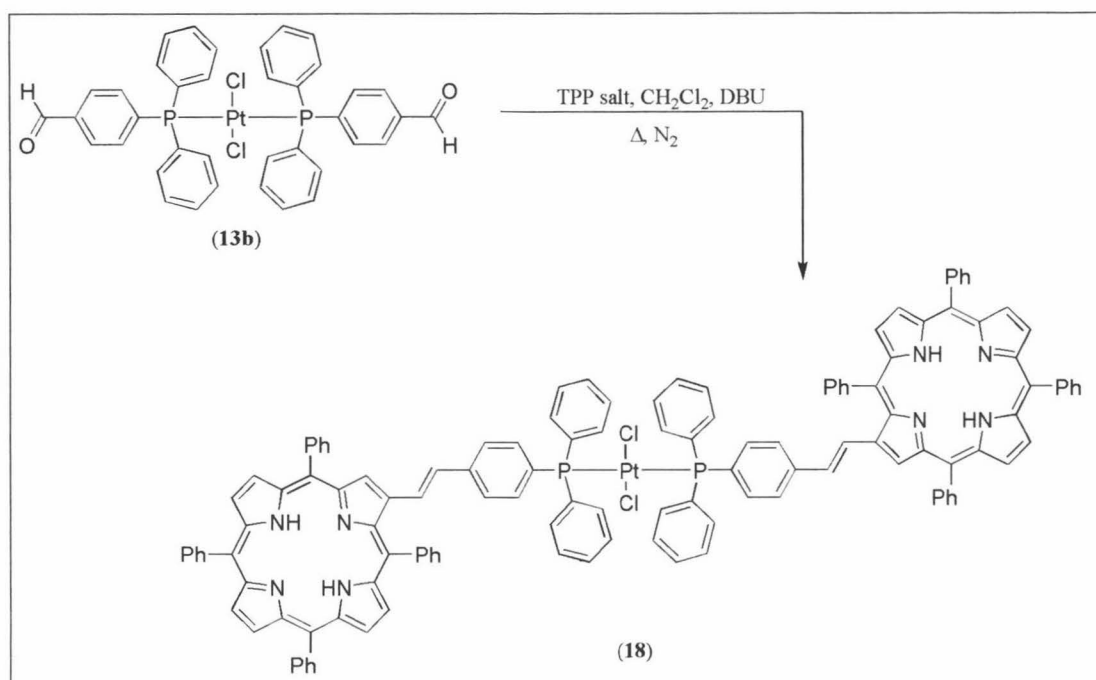


Figure 3.6

The attempted synthesis of platinum bis-phosphinoporphyrin complex.

Perhaps the most encouraging feature from the ¹H NMR spectrum is the doublet signal centred at 7.11 ppm (³J = 16.20 Hz), which shows the presence of the *trans*-vinylic linker. Both low-resolution and high-resolution mass spectrometry were used, however, the M⁺ ion was too weak to be measured. Similarly, fragments for (M-Cl)⁺ and (M-Cl₂)⁺ were also too weak. Currently, this compound remains only partially characterised.

3.2 Summary.

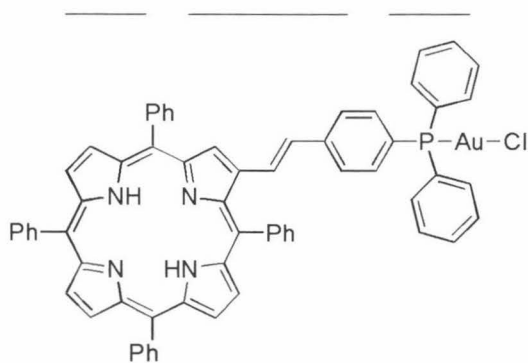
The synthesis of novel complexed phosphinoporphyrin conjugates, compounds (**14**) to (**18**), was successfully achieved by utilising Wittig chemistry of TPP phosphonium salt (**1**) with the appropriate complexed phosphine-aldehyde. In each individual case,

the Wittig conditions had to be optimised in order to obtain the sterically and thermodynamically favoured *trans*-isomer exclusively. In all the examples, the input of heat was sufficient to produce the *trans*-isomer. The NMR spectroscopy shows that the porphyrin has little effect on the proton environment of the phosphine, and vice versa. Likewise, the porphyrin has little effect on the environment of the phosphorus centre.

The synthesis of the ruthenium bis-phosfinoporphyrin complex showed that it is possible to have phosfinoporphyrin complexes that contain more than one porphyrin. This is especially encouraging, as the following chapter investigates the synthesis of a phosphine tris-aldehyde, and the attempted synthesis of the resulting phosfinoporphyrin trimer *via* the Wittig reaction.

3.3 Experimental procedures.

For general procedures used see Chapter Two, Section 2.5.1.



(14) Gold phosfinoporphyrin.

Au(4-PCHO) (**9**) (42.8 mg, 81.9 μmol) and TPP salt (**1**) (83.3 mg, 90 μmol) were heated at reflux temperature in dry toluene (~ 10 mL) for 5 minutes, then DBU (~ 70 μL , 468 μmol) was added. The reaction was deemed complete after 60 minutes (TLC analysis, 4% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$, $R_f = 0.90$), and the solvent was then removed *via* a rotary evaporator. The resulting residue was then purified *via* normal phase flash chromatography, eluting with CH_2Cl_2 . This fraction was then reduced to dryness,

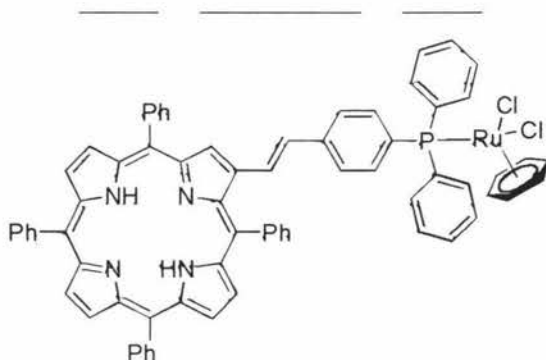
then recrystallised in CH_2Cl_2 /ethanol forming product (**14**) as a purple powder (66 mg, 71%).

$^1\text{H NMR}$ (270MHz, CDCl_3) δ /ppm: -2.57 (br s, 2H, N-H), 7.11 (d, $^3J = 16.18$ Hz, 1H, H_{vinylc}), 7.33 (dd, $^3J = 8.24$ Hz, $^4J = 2.14$ Hz, 2H, phosphine Ar- $H_{3,3'}$), 7.48-7.64 (m, 13H, phosphine Ar-H + H_{vinylc}), 7.74-7.86 (m, 12H, porphyrin Ar- $H_{\text{meta, para}}$), 8.19-8.28 (m, 8H, porphyrin Ar- H_{ortho}), 8.73-8.84 (m, 6H, $H_{\beta\text{-pyrrolic}}$), 9.03 (s, 1H, $H_{\beta\text{-pyrrolic}}$).

$^{31}\text{P NMR}$ (109MHz, CHCl_3) δ /ppm: 32.68 (s, 1P, $\text{TPPAr}_3\text{P-Au}$)

HRMS (positive FAB) m/z : M^+ for $\text{C}_{64}\text{H}_{45}\text{AuClN}_4\text{P}$: calculated $M^+ = 1132.2736$, observed $M^+ = 1132.2628$.

UV-Vis (CHCl_3): λ_{max} (log ϵ) 657.50 (3.48), 600.50 (3.86), 566.50 (4.03), 535.00 (4.25), 429.00 (5.28).



(15) *Ruthenium phosphinoporphyrin.*

Ru(4-PCHO) (**10**) (29 mg, 53.7 μmol) and TPP salt (**1**) (56.3 mg, 60.8 μmol) were heated at reflux temperature in dry CH_2Cl_2 (15 mL) for 5 minutes, then DBU (50 μL , 334 μmol) was added. The reaction was monitored by TLC (~3% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$, $R_f = 0.78$) and deemed complete after 60 minutes. The solvent was then removed *via* a rotary evaporator, and the residue purified by normal phase flash chromatography resulting in two fractions being obtained by gradient elution ($\text{CH}_2\text{Cl}_2 \rightarrow 4\% \text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$). The first fraction was then reduced to dryness *via* rotary evaporator, then the residue recrystallised from CH_2Cl_2 /ethanol to give (**15**) as a dark purple solid (22 mg, 36%).

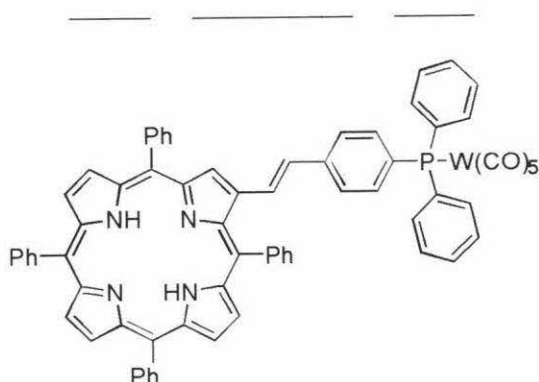
$^1\text{H NMR}$ (270MHz, CDCl_3) δ /ppm: -2.59 (br s, 2H, N-H), 5.39 (s, 6H, $\eta^6\text{-C}_6\text{H}_6$), 7.11 (d, $^3J = 16.48$ Hz, 1H, H_{vinylc}), 7.31-7.36 (m, 2H, phosphine Ar-H), 7.44-7.62 (m,

11H, phosphine Ar-*H* + *H*_{vinyl}), 7.65-7.82 (m, 14H, porphyrin Ar-*H*_{meta, para} + phosphine Ar-*H*), 8.18-8.28 (m, 8H, porphyrin Ar-*H*_{ortho}), 8.72-8.85 (m, 6H, *H*_{β-pyrrolic}), 9.03 (s, 1H, *H*_{β-pyrrolic}).

³¹P NMR (CHCl₃) δ/ppm: 29.71 (s, 1P, TPPAr₃P-Ru)

HRMS (positive FAB) *m/z*: MH⁺ for C₇₀H₅₂Cl₂N₄PRu: calculated MH⁺ = 1151.2351, observed MH⁺ = 1151.2361.

UV-Vis (CHCl₃): λ_{max} (log ε) 658.50 (3.68), 600.00 (3.95), 565.00 (4.10), 524.00 (4.35), 427.00 (5.37).



(16) *Tungsten phosphinoporphyrin.*

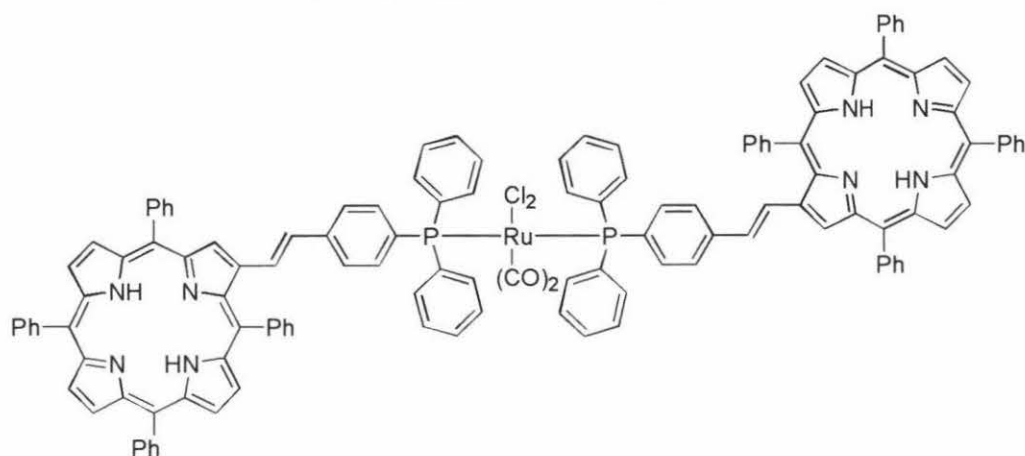
W(4-PCHO) (11) (50 mg, 81.4 μmol) and TPP salt (1) (70 mg, 75.6 μmol) were mixed in dry benzene under N₂, and then heated to approximately 60°C before DBU (40 μL, 267 μmol) was added. The solution immediately changed from crimson red to a very dark brown/black, and after 60 minutes, TLC analysis (4:1 CH₂Cl₂:hexane, R_f = 0.68) suggested the reaction was complete. After removing the solvent under reduced pressure, the residue was purified by normal phase flash column chromatography eluting with 4:1 CH₂Cl₂:*n*-hexane. This fraction was then recrystallised from CH₂Cl₂/ethanol, resulting in (16) as a dark brown/purple powder (67.6 mg, 73% yield).

¹H NMR (270 MHz, CDCl₃) δ/ppm: -2.58 (br s, 2H, N-*H*), 7.07 (d, ³*J* = 16.18 Hz, 1H, *H*_{vinyl}), 7.32 (dd, ³*J* = 8.24 Hz, ⁴*J* = 1.83 Hz, 2H, phosphine Ar-*H*_{3,3'}), 7.40-7.55 (m, 13H, phosphine Ar-*H* + *H*_{vinyl}), 7.72-7.82 (m, 12H, porphyrin Ar-*H*_{meta, para}), 8.18-8.28 (m, 8H, porphyrin Ar-*H*_{ortho}), 8.73-8.85 (m, 6H, *H*_{β-pyrrolic}), 9.00 (s, 1H, *H*_{β-pyrrolic}).

^{31}P NMR (109 MHz, CHCl_3) δ/ppm : 20.38 (t, $^1J_{\text{P-W}} = 121.58$ Hz, 1P, $\text{TPPAr}_3\text{P-W}$).

HRMS (positive FAB) m/z : M^+ for $\text{C}_{69}\text{H}_{45}\text{N}_4\text{O}_5\text{PW}$: calculated $\text{M}^+ = 1224.2637$, observed $\text{M}^+ = 1224.2603$.

UV-Vis (CHCl_3): λ_{max} ($\log \epsilon$) 657.50 (3.42), 600.00 (3.86), 565.50 (4.05), 524.50 (4.31), and 428.00 (5.36).



(17) *Ruthenium phosphinoporphyrin dimer.*

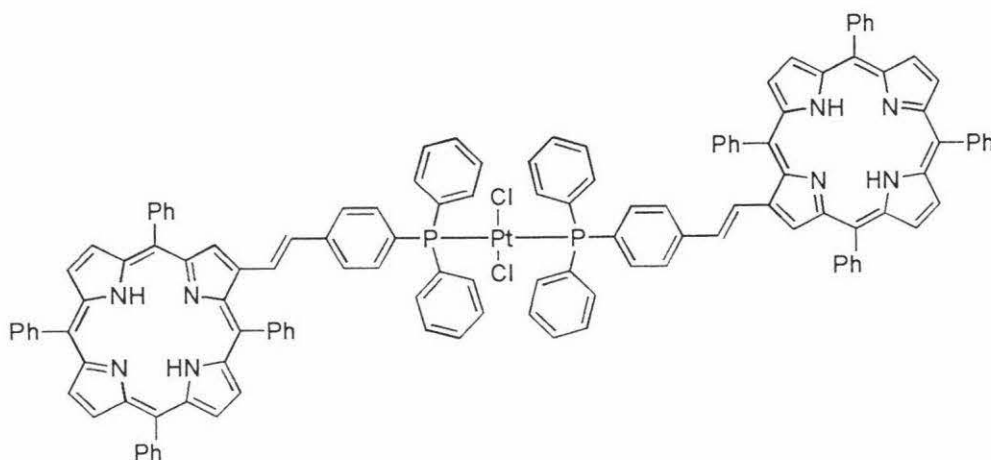
$\text{Ru}(4\text{-PCHO})_2$ (**12**) (15 mg, 18.55 μmol) and TPP salt (**1**) (36 mg, 39 μmol) were dissolved in dry CH_2Cl_2 (10 mL) then heated until at reflux temperature. DBU (40 μL , 267 μmol) was then added and the reaction monitored by TLC (CH_2Cl_2 , $R_f = 0.84$). After 30 minutes, the reaction was deemed complete and the solvent removed *via* rotary evaporator. The residue was then purified by flash column chromatography, resulting in two fractions being obtained by gradient elution ($\text{CH}_2\text{Cl}_2 \rightarrow 4\% \text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$). The first fraction was then reduced to dryness *via* rotary evaporator, and the residue recrystallised from $\text{CH}_2\text{Cl}_2/\text{ethanol}$ to give (**17**) as a dark purple solid (17 mg, 45%).

^1H NMR (270 MHz, CDCl_3) δ/ppm : -2.58 (br s, 4H, N-H), 7.05 (d, $^3J = 16.02$ Hz, 2H, H_{vinyllic}), 7.25-7.40 (m, $\sim 10\text{H}$, phosphine Ar-H + H_{vinyllic}), 7.52-7.59 (m, $\sim 10\text{H}$, phosphine Ar-H), 7.71-7.79 (m, $\sim 24\text{H}$, porphyrin Ar- $H_{\text{meta, para}}$), 7.92-8.11 (m, $\sim 10\text{H}$, phosphine Ar-H), 8.17-8.26 (m, 16H, porphyrin Ar- H_{ortho}), 8.74-8.85 (m, 12H, $H_{\beta\text{-pyrrolic}}$), 9.00 (s, 2H, $H_{\beta\text{-pyrrolic}}$).

^{31}P NMR (109MHz, CH_2Cl_2) δ/ppm : 17.25 (s, 2P, -P-Ru-P-).

HRMS (positive FAB) m/z : M^+ for $C_{130}H_{90}Cl_2N_8O_2P_2Ru$: calculated $M^+ = 2028.5082$, observed $M^+ = 2028.5066$.

UV-Vis ($CHCl_3$): λ_{max} (log ϵ) 655.50 (3.89), 599.50 (4.29), 565.00 (4.47), 524.50 (4.72), 427.00 (5.77).



(18) *Attempted synthesis of platinum phosphinoporphyrin dimer.*

$Pt(4-PCHO)_2$ (**13b**) (17.5 mg, 20.7 μmol) and TPP salt (**1**) (40 mg, 43.2 μmol) were dissolved in dry CH_2Cl_2 (10 mL) and heated at reflux temperature under N_2 for 5 minutes. DBU (40 μL , 267 μmol) was then added, and TLC analysis (4% CH_3OH/CH_2Cl_2) deemed the reaction complete after 45 minutes ($R_f = 0.27$). The solvent was removed *via* a rotary evaporator, then the resulting residue was purified by normal phase flash chromatography eluting with 5% CH_3OH/CH_2Cl_2 . This fraction was then recrystallised from $CH_2Cl_2/ethanol$, giving (**18**) as purple solid (20.6 mg, 9.97 μmol , 48%).

1H -NMR (270 MHz, $CDCl_3$) δ /ppm: -2.59 (br s, 4H, N-H), 7.11 (d, $^3J = 16.20$ Hz, 2H, H_{vinyl}), 7.31-7.36 (m, ~4H, phosphine Ar-H), 7.47-7.58 (m, ~26H, phosphine Ar-H + H_{vinyl}), 7.64-7.82 (m, ~24H, porphyrin Ar- $H_{meta, para}$), 8.18-8.28 (m, ~16H, porphyrin Ar- H_{ortho}), 8.71-8.84 (m, 12H, $H_{\beta\text{-pyrrolic}}$), 9.02 (s, 2H, $H_{\beta\text{-pyrrolic}}$).

2.6 References.

- (1) Märkl, G.; Reiss, M.; Kreitmeier, P.; Nöth, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*(20), 2230-2234.

Chapter Four

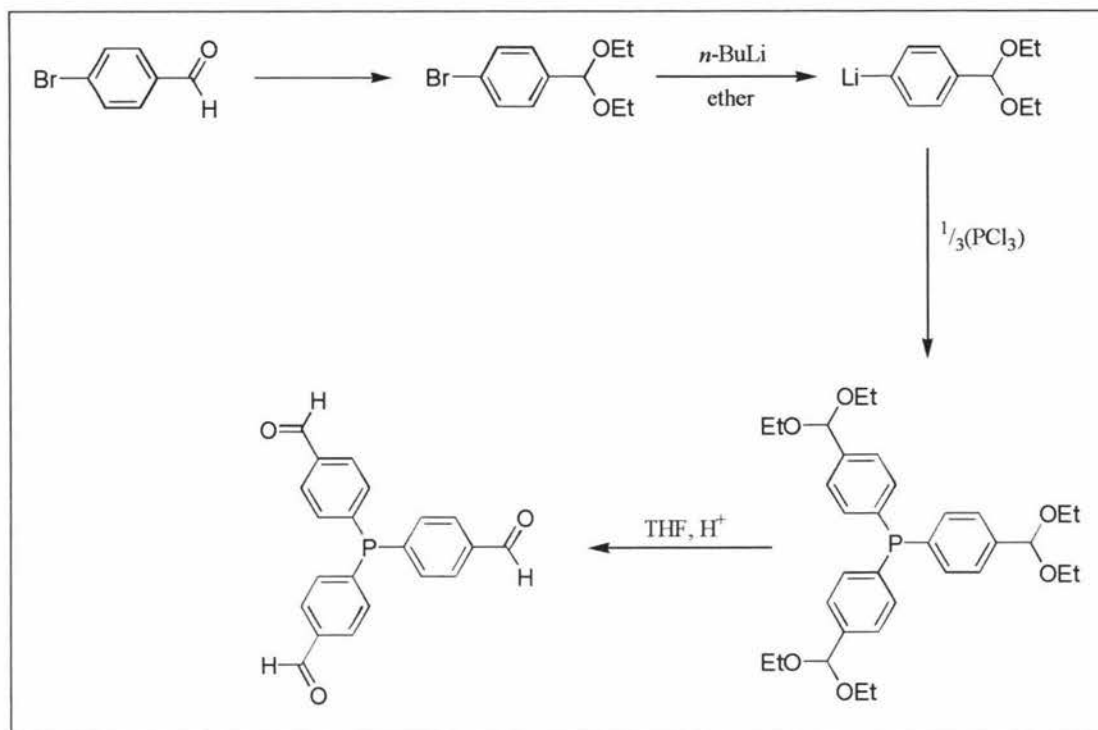
Attempted synthesis of Tris(4-formylphenyl)phosphine

The synthesis of a bis-phosfinoporphyrin complex from ruthenium bis(phosphine-aldehyde) was successful. This chapter describes the synthesis and characterisation of a phosphine tris-aldehyde. This tris-aldehyde is a key compound, as Wittig reaction with TPP phosphonium salt should yield a novel phosfinoporphyrin trimer. In this case, the single phosphine moiety will act as a “central hub”, essentially providing a connection between the three porphyrins.

4.1 Previous reports on Tris(4-formylphenyl)phosphine.

There are two general methods for synthesising tris(4-formylphenyl)phosphine, $P(4\text{-CHO})_3$. The first such publication was in 1978 by Bartlett *et al.*¹ (see scheme 4.1). Their method firstly involves the protection of *p*-bromobenzaldehyde. Next, lithiation of the di-ethoxy protected bromobenzaldehyde, followed by condensation with phosphorus trichloride affords the triacetal phosphine. At this stage, the product was purified by chromatography on Florisil (10% ether/petroleum ether), followed by vacuum distillation. For the last step, acid-catalysed deprotection results in the desired compound in approximately 45% overall yield.

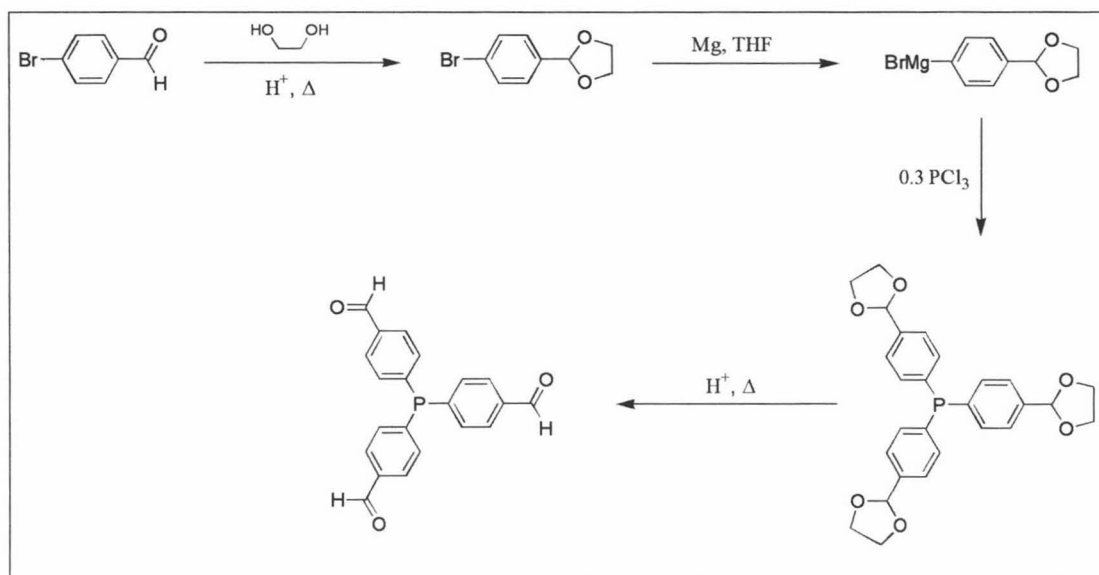
Bartlett *et al.* then converted the aldehyde groups to methamine groups, followed by complexation with gold to form an undecane cluster, $(Ar_3P)_7Au_{11}X_3$ ($X = I$ or CN).



Scheme 4.1

Bartlett's synthesis of tris(4-formylphenyl)phosphine.

Recently, Chalier *et al.*² also published a synthesis for $\text{P}(\text{4-CHO})_3$. Their methodology followed the Grignard method of Schiemenz and Kaack,^{3, 4} the same method used to synthesise 4-PCHO (5). This method involved the cyclic protection of *p*-bromobenzaldehyde followed by reaction of the resulting dioxolane with Mg to form the Grignard reagent. Reaction of this Grignard with phosphorus trichloride, followed by an acid-catalysed deprotection step yields the desired product, $\text{P}(\text{4-CHO})_3$, in an overall yield of approximately 25% (see scheme 4.2). Chalier *et al.* then reduced the aldehyde groups to hydroxyl groups.



Scheme 4.2

Chalier's synthesis of tris(4-formylphenyl)phosphine.

For this project, the latter methodology was chosen. Despite the apparent low overall yields, the Grignard method was selected primarily because of familiarity with the method, and because this procedure is a tested and published preparation.

4.1.1 Synthesis of Tris(4-formylphenyl)phosphine oxide.

The attempted synthesis of tris(4-formylphenyl)phosphine was carried out using the Grignard method following the same procedure of Chalier *et al.*² The first two steps, the cyclic protection of *p*-bromobenzaldehyde followed by reaction with Mg to form the Grignard reagent, is exactly the same as for the synthesis of 4-PCHO (**5**). Reaction of this Grignard with freshly distilled phosphorus trichloride then gave the crude protected product. Purification by the literature method involves extraction with CH_2Cl_2 followed by removal of the solvent under reduced pressure, then crystallisation from THF-ethanol (4:1) at 4°C. However in practice, the crystallisation was not successful. TLC analysis indicated two products (CH_2Cl_2 , $R_f = 0.73, 0.00$), which were isolated by column chromatography using gradient elution. The second fraction afforded the oxidised protected product, (**19**), as a yellow oil in 64% yield. Analysis of the ^{31}P NMR spectrum confirmed the product was the oxidised species, giving a resonance at a chemical shift of 27.30 ppm, which is characteristic for P(V) compounds. The first fraction was thought to be a Wurtz coupling by-product, as the ^{31}P NMR indicated the absence of phosphorus.

The final step of acid-catalysed deprotection yielded the crude product. Purification by column chromatography eluting with 5% CH₃OH/CH₂Cl₂ afforded the product of oxidation, **(20)**, as a pale yellow solid in an overall yield of 20% based upon *p*-bromobenzaldehyde (see figure 4.1).

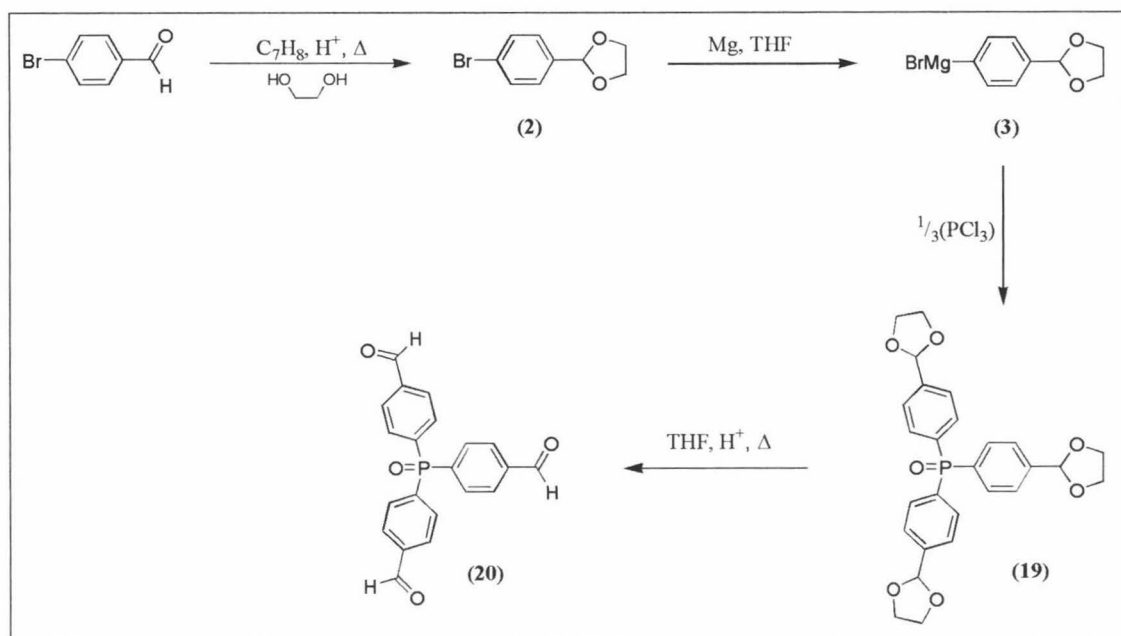


Figure 4.1

The synthesis of tris(4-formylphenyl)phosphine oxide.

Despite repeated attempts, the desired compound, tris(4-formylphenyl)phosphine, was never obtained. Oxidation always occurred during the third step; hence the product isolated was the P(V) compound **(20)**.

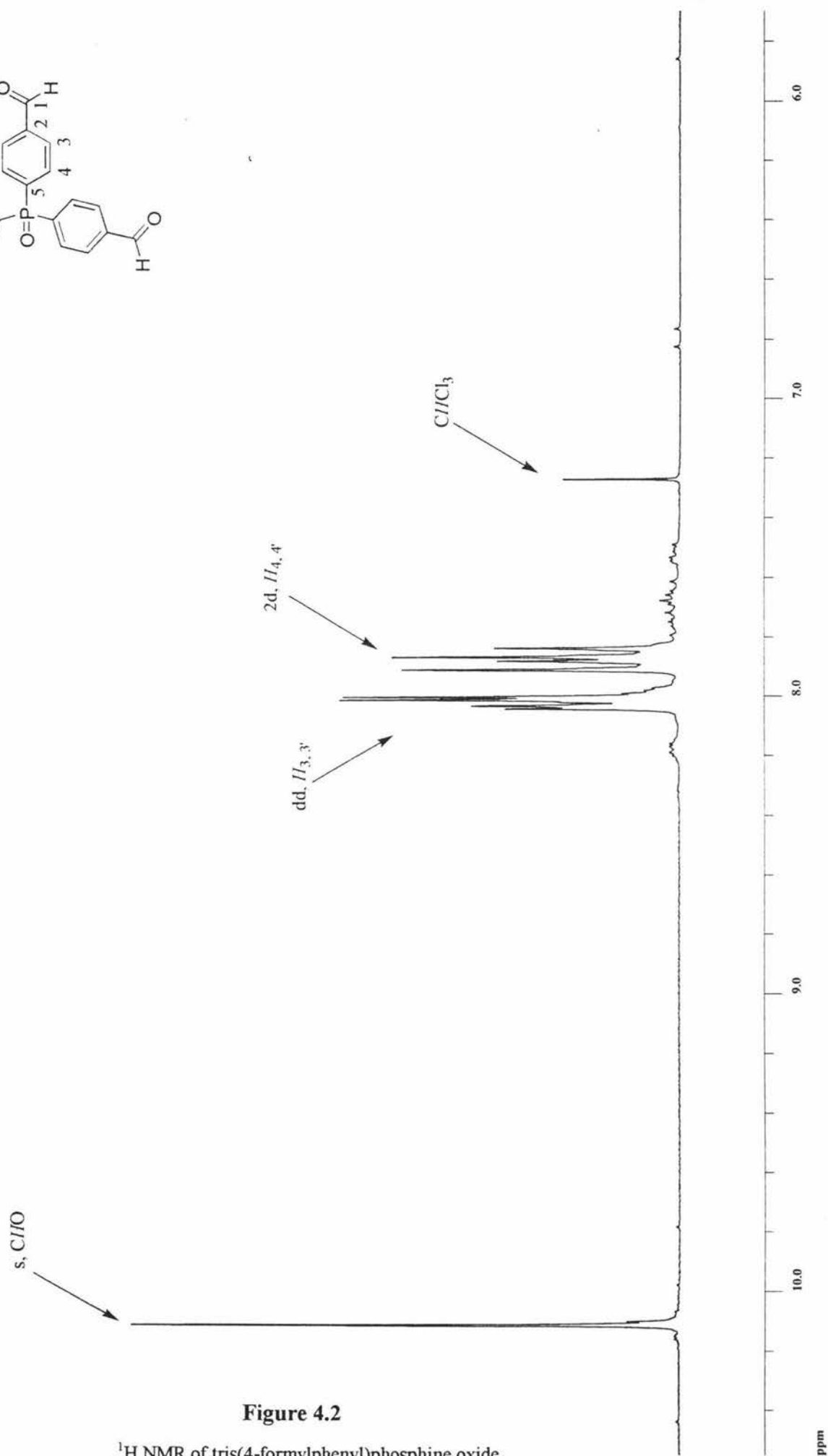
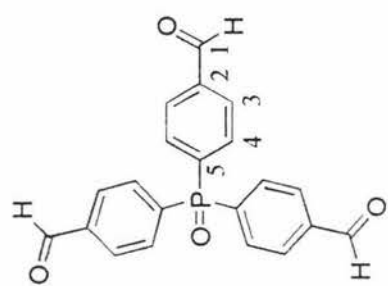
4.1.2 Compound characterisation.

Both compounds **(19)** and **(20)** were characterised by ¹H NMR and ³¹P NMR spectroscopy, with **(20)** also being characterised with ¹³C NMR, infrared spectroscopy, and high-resolution mass spectroscopy.

As described earlier, (19) was confirmed as the oxidised protected product by ^{31}P NMR, giving a resonance at 27.30 ppm which is consistent with P(V) compounds. The ^1H NMR of (20) (see figure 4.2) was similar to that of 4-(diphenylphosphino)benzaldehyde (5), and was relatively straightforward to assign due to the high amount of symmetry. The characteristic downfield resonance of the aldehyde proton appears at 10.11 ppm, and has a similar chemical shift to that of (5) (10.01 ppm). A doublet of doublets centred at 8.02 ppm is assigned to the $\text{H}_{3,3'}$ protons, which displays a strong three bond coupling to the adjacent $\text{H}_{4,4'}$ protons ($J = 8.35$ Hz), and a weaker four-bond coupling to the aldehyde proton ($J = 2.86$ Hz). Two partially overlapping doublet signals appear at 7.89 ppm ($J = 11.64$ Hz) and 7.86 ppm ($J = 11.64$ Hz), and are assigned to the $\text{H}_{4,4'}$ protons.

The ^{13}C NMR spectrum of (20) was also straightforward to assign due to the three-fold symmetry. The characteristic downfield resonance of the aldehyde carbon appears at 191.05 ppm, which is consistent with all the other aldehydes synthesised thus far. An apparent doublet signal centred at 138.85 ppm ($J = 3.00$ Hz) is assigned to the C_2 carbon. As observed with the phosphine-aldehyde complexes, the carbon-phosphorus coupling constant of signal for the *ipso* carbon, C_5 , dramatically increases upon coordination. In the case of (20), oxidation has the effect of increasing the coupling constant to 101.60 Hz, which is typical for phosphine oxide compounds ($\text{O}=\text{PPh}_3$ $^1J_{\text{C-P}} = 103.38$ Hz). Two more doublet signals appear further upfield centred at 132.56 ppm ($J = 11.00$ Hz) and 129.57 ppm ($J = 13.00$ Hz), and are assigned to the C_4 and C_3 carbons respectively.

The ^{31}P NMR spectrum of (20) gave a signal at 26.17 ppm, which is consistent with P(V) compounds, and is comparable to the complexed phosphine-aldehydes synthesised in Chapter Two. Infrared spectroscopy confirmed the presence of the aldehyde carbonyl group, with a characteristic $\text{C}=\text{O}$ stretch at 1704 cm^{-1} . High-resolution mass spectrometry was also employed to support the characterisation as (20), with a very accurate mass reading for the MH^+ ion.

**Figure 4.2**

^1H NMR of tris(4-formylphenyl)phosphine oxide.

4.2 Attempted synthesis of phosphinoporphyrin trimer.

Despite only being able to obtain the product of oxidation, it was decided to continue using (20) for further reactions. In fact, a search of the literature revealed no reports of the synthesis, or reactions of tris(4-formylphenyl)phosphine oxide.

The attempted synthesis of a phosphinoporphyrin trimer was carried out by reacting just over three equivalents of TPP phosphonium salt (1) with (20) under optimised Wittig conditions, with DBU as the base and C₆H₆ at reflux temperature (see figure 4.3).

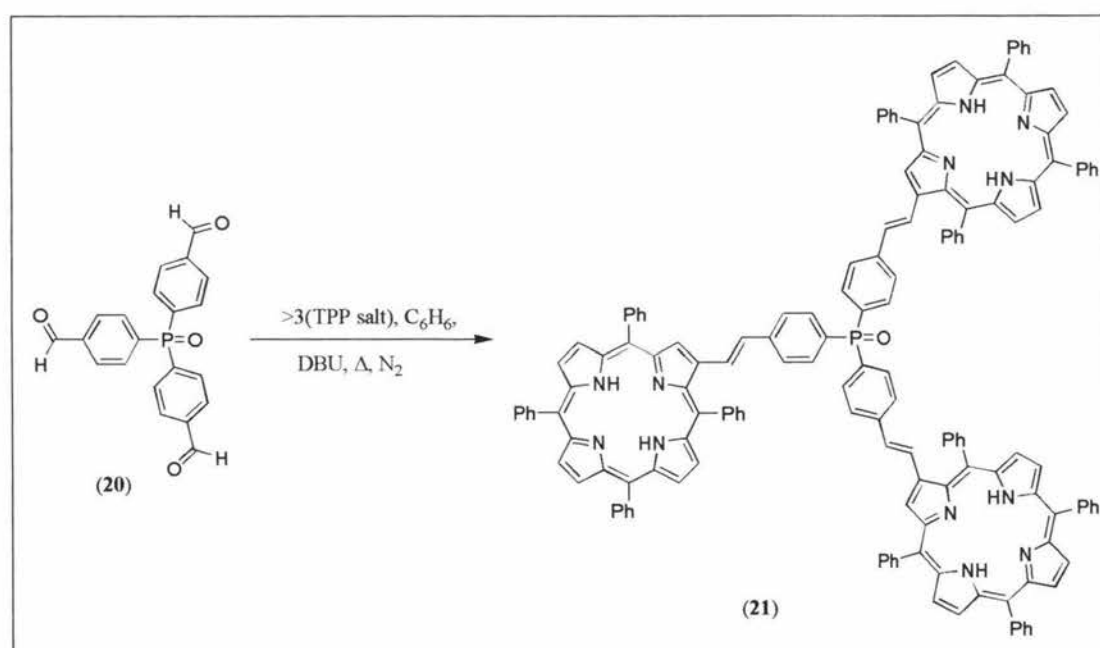


Figure 4.3

The attempted synthesis of a phosphinoporphyrin trimer.

TLC analysis (2% CH₃OH/CH₂Cl₂) indicated two minor products ($R_f = 0.86, 0.00$), presumably methyl TPP and unreacted TPP phosphonium salt, and one major product ($R_f = 0.57$). This major product was isolated by column chromatography using gradient elution, affording (21) as a purple solid in 86% yield. Unfortunately, difficulties were experienced when trying to purify the compound to spectroscopic quality. However, the ¹H NMR did indicate the presence of the *trans* vinylic linker, giving a distinctive doublet signal at 7.20 ppm ($J = 16.17$ Hz). High-resolution mass

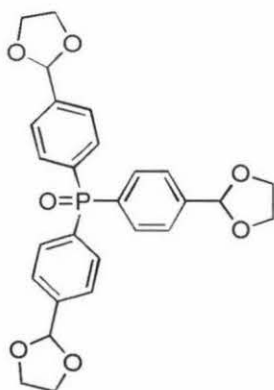
spectrometry also confirmed the compound as (21), giving a very accurate mass reading for the MH^+ ion.

4.2 Summary.

The synthesis of tris(4-formylphenyl)phosphine was severely hindered due to air oxidation. Despite repeat attempts, only the product of oxidation, (20), was obtained. The synthesis of a novel phosphinoporphyrin trimer was attempted by utilising Wittig chemistry of TPP phosphonium salt (1) with (20). Analysis of the crude product indicated the reaction was successful, however, due to restrictions in time, refinements to the reaction conditions and further purification of the product could not be fulfilled.

4.3 Experimental procedures.

For general procedures used see Chapter Two, section 2.5.1.



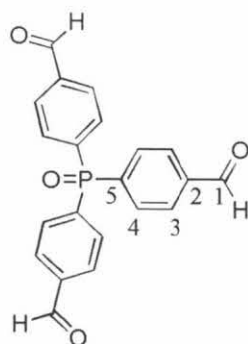
(19) *Tris[4-(1,3-dioxolan-2-yl)phenyl]phosphine oxide.*

Dry THF (150 mL) and Mg turnings (633 mg, 26 mmol) were mixed in a three-necked flask under argon. (2) (5.598 g, 24.4 mmol) in 5 mL THF was added dropwise *via* pressure equalising dropping funnel. After ~1 mL, a single crystal of I_2 was added to initiate the reaction. After the addition was complete, the flask was placed in

a sonicator until the Mg had disappeared, resulting in a yellow/brown solution (**3**). Whilst the Grignard reagent was cooling on ice/water, PCl_3 was firstly heated to reflux temperature to remove dissolved HCl, then distilled at room temperature under argon. The PCl_3 (710 μL , 8.15 mmol) was diluted to 20 mL with THF then added drop-wise *via* pressure equalising dropping funnel whilst maintaining the reaction mixture at $\sim 5^\circ\text{C}$. After the addition was complete, the yellow solution was stirred at room temperature overnight, before heating to reflux temperature for three hours. After cooling, saturated NaHCO_3 (50 mL) was added, forming a strong white emulsion (probably Mg salt) plus a yellow organic phase. After extracting with CH_2Cl_2 , the organic phase was dried over MgSO_4 , and then the filtered solution was reduced in volume affording a yellow oil. TLC analysis indicated two products (CH_2Cl_2 , $R_f = 0.73, 0.00$), which were isolated by normal phase flash chromatography (CH_2Cl_2 then 5% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$). Once the solvent was removed, the second fraction gave (**19**), the product of oxidation, as a yellow oil (2.5109 g, 64%). The first fraction afforded a yellow oil (1.2605 g), and is possibly a Wurtz coupling product.

$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : 4.02-4.15 (m, 12H, $-\text{CH}_2\text{CH}_2-$), 5.85 (s, 3H, $-\text{CH}-$), 7.55-7.72 (m, 12H, Ar-H).

$^{31}\text{P NMR}$ (109MHz, CH_2Cl_2) δ/ppm : 27.30 (s, 1P, $\text{Ar}_3\text{-P=O}$).



(**20**) *Tris(4-formylphenyl)phosphine oxide.*

(**19**) (~ 2.5100 g, 5.24 mmol) was firstly dissolved in THF (50 mL), then 2M HCl (~ 10.5 mL, 21 mmol) was added. The solution was then heated at reflux temperature for approximately 60 minutes, and then once cooled, extracted with CH_2Cl_2 (50 mL), before being neutralised with saturated NaHCO_3 (50 mL). The organic phase was

dried over MgSO_4 , and then concentrated to a yellow oil that was purified by normal phase flash chromatography. The first and main fraction was collected with 5% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$. After removing the solvent *via* rotary evaporator, the resulting yellow oil was placed under partial vacuum in a desiccator, affording (**20**) as a pale yellow solid (706 mg, 37%).

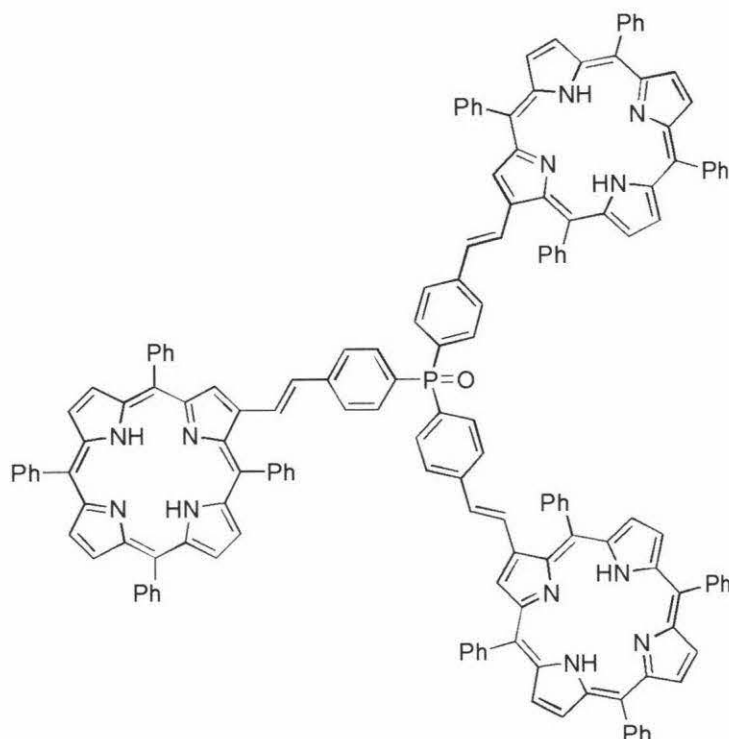
$^1\text{H NMR}$ (270 MHz, CDCl_3) δ/ppm : 7.86 (d, $^3J = 11.64$ Hz, 3H, Ar- $H_{4 \text{ or } 4'}$), 7.89 (d, $^3J = 11.64$ Hz, 3H, Ar- $H_{4 \text{ or } 4'}$), 8.02 (dd, $^3J = 8.35$ Hz, $^4J = 2.86$ Hz, 6H, Ar- $H_{3,3'}$), 10.12 (s, 3H, -CHO).

$^{13}\text{C NMR}$ (68MHz, CDCl_3) δ/ppm : 129.57 (d, $^3J_{\text{C-P}} = 13.00\text{Hz}$, C_3), 132.56 (d, $^2J_{\text{C-P}} = 11.00\text{Hz}$, C_4), 137.11 (d, $^1J_{\text{C-P}} = 101.06\text{Hz}$, C_5), 138.85 (d, $^4J_{\text{C-P}} = 3.00\text{Hz}$, C_2), 191.05 (s, C_1).

$^{31}\text{P NMR}$ (109MHz, CH_2Cl_2) δ/ppm : 26.17 (s, 1P, Ar $_3$ -P=O).

IR (Nujol mull) cm^{-1} : 1704 (s) $\nu(\text{C=O})$.

HRMS (positive FAB) m/z : MH^+ for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{P}$: calculated $\text{MH}^+ = 363.0786$, observed $\text{MH}^+ = 363.0770$.



(21) Attempted synthesis of phosphinoporphyrin trimer.

$P(4\text{-CHO})_3$ oxide (**20**) (10 mg, 27.6 μmol) and TPP phosphonium salt (**1**) (83 mg, 89.7 μmol) were dissolved in dry C_6H_6 (5 mL) and heated to reflux temperature. DBU (50 μL , 331 μmol) was added and reflux was continued for 30 minutes. TLC analysis (2% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$) indicated the formation of two minor products ($R_f = 0.86$, 0.00), and one major product ($R_f = 0.57$). The solvent was removed under reduced pressure and the residue purified by flash column chromatography using gradient elution ($\text{CH}_2\text{Cl}_2 \rightarrow 2\% \text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$), where one main band was collected whilst eluting with 2% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$. Removal of the solvent under reduced pressure resulted in a purple residue, which recrystallised from $\text{CH}_2\text{Cl}_2/\text{ethanol}$, giving a purple solid (52.3 mg, 86%).

HRMS (positive FAB) m/z : MH^+ for $\text{C}_{156}\text{H}_{106}\text{N}_{12}\text{OP}$: calculated $\text{MH}^+ = 2193.8342$, observed $\text{M}^+ = 2193.8350$.

4.4 References.

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Chapter Five

Investigation into Phosphinoferrocenes.

To date, the most common types of phosphine-ferrocene compounds are those which have the phosphine attached to the C_P ring *via* a transition metal,^{1, 2} or where one of the aryl rings of the phosphine is substituted with the C_P ring of the ferrocene^{3, 4} (see figure 5.1). These types of compounds are of interest because many are useful transition-metal complexes. The methodology developed in this project will have the proposed phosphine and ferrocene moieties connected together *via* the vinylic bridge, which is similar to the phosphinoporphyryns described earlier.

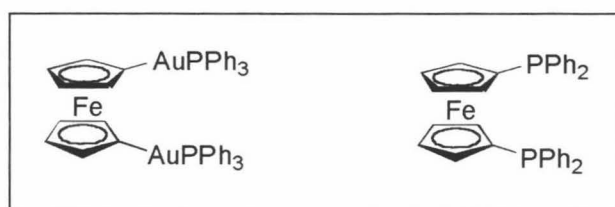


Figure 5.1

Common types of phosphine-ferrocene compounds.

The main objective for this investigation was to establish the feasibility of synthesising phosphine functionalised ferrocenes *via* Wittig chemistry. Hence, this chapter describes the synthesis and characterisation of novel phosphinoferrocene compounds.

To the best of the author's knowledge, the compounds described in this chapter are the first of their kind to be synthesised, especially as the ferrocene is functionalised *via* the vinylic bridge to the phosphine.

5.1 Synthesis of phosphinoferrocene monomer.

The phosphonium salt of choice in this investigation is the ferrocene methyl phosphonium salt (**22**). A novel phosphinoferrocene monomer was synthesised by utilising Wittig chemistry of ferrocene phosphonium salt (**22**) with 4-PCHO (**5**) (see figure 5.2). However, the use of ferrocene phosphonium salt requires vastly different Wittig conditions compared to the TPP phosphonium salt. In order to form the ferrocene phosphonium ylide, a relatively strong base is required, so potassium tertiary butoxide is used instead of DBU. In addition to this, non-halogenated solvents, such as THF, must be used to avoid reaction of the base with the solvent.

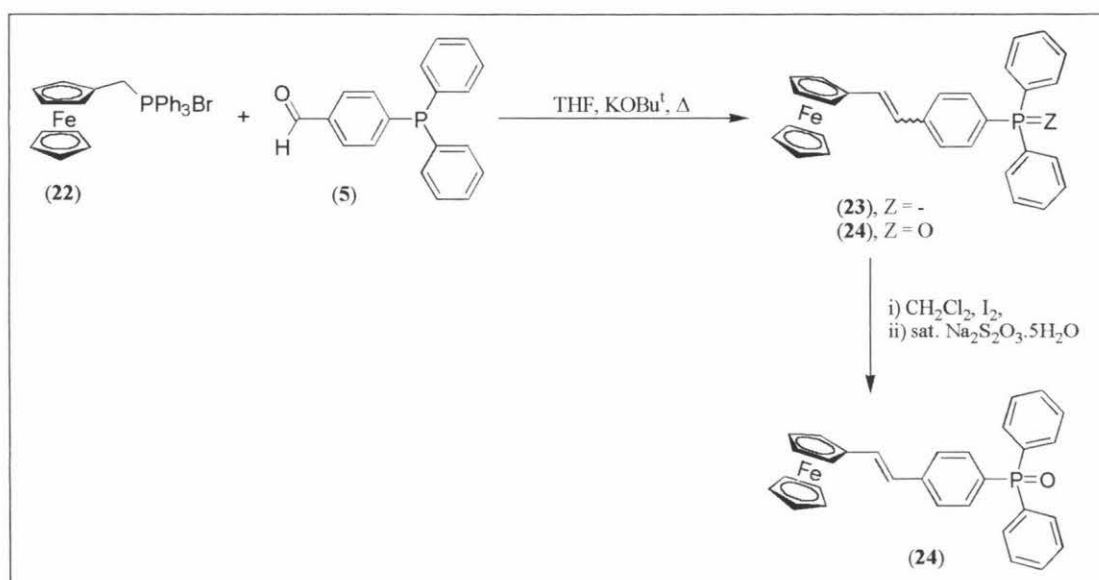


Figure 5.2

The synthesis of a phosphinoferrocene monomer.

Purification of the crude product by column chromatography using gradient elution yielded two main bands. The first band afforded a *cis/trans* mixture of the desired product, (**23**). ¹H NMR analysis indicated a *cis/trans* ratio of 1:1, and ³¹P NMR gave a resonance at a chemical shift of -6.07 ppm, which is consistent with P(III) compounds. The second band afforded a *cis/trans* mixture of the phosphine oxide, (**24**). This was confirmed by the presence of a signal at 27.43 ppm in the ³¹P NMR. Conversion of the *cis/trans* mixture to the *trans*-isomer was achieved with the aid of iodine.⁵ In the presence of iodine, the *cis*-isomer is converted to the

thermodynamically more stable *trans*-isomer, and the ferrocene moiety is oxidised to the corresponding ferrocenium ion. After isomerisation was completed, removal of iodine and reduction of the ferrocenium moiety back to ferrocene was achieved using an aqueous sodium thiosulphate work-up. A final purification step using column chromatography eluting with 2% CH₃OH/CH₂Cl₂ affords the *trans* phosphine-oxide (**24**) exclusively, as a rust coloured solid.

5.1.1 Compound characterisation.

The phosphinoferrocene oxide (**24**) was characterised using the usual spectroscopic methods. The ¹H NMR spectrum (see figure 5.3) displayed all the characteristic hallmarks of the phosphine and the ferrocene moieties, as well as the vinylic bridge. The ferrocene protons are split into three distinct signals, with a singlet at 4.15 ppm being assigned to the unsubstituted C_P ring. The protons of the substituted C_P ring appear as two triplet signals further downfield at 4.33 ppm and 4.49 ppm (both *J* = 1.76 Hz). Two distinctive doublet signals centred at 6.70 ppm and 7.01 ppm correspond to the two protons of the vinylic bridge. The coupling constants for these two doublets measured 16.26 Hz, which typifies the *trans* arrangement. The multiplet signals of the phosphine protons appear further downfield at 7.44-7.58 ppm and 7.63-7.71 ppm.

The ¹³C NMR spectrum of (**24**) displays the upfield resonances expected of a ferrocene moiety. Singlet peaks at 67.19 ppm and 69.50 ppm are associated with the CH carbons of the substituted C_P ring. Another singlet peak at 69.30 ppm is assigned to the five equivalent carbons of the unsubstituted C_P ring, C₁, and the signal further downfield at 82.38 ppm is assigned to the quaternary C_P carbon, C₄. Other main features of the spectrum are the resonances for the two vinylic protons (124.52 ppm and 130.11 ppm), and the *ipso* carbon, C₇. This doublet signal is centred at 132.34 ppm and has a coupling constant of 103.06 Hz, which is consistent with a phosphine-oxide compound.

A single resonance is observed in the ³¹P NMR spectrum at 27.43 ppm, confirming the presence of a P(V) compound. High-resolution mass spectrometry also confirmed the product as (**24**), giving a very accurate mass reading.

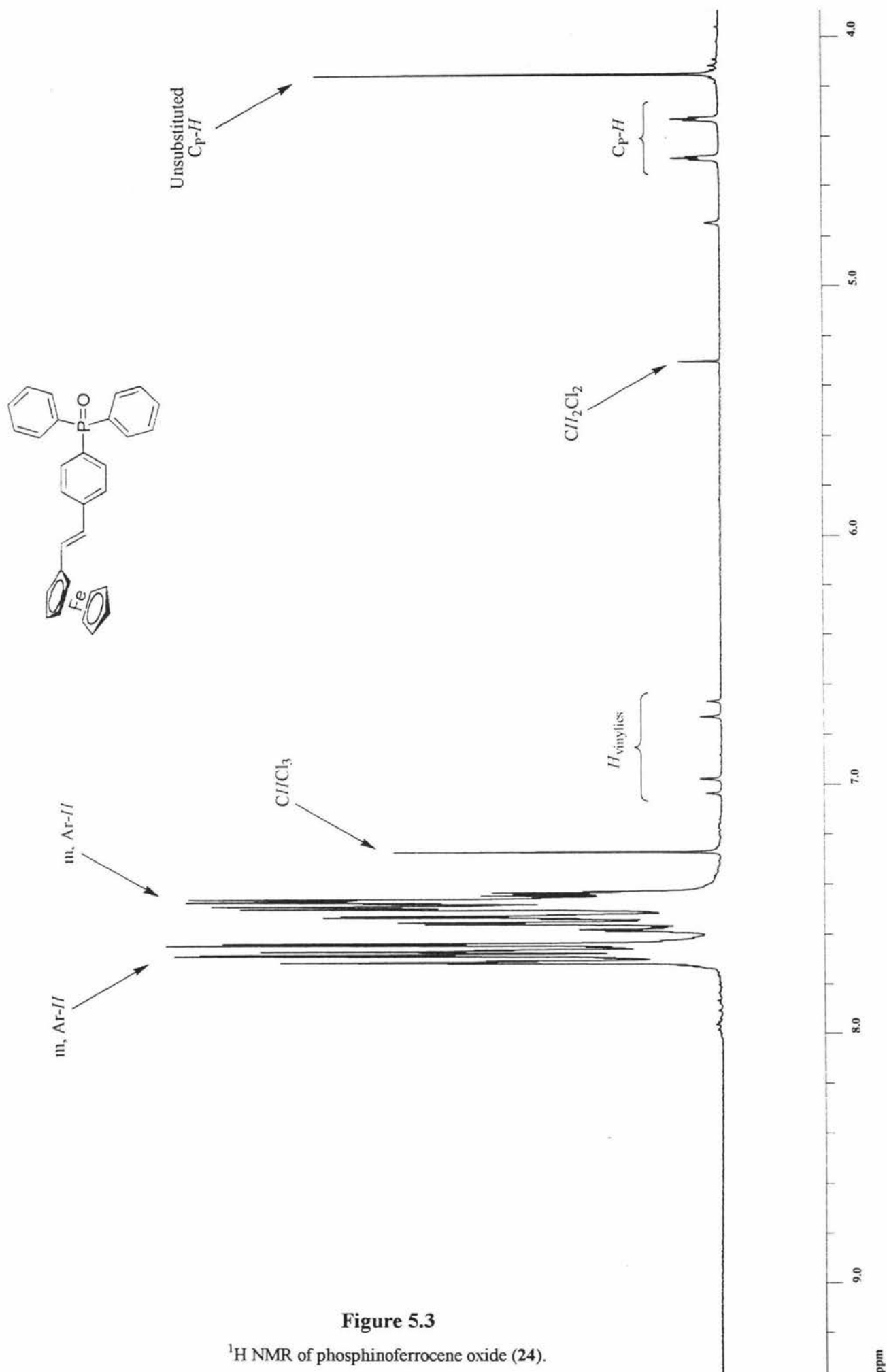


Figure 5.3

 ^1H NMR of phosphinoferrrocene oxide (24).

5.2 Synthesis of phosphinotrisferrocene oxide.

The synthesis of a phosphinotrisferrocene compound was attempted by the reaction of 3.5 equivalents of ferrocene phosphonium salt (**22**) with $\text{O}=\text{P}(\text{4-CHO})_3$ (**20**) (see figure 5.4).

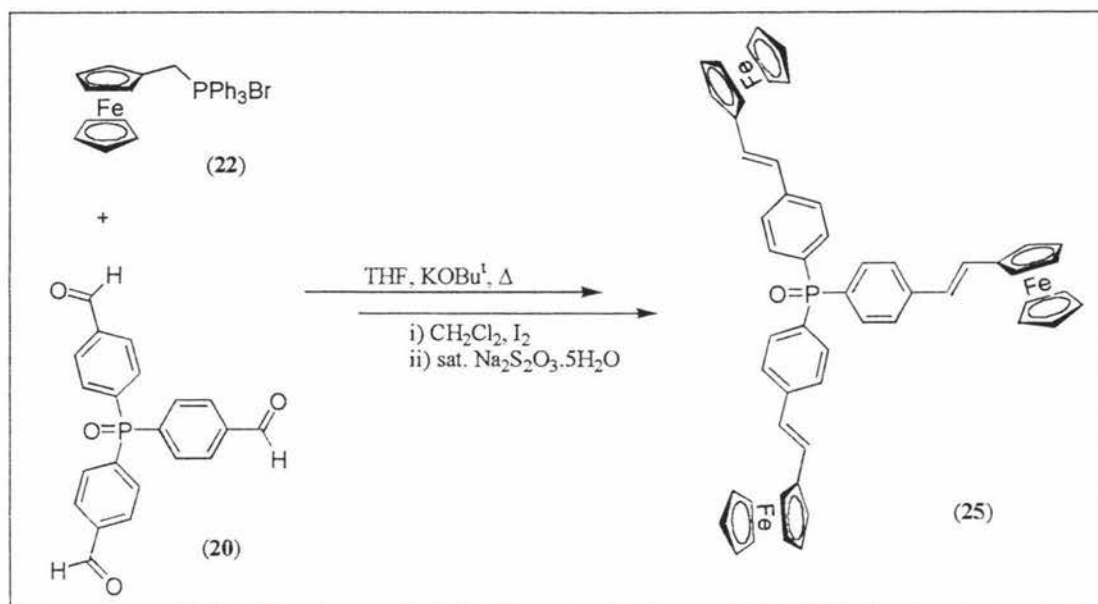


Figure 5.4

The attempted synthesis of a phosphinotrisferrocene trimer.

Purification by column chromatography using gradient elution afforded a *cis/trans* mixture of the desired phosphinotrisferrocene oxide, (**25**). Isomerisation using iodine, followed by an aqueous sodium thiosulphate work-up yielded the desired product. Column chromatography eluting with 2% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ afforded the *trans* isomer of (**25**) as a rust coloured solid. Unfortunately, purification difficulties resulted in (**25**) being characterised by high-resolution mass spectrometry only. The result was very encouraging, and is worthy of further investigation.

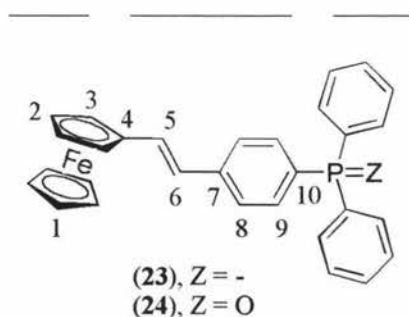
5.3 Summary.

The synthesis of a novel phosphinoferrocene compound was successful. Although the product (**24**) was obtained after the isomerisation step, air oxidation is regarded as not being a significant problem. To avoid air oxidation, the complexed phosphine-aldehyde could be used in the Wittig reaction instead of (**5**).

The synthesis of a novel phosphinoferrocene trimer was also attempted by utilising Wittig chemistry of ferrocene phosphonium salt (**22**) with $\text{O}=\text{P}(\text{4-CHO})_3$ (**20**). Analysis of the crude product indicated the reaction was successful, however due to restrictions in time, further purification steps could not be completed.

5.4 Experimental procedures.

For general procedures used see Chapter Two, section 2.5.1. Where possible, reactions described in this chapter were carried out shielded from ambient light.



(**23**) and (**24**) *Phosphinoferrocene.*

Step one: The ferrocene phosphonium salt (**22**) (50 mg, 92.4 μmol) was stirred in dry THF (10 mL) forming a suspension. Addition of potassium tertiary butoxide (~25 mg, 222 μmol) changed the solution to a characteristic red colour associated with the ylide. After heating until at reflux temperature, a solution of 4-PCHO (**5**) (21 mg, 72.3 μmol) in THF (2 mL) was added. The solution gradually changed to a rust colour, and

TLC analysis after 120 minutes deemed the reaction complete (20% ethyl acetate/hexane, $R_f = 0.64$). The solvent was removed under reduced pressure and the resulting residue purified by flash column chromatography. Three bands were obtained, the first while eluting with hexane, and the second while eluting with ethyl acetate, and the third while eluting with ~2% CH₃OH/CH₂Cl₂. Removal of the solvent afforded methyl ferrocene (<5 mg) from the first fraction, and the second fraction afforded a *cis/trans* mixture of the desired product, (**23**) as a dark rust coloured solid (20 mg), and the third fraction afforded a *cis/trans* mixture of the oxidised product, (**24**) as a dark rust coloured solid (10 mg).

³¹P NMR (109MHz, CH₂Cl₂) δ/ppm: -6.07 (s, 1P, F_cAr₃-P), 27.43 (s, 1P, F_cAr₃-P=O).

Step two (isomerisation): The *cis/trans* phosphinoferrocene mix (**23**) (20 mg, 42.3 μmol) was dissolved in dry CH₂Cl₂ (5 mL) before the addition of I₂ (33 mg, 130 μmol). After stirring in the dark at room temperature for three hours, the reaction was quenching with saturated Na₂S₂O₃ (15 mL), and then the solution was vigorously stirred for 20 minutes. The now rust coloured organic layer was then extracted with CH₂Cl₂ (30 mL), dried over K₂CO₃, filtered, then the solvent removed under reduced pressure. The resulting residue was then purified by flash column chromatography; in which one band was obtained eluting with 3% CH₃OH/CH₂Cl₂. Removal of the solvent afforded the *trans*-isomer of the product of oxidation, (**24**), as a rust coloured solid (15 mg).

A similar procedure was also used for isomerising the *cis/trans* phosphinoferrocene oxide (**24**) mix to the *trans* product exclusively. The combined yields totalled 23 mg, 65%.

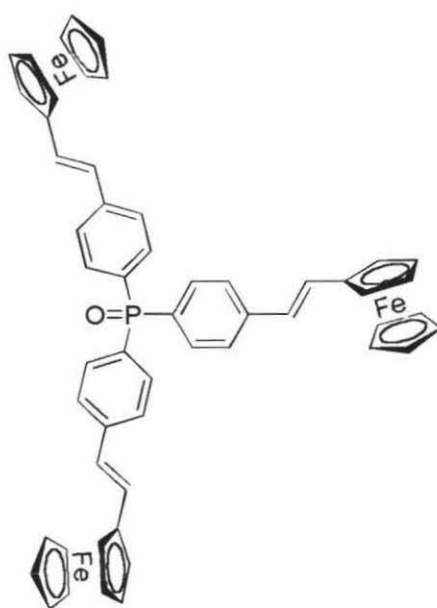
¹H NMR (270 MHz, CDCl₃) δ/ppm: 4.15 (s, 5H, C_p-H), 4.33 (t, $J = 1.76$ Hz, 2H, C_p-H), 4.49 (t, $J = 1.76$ Hz, 2H, C_p-H), 6.70 (d, $^3J = 16.26$ Hz, 1H, H_{vinylic}), 7.01 (d, $^3J = 16.26$ Hz, 1H, H_{vinylic}), 7.44-7.58 (m, Ar-H)*, 7.63-7.71 (m, Ar-H)*.

* The optimum integrated value could not be determined due to the presence of an inseparable phosphine oxide impurity.

$^{13}\text{C-NMR}$ (67 MHz, CDCl_3) δ/ppm : 67.19 (s, C_2 or C_3), 69.30 (s, C_1), 69.50 (s, C_2 or C_3), 82.38 (s, C_4), 124.52 (s, C_5 or C_6), 128.39 (d, $J_{\text{C-P}} = 12.01$ Hz, C_8 or C_9), 130.11 (s, C_5 or C_6), 131.84 (s, C_7), 131.98 (d, $J_{\text{C-P}} = 10.01$ Hz, C_8 or C_9), 132.34 (d, $^1J_{\text{C-P}} = 103.06$ Hz, C_{10}).

$^{31}\text{P-NMR}$ (109MHz, CH_2Cl_2) δ/ppm : -6.03 (s, 1P, $\text{FcAr}_3\text{-P}$), 27.43 (s, 1P, $\text{FcAr}_3\text{-P=O}$).

HRMS (positive FAB) m/z : MH^+ for $\text{C}_{30}\text{H}_{26}\text{FeOP}$: calculated $\text{MH}^+ = 489.1071$, observed $\text{MH}^+ = 489.1076$.



(25) *Phosphinotrisferrocene oxide.*

The ferrocene phosphonium salt (**22**) (78 mg, 145 μmol) was stirred in dry THF (10 mL) before the addition of potassium tertiary butoxide (18 mg, 160 μmol). After heating the red coloured solution to reflux temperature, a solution of O=P(4-CHO)_3 (**20**) (15 mg, 41.4 μmol) in THF (2 mL) was added and the solution gradually changed to the rust colour of ferrocene. TLC analysis (3% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$) deemed the reaction was complete after 60 minutes ($R_f = 0.55$), and after the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography. A small amount of methyl ferrocene was collected whilst eluting with CH_2Cl_2 , and one main fraction was collected whilst eluting with 3% $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$. This fraction was reduced to dryness, and then isomerised with I_2

using the same procedure as mentioned above, affording a dark rust coloured solid (25).

HRMS (positive FAB) m/z : M^+ for $C_{54}H_{45}Fe_3OP$: calculated $M^+ = 908.1256$, observed $M^+ = 908.1259$.

5.5 References.

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Chapter Six

Conclusions and Future Work

The primary aim of this research project was to formulate an efficient methodology for synthesising complexed phosphinoporphyrin conjugates containing vinylic linker groups. A secondary aim of investigating the synthesis of phosphinoferrocene conjugates containing vinylic linker groups was also pursued.

Wittig chemistry was proposed as the methodology of choice for synthesising the desired phosphinoporphyrin conjugates. The required precursors, *meso*-tetraphenylporphyrin phosphonium salt (1), and 4-(diphenylphosphino)benzaldehyde (5) were successfully synthesised. Initial Wittig reactions performed with (1) and (5) were severely limited due to oxidation, and only a small portion of the desired phosphinoporphyrin (6) was obtained. The remainder was identified as the phosphinoporphyrin oxide (7). To avoid this air oxidation, a new methodology was pursued – complexation before the Wittig reaction. Reaction of (5) with the appropriate transition metal led to the simple and efficient synthesis of a range of complexed phosphine-aldehydes. They include complexes of gold (9), ruthenium (10), and tungsten (11). Complexes containing two phosphine-aldehydes were also synthesised, specifically complexes of ruthenium (12) and platinum (13).

The primary goal of synthesising novel complexed phosphinoporphyrins was achieved by Wittig reaction of TPP phosphonium salt (1) with the appropriate complexed phosphine-aldehydes, (9)-(13). The resulting desired compounds include phosphinoporphyrin complexes of gold (14), ruthenium (15), and tungsten (16). A bis-phosphinoporphyrin complex was also synthesised by Wittig reaction between (1) and (12), resulting in the ruthenium bis-phosphinoporphyrin complex, (17). In general, the Wittig reaction proved to be a successful and efficient methodology, producing the target compounds in yields ranging from 45% to 73%. In each individual case, the use of heat was necessary in order to obtain the sterically and

thermodynamically favoured *trans*-isomer exclusively. Overall, this study confirmed both the viability and the flexibility of the proposed methodology.

The remaining phosphinoporphyrin study focused on the synthesis of a phosphinoporphyrin trimer. The synthesis of the phosphine tris-aldehyde precursor, tris(4-formylphenyl)phosphine oxide, (**20**) was successful. Although the product from air oxidation was isolated, it was decided to continue the study to establish the feasibility of the proposed methodology. The use of Wittig chemistry proved successful, as reaction of (**1**) with (**20**) yielded the desired phosphinoporphyrin trimer, (**21**).

The final goal of this project was to investigate the practicability of synthesising phosphinoferrocenes *via* Wittig chemistry. Preliminary Wittig reactions were carried out using a ferrocene phosphonium salt (**22**) and (**5**), resulting in the synthesis of a phosphinoferrocene monomer, (**24**). Given the success of this reaction, Wittig reaction of (**22**) with (**20**) was tried in an attempt to synthesis a phosphinotriferrocene (**25**). Overall, this introductory investigation into the synthesis of phosphinoferrocenes *via* Wittig chemistry was successful, completing the research carried out for this thesis.

There are many areas of this project that can be extended further. The primary objective of any future work will focus on preventing oxidation during the synthesis of tris(4-formylphenyl)phosphine. Perhaps complexation during the synthesis of tris(4-formylphenyl)phosphine could be a solution, as this will also result in the desired complexed tris-aldehyde. Subsequent Wittig reaction should then yield the desired complexed phosphinoporphyrin trimer. Another area worth investigating is using 2-(diphenylphosphino)benzaldehyde, as functionalisation at the *ortho* position may introduce different steric and physical constraints and properties. A second goal is to extend the phosphinoferrocene research. Given the success of the preliminary investigation, synthesis of complexed phosphinoferrocenes should be relatively straightforward, and will provide a wealth of further chemistry.