Phosphine – Porphyrin Conjugates

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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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Last but not least, I would like to thank my mum, dad, and sister for their unconditional support, and providing encouragement for me to complete this thesis.

Table of Contents

List of Figures

List of Tables and Schemes.

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
$O{=}P(4\text{-}CHO)_3$	Tris(4-formylphenyl)phosphine oxide
$P(4\text{-}CHO)_3$	Tris(4-formylphenyl)phosphine
Ph	Phenyl
PPh_3	Triphenylphosphine
$Pt(4\text{-}PCHO)_2$	Platinum bis(phosphine-aldehyde) complex
Ru(4-PCHO)	Ruthenium phosphine-aldehyde
$Ru(4\text{-}PCHO)_2$	Ruthenium bis(phosphine-aldehyde) complex
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TPP	*meso*-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.

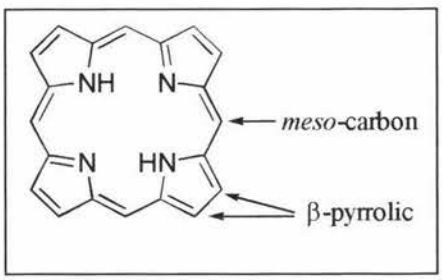

Figure 1.1

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.

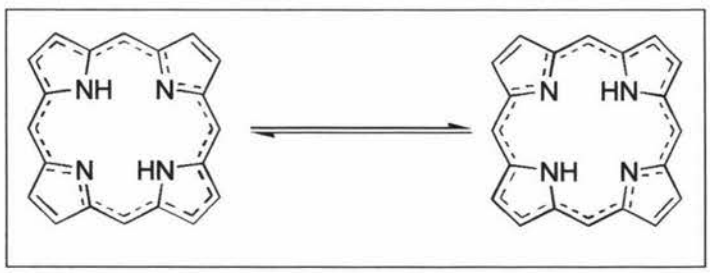

Figure 1.2

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.

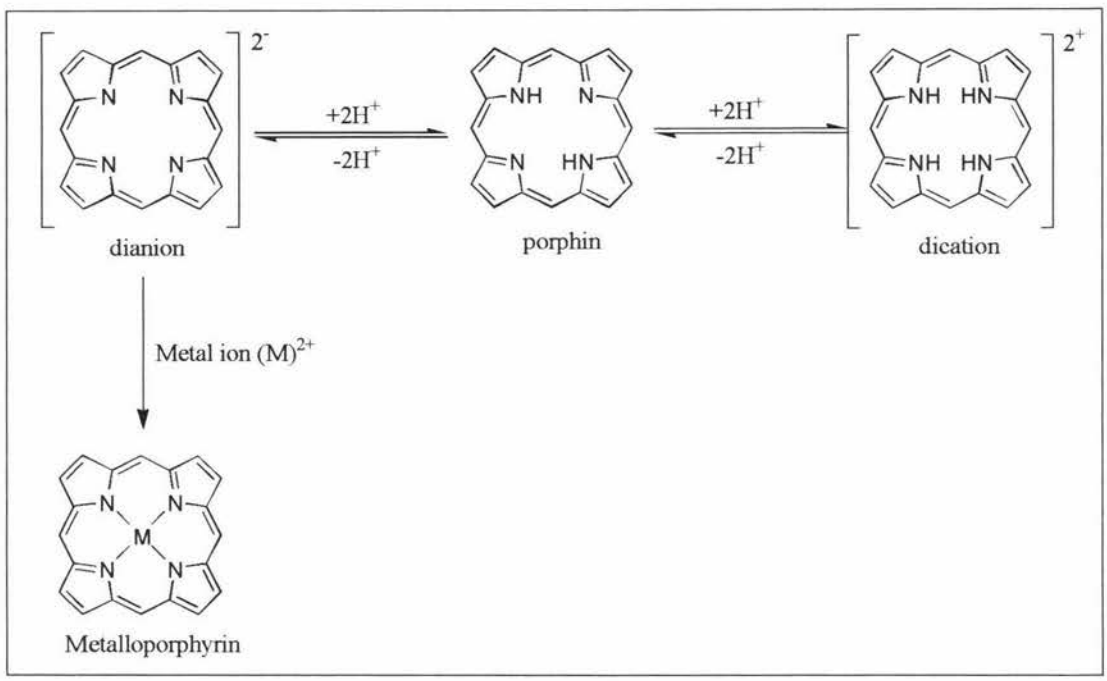

Figure 1.3

The acid-base chemistry of the porphin 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 π-π^* and n-π^* 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 ^{1}H 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.

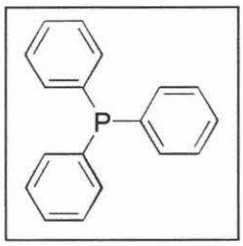

Figure 1.4

The triphenylphosphine molecule.

Triphenylphosphine (PPh_3) has been described by some authors as one of the most important ligands in transition metal chemistry[2] and one of the most widely used ligands in coordination chemistry.[3] PPh_3 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, PPh_3 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.

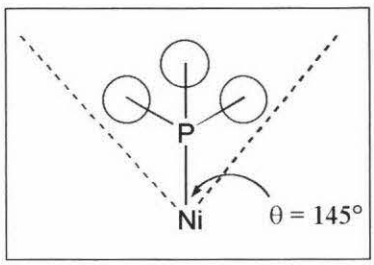

Figure 1.5

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.

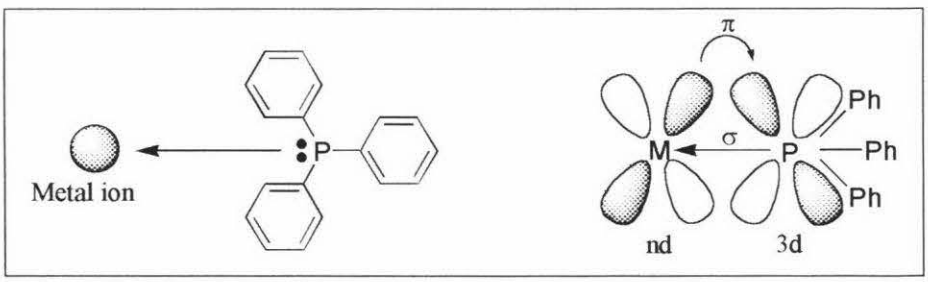

Figure 1.6

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 [$RhCl(PPh_3)_3$] 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. $[RhCl(PPh_3)_3]$ 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).

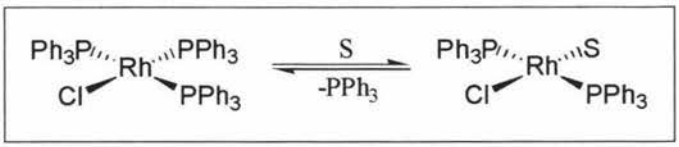

Figure 1.7

The formation of the solvated $[RhCl(PPh_3)_2S]$ complex.

The catalytic cycle is then initiated by the oxidative addition of H_2 to $[RhCl(PPh_3)_2S]$, 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.

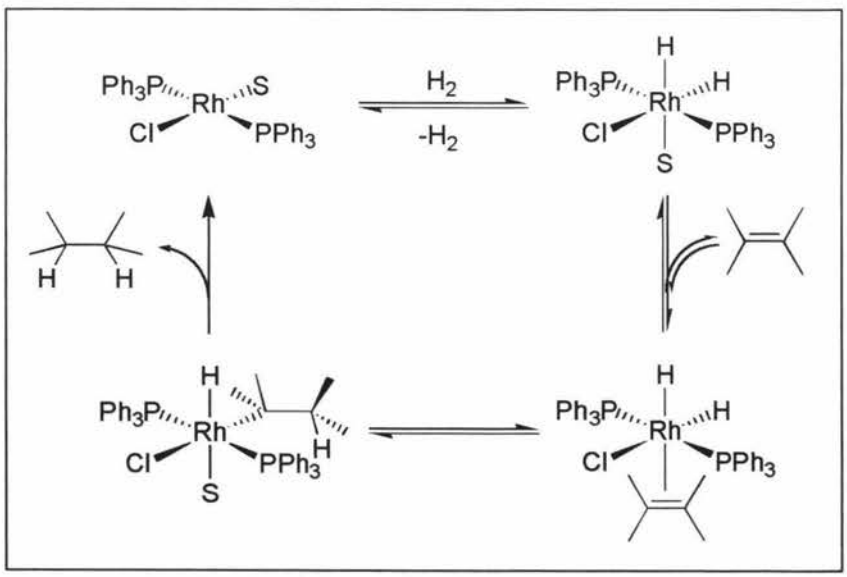

Figure 1.8

Simplified catalytic cycle of the hydrogenation of an alkene by species derived from $[RhCl(PPh_3)_3]$.

The size of the R groups on the alkene used in the above catalytic cycle is also important. For the $[RhCl(PPh_3)_3]$ 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 $[RhCl(PPh_3)_3]$ 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.

Reaction Type.	Catalyst
Hydrogenation	$[RhCl(PPh_3)_3]$, $[IrH(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_2]$
Hydroformylation	$[RhH(CO)(PPh_3)_3]$, $[CoH(CO)_3PPh_3]$, $[RhCl(CO)(PPh_3)_2]$
Hydrosilation	$[NiCl_2(PPh_3)_2]$, $[Pd(PPh_3)_4]$
Oxidation	$[Pt(PPh_3)_4]$, $[IrCl(CO)(PPh_3)_2]$
Polymerisation	$[(\pi\text{-}C_3H_6)Ni(PPh_3)]$

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 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 maybe be bi-,[20, 23] tri-,[21, 33] or even tetra[21] 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.

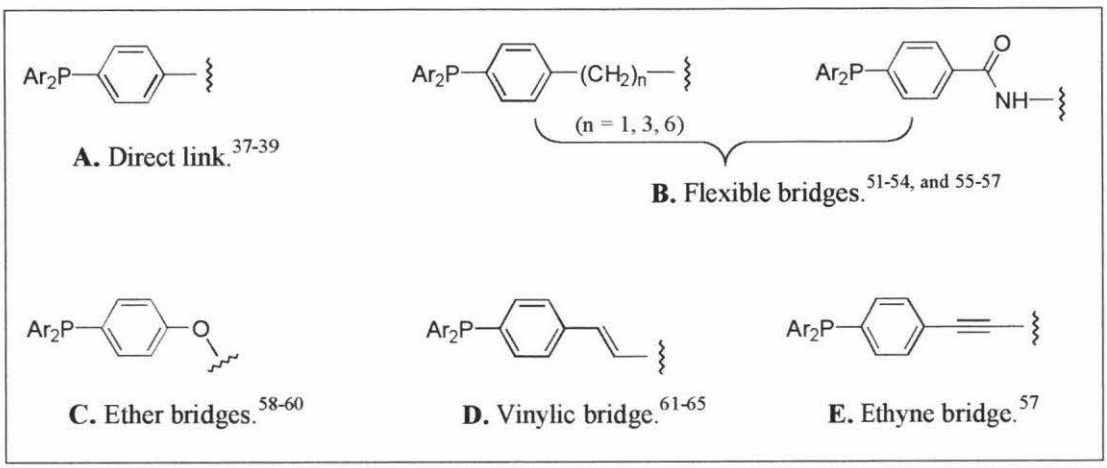

Figure 1.9

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

form its corresponding phosphorus ylide. This ylide then reacts with a carbonyl compound to form the vinylic bridge.

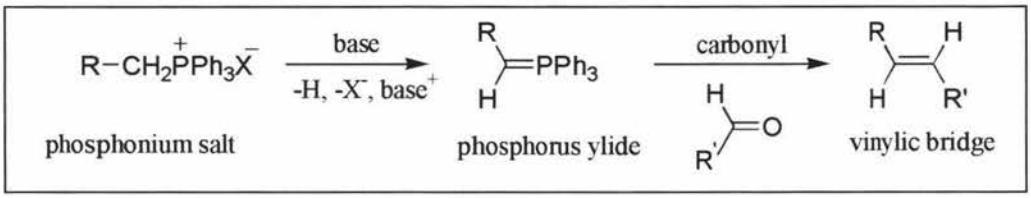

Figure 1.10

The Wittig reaction.

In theory, the nature of the R groups will have an influence on the stereospecificity. If R is an electron withdrawing substituent, then the thermodynamic *trans* product is favoured. This *trans* product is also more sterically favoured. If R is an electron donating substituent, then the kinetic *cis* product is favoured. However, in practice, mixtures of both the *cis* and *trans* isomers are formed with one isomer more abundant than the other, so an isomerisation step is often required to convert the mixture to the *trans*-isomer exclusively.

An example of a tertiary aryl phosphine containing a vinylic bridge *via* the Wittig reaction is that of Zhmurova *et al.*[61] They reacted benzothiazole phosphorus ylide with 4-(diphenylphosphino)benzaldehyde to form the product shown in the figure below.

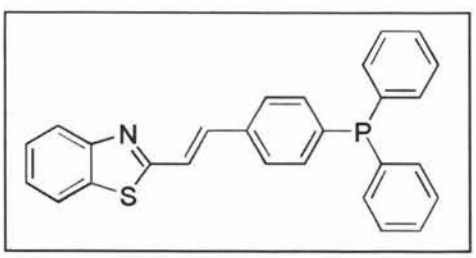

Figure 1.11

An early example of a phosphine with a vinylic bridge.

1.3.3 Porphyrin-functionalised phosphines (phosphinoporphyrins).

To date, there are only a small number of phosphinoporphyrins in the literature. In 1995, Märkl *et al.*[39] reported the synthesis of the first such phosphinoporphyrin. This

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 $W(CO)_5THF$, giving the first such reported porphyrin containing a bound transition metal complex fragment.

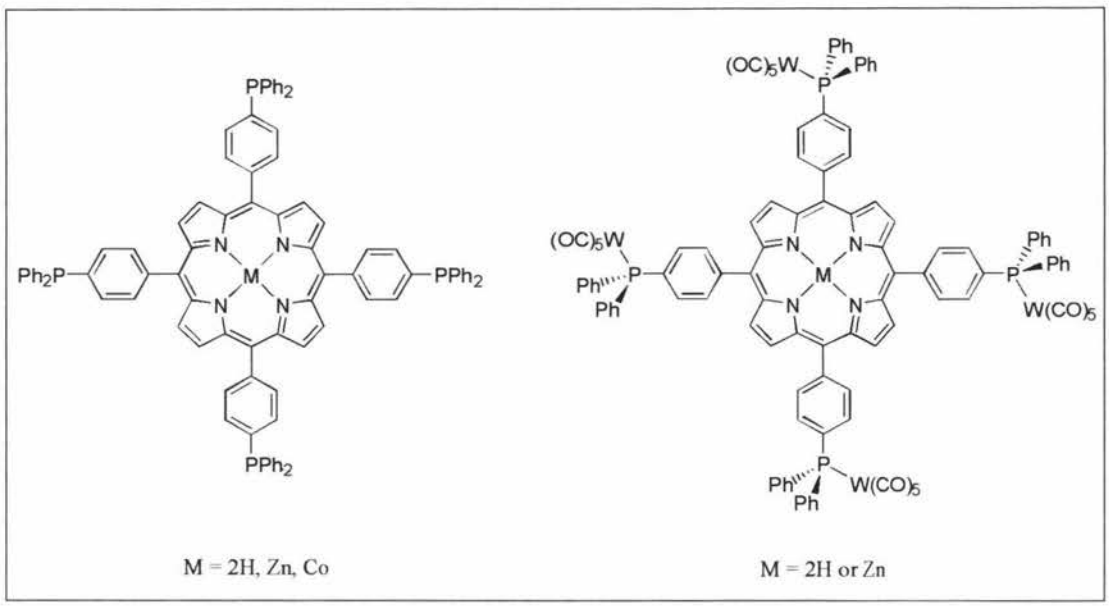

Figure 1.12

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.

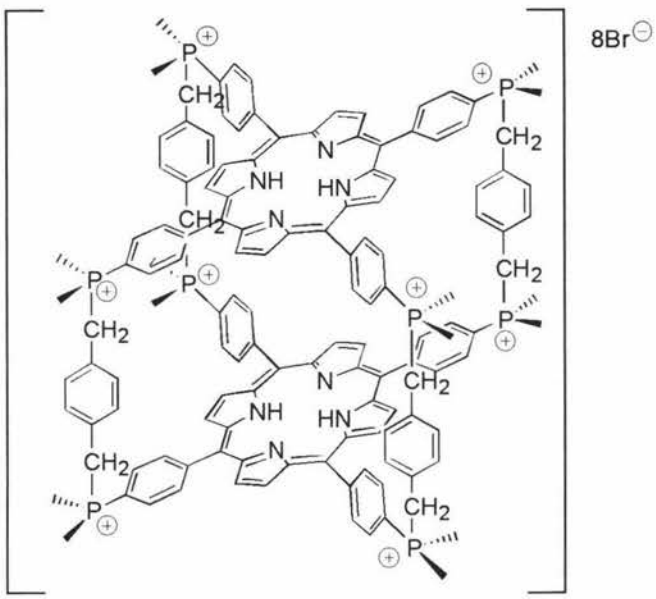

Figure 1.13

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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