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# Advances in Polyaromatic and Ferrocenyl Phosphine Chemistry 

by

## Andrew Lake

A Doctoral Thesis

Submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of
Loughborough University

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#### Abstract

Condensation of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ with a range of polyaromatic substituted secondary amines afforded a new set of "hybrid" phosphine ligands of the type $\left\{\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}$ and $\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2} \mathrm{CH}_{3} \quad(\mathrm{R}=$ various planar aromatic groups). The coordination chemistry of these new mono and bidentate ligands towards a range of transition metal centres including $\operatorname{Mo}(0), \mathrm{Au}(\mathrm{I}), \mathrm{Rh}(\mathrm{I})$, $\mathrm{Ni}(\mathrm{II}), \mathrm{Pd}(\mathrm{II}), \mathrm{Pt}(\mathrm{II})$ and $\mathrm{Ru}(\mathrm{II})$ was investigated. Ditertiary phosphines of the form $\left\{\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}$ were found to be capable of bridging two transition metal centres in addition to forming rare examples of nine-membered cis- and transchelate complexes. Single crystal X-ray analysis of these coordination compounds revealed several types of inter- and intramolecular packing interactions (including a $\mathrm{C}-\mathrm{H} \cdots \mathrm{Pt}$ interaction and slipped intermolecular $\pi \cdots \pi$ stacking), and also confirmed the rare trans-diphosphine coordination mode. Fluorescent emission measurements have been undertaken on these new tertiary phosphines and their coordination compounds, and these luminescent properties are discussed. A preliminary investigation into the chemosensory behaviour of selected compounds has been undertaken.

Using $\mathrm{RPCH}_{2} \mathrm{OH}\left(\mathrm{RP}=\mathrm{Ph}_{2} \mathrm{P}, \mathrm{Cy}_{2} \mathrm{P}\right.$ or $\mathrm{AdP}=1,3,5,7,-$ tetramethyl $-2,4,8-$ trioxa $-6-$ phosphaadamantane) as a versatile precursor, a range of ferrocenyl ( Fc ) tertiary phosphines have been prepared from a selection of primary and secondary amines. The coordination chemistry of these new mono and bidentate ligands towards several transition metal centres including $\mathrm{Cr}(0), \mathrm{Mo}(0), \mathrm{Au}(\mathrm{I}), \mathrm{Rh}(\mathrm{I}), \mathrm{Ru}(\mathrm{II}), \mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ was investigated. In particular, the previous chemistry was expanded to prepare several new diferrocenyl phosphines of the form $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PR}\right) \mathrm{CH}_{2}\right\}_{2}$. In a similar manner to their polyaromatic counterparts, these ditertiary phosphines were found to be capable of coordination through both bridging and cis- / trans-chelating modes. Notably, single crystal X-ray analysis was used to confirm the formation of an extremely rare example of a dimeric trans, trans $\left.-[\mathrm{Rh}(\mathrm{CO}) \mathrm{Cl} \text { \{phosphine }\}_{2}\right]_{2}$ complex; thought to be the first crystallographically characterised metallacycle containing an $\mathrm{Rh}_{2} \mathrm{Fe}_{4}$ arrangement of metal centres. In addition to this $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PR}\right) \mathrm{CH}_{2}\right\}_{2}$ chemistry, a rare example of a triferrocenyl ditertiary


phosphine, $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$, was prepared, as well as a macrocyclic ditertiary ferrocenyl phosphine, $\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2}$. The coordination chemistry of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$ led to the formation of two unusual examples of pentametallic diphosphine coordination complexes with a $\mathrm{Fe}_{3} \mathrm{Au}_{2}$ and $\mathrm{Fe}_{3} \mathrm{Ru}_{2}$ arrangement of metal centres. The development of a new phosphinoamine, $\left(\mathrm{Ph}_{2} \mathrm{P}\right)_{2} \mathrm{NCH}_{2} \mathrm{Fc}$, and a new ferrocenyl iminophosphine, $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2} \mathrm{Fc}$, are also discussed, in addition to a brief investigation of their coordination chemistry. Electrochemical measurements have also been undertaken on these ferrocenyl ligands and their respective coordination compounds (when purity, yield and stability would allow), and their redox chemistry discussed.

A series of novel phosphorus(III) containing ligands of the forms (R) $\mathrm{N}_{\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}}$ and (R) $\mathrm{NHCOCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}(\mathrm{R}=$ functionalised planar aromatic or ferrocenyl group) have been prepared. The phosphines were found to readily coordinate several transition metals including $\operatorname{Pt}(\mathrm{II}), \mathrm{Pd}(\mathrm{II})$ and $\mathrm{Ru}(\mathrm{II})$ to form a series of new cischelate and bridged bimetallic complexes. Analysis by single crystal X-ray diffraction revealed several types of inter- and intramolecular hydrogen bonding within the molecular structures of the phosphines and their coordination compounds, including the formation of several intermolecular 1D chains and the presence of an intramolecular $\mathrm{N}-\mathrm{H} \cdots \mathrm{N}$ bond, which forces a "scorpion-like" conformation.

Keywords: Tertiary phosphine, Mannich based condensation, Ferrocenyl compounds, Coordination chemistry, Late-transition metals, Trans-spanning diphosphines, X-ray crystallography, Electrochemical studies, Luminescent studies, Chemosensors.

## Dedication

Dedicated to Paula, my parents Jenny and Michael, and my grandparents Jean and John for their love and support.

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## ABBREVIATIONS AND SYMBOLS

| A | Angström unit ( $10^{-10} \mathrm{~m}$ ) |
| :---: | :---: |
| abs. | absolute |
| atm | atmospheres |
| Ar | Aryl ring |
| arom. | aromatic |
| b | broad |
| BOC | tert-Butyloxycarbonyl |
| bpy | 2,2'-bipyridine |
| Bs | broad singlet |
| ca. | circa |
| $\mathrm{CDCl}_{3}$ | Deuterated chloroform |
| $\mathrm{CHCl}_{3}$ | Chloroform |
| CHN | Carbon, Hydrogen, Nitrogen elemental analysis |
| $\mathrm{cm}^{-1}$ | Wavenumber |
| cod | Cycloocta-1,5-diene |
| COSY | COrrelation SpectroscopY |
| cot | cyclooctene |
| CSD | Cambridge Structural Database |
| CT | Charge Transfer |
| Cy | Cyclohexyl, $\mathrm{C}_{6} \mathrm{H}_{11}$ |
| p-cym | $\eta^{6}-p-\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Pr}$ |
| Cytop | 1,3,5,7,-tetramethyl-2,4,8-trioxa-6-phospha-adamantane, see also |
|  | PAd. |
| d | days |
| d | doublet |
| dd | doublet of doublets |
| D | Deuterium |
| DCM | Dichloromethane, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ |
| DEPT | Distortionless Enhancement by Polarization Transfer |
| DMF | Dimethylformamide, $\mathrm{HC}(\mathrm{O}) \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}$ |
| DMSO | Dimethyl sulfoxide, $\mathrm{OS}\left(\mathrm{CH}_{3}\right)_{2}$ |
| ee. | enantiomeric excess |


| equiv. | molar equivalent |
| :---: | :---: |
| Et | Ethyl, $-\mathrm{CH}_{2} \mathrm{CH}_{3}$ |
| $\mathrm{Et}_{2} \mathrm{O}$ | Diethyl ether, $\left(\mathrm{CH}_{3} \mathrm{CH}_{2}\right)_{2} \mathrm{O}$ |
| EtOH | Ethanol, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ |
| FAB-MS | Fast Atom Bombardment Mass Spectroscopy |
| Fc | Ferrocenyl, $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}$ |
| FT | Fourier Transform |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| g | grams |
| h | hours |
| HMQC | Heteronuclear Multiple Quantum Coherence |
| HOMO | Highest Occupied Molecular Orbital |
| Hz | hertz |
| ${ }^{i} \mathrm{Pr}$ | Iso-propyl, $-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$ |
| IR | Infra Red spectroscopy |
| J | Coupling constant, Hz |
| LUMO | Lowest Unoccupied Molecular Orbital |
|  | multiplet |
| M | Molarity, mol dm ${ }^{-3}$ |
| MALDI | Matrix-Assisted Laser Desorption / Ionization |
| mm | millimetre, $1 \times 10^{-3}$ meter |
| $\boldsymbol{\mu M}$ | Micro molar, $1 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3}$ |
| mA | milliamp, $1 \times 10^{-3} \mathrm{amp}$ |
| Me | Methyl, - $\mathrm{CH}_{3}$ |
| MeOH | Methanol, $\mathrm{CH}_{3} \mathrm{OH}$ |
| MHz | megahertz, $1 \times 10^{6} \mathrm{~Hz}$ |
| min | minutes |
| mol | mole |
| mmol | millimole, $1 \times 10^{-3} \mathrm{~mol}$ |
| MS | Mass Spectrometry |
| $\mathrm{mV}^{-1}$ | per millivolt, $1 \times 10^{-3} \mathrm{~V}$ |
| m/z | mass-to-charge ratio |
| ${ }^{n} \mathbf{B u}$ | $n$-butyl, - $\mathrm{C}_{4} \mathrm{H}_{10}$ |
| ${ }^{n} \mathrm{BuLi}$ | $n$-butyllithium, $\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{Li}$ |


| nm | nanometer, $1 \times 10^{-9}$ meter |
| :---: | :---: |
| NMR | Nuclear Magnetic Resonance |
| nbd | Norbornadiene, $\mathrm{C}_{7} \mathrm{H}_{8}$ |
| $p$ | para |
| PAd | 1,3,5,7,-tetramethyl-2,4,8-trioxa-6-phospha-adamantane, see also |
|  | Cytop. |
| PET | Photoinduced Electron Transfer |
| Ph | phenyl, - $\mathrm{C}_{6} \mathrm{H}_{5}$ |
| ppm | parts per million |
| ${ }^{i} \mathrm{Pr}$ | iso-propyl, $-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$ |
| Pyr | pyrenyl, - $\mathrm{C}_{16} \mathrm{H}_{9}$ |
| q | quartet |
| RT | Room Temperature |
| s | singlet |
| sept | septet |
| ${ }^{\text {t Bu }}$ | tert-butyl, - $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}$ |
| THF | Tetrahydrofuran, $\left(\mathrm{CH}_{2}\right)_{4} \mathrm{O}$ |
| tht | Tetrahydrothiophene, $\left(\mathrm{CH}_{2}\right)_{4} \mathrm{~S}$ |
| t | triplet |
| TMEDA | Tetramethylethylenediamine, $\left\{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NCH}_{2}\right\}_{2}$ |
| V | Voltage |
| w | weak |
| w/v | Weight by volume |
| w/w | Weight by weight |
| 0 | degrees |
| ${ }^{\circ} \mathrm{C}$ | degrees centigrade |
| $\delta$ | chemical shift |
| $v$ | frequency |
| $\lambda$ | wavelength ( $\mathrm{cm}^{-1}$ ) |
| $\lambda_{\text {em }}$ | emission wavelength ( $\mathrm{cm}^{-1}$ ) |
| $\lambda_{\text {ex }}$ | excitation wavelength ( $\mathrm{cm}^{-1}$ ) |
| $\left\{{ }^{1} \mathbf{H}\right\}$ | proton decoupled |
| Ф | quantum yield, (photons emitted / photons absorbed) |
| \% | Percentage |

Chapter 1
Introduction

### 1.1 Introduction

Phosphorus(III) ligands, particularly tertiary phosphines $\mathrm{PR}_{3}[\mathrm{R}=$ aromatic or an aliphatic substituent], are a fascinating group of compounds that are arguably at the centre of our understanding of modern coordination chemistry and catalysis. ${ }^{3-6}$ The chemistry of this important class of compound is centred around the ability of the central pyramidal phosphorus atom to readily stabilise a huge variety of electron deficient species, particularly transition metal centres, through the formation of new $\mathrm{P}-\mathrm{M}$ bonds. This ability has seen tertiary phosphines play important roles in numerous areas of industrial and academic significance ranging from catalysts for a wide range of organic transformations, ${ }^{7-17}$ to reagents used within selective metal extraction, ${ }^{18-20}$ to building blocks used in supramolecular chemistry, ${ }^{21-23}$ and to therapeutic applications such as anticancer drugs ${ }^{24-28}$ and biological imaging agents. ${ }^{29-31}$ Many tertiary phosphines have been reported to date, and some pertinent examples include the ditertiary phosphines, dppm [bis(diphenylphosphino)methane], ${ }^{16,32-34}$ dppe [1,2-bis(diphenylphosphine)ethane], ${ }^{35-}$ 38 dppp [1,3-bis(diphenylphosphino)propane], ${ }^{39-42}$ dppf $\quad\left[1,1^{\prime}-\right.$ bis(diphenylphosphino)ferrocene $]^{43-46}$ and binap $\quad\left[2,2^{\prime}-b i s(d i p h e n y l p h o s p h i n o)-\right.$ 1,1'binaphthyl] ${ }^{47-49}$ (Figure 1.1).


Figure 1.1 Examples of ditertiary phosphines.

The versatility / significance associated with tertiary phosphines, orientates from two key areas;
i) The ease with which R substituents attached to the central phosphorus atom can be controllably varied.
ii) The influence that these R groups have upon the intrinsic properties of the resulting phosphines, such as steric and electronic effects, bite angle (for ditertiary phosphines), solubility and chirality.

As a result, phosphines can be readily tailored to suit specific applications, simply by the controlled variation of their R substituents. For example, all of the ditertiary phosphines shown in Figure 1.1 contain two $\mathrm{Ph}_{2} \mathrm{P}-$ moieties, and yet, by just varying the remaining R substituent their coordination chemistry, and thus their catalytic properties, are notably different. ${ }^{16,17,32,33,36,50,51}$ For example, Zou et al. ${ }^{16}$ recently reported that whilst dppm, dppe, dppp, dppf and binap were all able to catalyse the conjugated addition of aryl boronic acid to N,N-dimethylacrylamide (Equation 1.1), the structure of the diphosphine had a remarkable influence upon the selectivity and yield of the resulting saturated product (1.1).


When diphosphines capable of forming stable chelate complexes were used (dppp, dppf, binap), $\mathbf{1 . 1}$ was obtained in excellent selectivity and yield over its unsaturated counterpart (1.2) [ca. 99:1 (1.1:1.2), 93\% respectively], whilst comparatively low selectivity and yields [ca. 77:23 (1.1:1.2), 42\% respectively] were observed when more constrained diphosphines were applied (dppm and dppe). Zou suggested that this enhanced selectivity and yield was due to the formation of stable chelate complexes during the catalytic cycle when dppp, dppf or binap were used, which in turn lowered the occurrence of a coordinately unsaturated Rh species which lead to the formation of $\mathbf{1 . 2}$. ${ }^{16}$

The ability to controllably vary the R substituents attached to a phosphorus atom is therefore key to influencing the properties of the resulting phosphine. As a consequence, many methods have been developed over the years to selectively incorporate different R substituents around a phosphorus centre, such as free radical addition and nucleophilic substitution. These strategies have been extensively reviewed by McAuliffe, ${ }^{52}$ Gilheany and Mitchell, ${ }^{53}$ and more recently by Quin, ${ }^{54}$ Woollins, ${ }^{55}$ Allen, ${ }^{56}$ Smith and Downing. ${ }^{6}$

In addition to the above methods, we ${ }^{1,4,21-23,57-60}$ and others ${ }^{7,61-64}$ have shown a phosphorus based Mannich transformation to be a particularly efficient and versatile route towards catalytically and coordinatively important tertiary phosphines. This synthetic strategy, as outlined in Equation 1.2, involves reaction of a hydroxymethyl tertiary phosphine synthon $\mathrm{R}_{2} \mathrm{PCH}_{2} \mathrm{OH}\left[\mathrm{R}_{2} \mathrm{PCH}_{2} \mathrm{OH}\right.$ readily preformed ${ }^{7,58,60}$ or prepared in-situ ${ }^{61,62,65}$ from equimolar amounts of $\left(\mathrm{CH}_{2} \mathrm{O}\right)_{n}$ and $\left.\mathrm{R}_{2} \mathrm{PH}\right]$ with an aromatic or aliphatic amine of choice. This has routinely allowed the preparation of both functionalised mono- and di-tertiary phosphines, depending upon the stoichiometry used.


Equation 1.2

In addition to its versatility, this synthetic procedure offers many advantages over classical methods of tertiary phosphine synthesis, as reactions are usually performed in one-pot, are high yielding, and involve cheap, commercially available starting materials. ${ }^{60}$ Some pertinent examples of tertiary phosphines recently prepared by this method are shown in Figure 1.2. ${ }^{7,21,58,61,65}$

1.3

1.6

1.4

1.5


1.7

Figure 1.2 Tertiary phosphines prepared via Mannich based condensation.

Given the general significance of tertiary phosphines, the remainder of this chapter will seek to review previously reported tertiary phosphine compounds that are relevant to this research, thereby focusing upon novel tertiary phosphines bearing polyaromatic groups, such as anthracene and pyrene, as well as ferrocenyl substituents. During each section common synthetic strategies will be discussed, in addition to highlighting key coordination compounds and relevant applications.

### 1.2 Tertiary Phosphines Bearing Anthracenyl or Pyrenyl Groups

Surprisingly, given the general significance of phosphorus, ${ }^{6,55,56}$ and the importance of pyrenyl $\left(-\mathrm{C}_{16} \mathrm{H}_{9}\right)$ and anthracenyl $\left(-\mathrm{C}_{14} \mathrm{H}_{9}\right)$ groups within non-phosphorus based chemistry, ${ }^{66-73}$ relatively few examples of tertiary phosphines bearing anthracenyl and pyrenyl moieties have been reported to date. Of those that have been reported, many display novel coordination ${ }^{3,65,74-79}$ and luminescent properties. ${ }^{65,76,77,80-85}$ The versatility of anthracene and pyrene within tertiary phosphine synthesis can be readily illustrated by some of the previous examples of compounds reported in the literature. In these cases, the anthracenyl and pyrenyl groups are commonly employed as substituents directly bonded to phosphorus, ${ }^{74,75,82,86-88}$ as rigid backbones for accessing mono- and ditertiary phosphines ${ }^{65,77-79,84,85}$ or as
substituents indirectly bound to phosphorus through an alkyl or aryl tether (Figure 1.3). ${ }^{76,80,81,83,89,90}$

1.7

1.8

1.9

Figure 1.3 Examples of anthracenyl and pyrenyl tertiary phosphines.

Over the years, a variety of synthetic strategies, such as condensation, ${ }^{65,76,77,79,84}$ nucleophilic substitutions ${ }^{78,85}$ and peptide couplings, ${ }^{89}$ have been used to prepare tertiary phosphines bearing anthracenyl and pyrenyl substituents. For example, tertiary phosphines with a $\mathrm{P}-\mathrm{Ar}(\mathrm{Ar}=$ anthracenyl or pyrenyl) connectivity have been routinely prepared via phosphorylation reactions, which involve, treatment of polyaromatic groups with an organometallic base (e.g. $\left.{ }^{n} \mathrm{BuLi}\right)$ followed by reaction of the resulting salt with a halophosphine. ${ }^{74,75,86,87,91}$ Recently, Hu et al. used this procedure to prepare the pyrenyl-ditertiary phosphine 1.8 , in good yield (75\%) (Scheme 1.1). ${ }^{74}$


Scheme 1.1
Yamaguchi et al. also used this methodology to prepare the tri-anthracenyl monophosphine 1.10, in reasonable yield (59\%) (Scheme 1.2). ${ }^{87}$

1.10

Scheme 1.2

In contrast, the alkyl linked mono- and ditertiary phosphines $\mathbf{1 . 1 1}$ and $\mathbf{1 . 1 2}$ were prepared, in reasonable yield (41 and 71\% respectively), by the reaction of premetalated $\mathrm{PHPh}_{2}$ with the respective alkyl halides (Figure 1.4). ${ }^{79,80}$



Figure 1.4

More functionalised tertiary phosphines bearing anthracenyl and pyrenyl substituents have also been reported in the literature. Zhang et al. reported the preparation of the hexadentate $\left(\mathrm{P}_{2} \mathrm{~N}_{4}\right)$ ditertiary phosphine $\mathbf{1 . 1 3}$ (Equation 1.3). ${ }^{78}$ The phosphine was prepared, in reasonable yield (57\%), by treatment of the preformed dipyridenyl amine with $\mathrm{Ph}_{2} \mathrm{PLi}$ (Equation 1.3).

1.13

Equation 1.3

In contrast, Xing et al. described the preparation of the chiral ditertiary phosphine 1.14, in excellent yield (94\%), by peptide coupling of the commercially available chiral diphosphine, (3R,4R)3,4-bis(diphenylphosphine)-pyrrolidine (Pyrphos), with 1-pyrenebutyric acid in the presence of the peptide coupling reagent DCC (dicyclohexylcarbodiimide) (Equation 1.4). ${ }^{89}$

1.14

Jeon et al. ${ }^{76}$ reported the preparation of a similarly substituted pyrene appended monophosphine 1.15, in low yield (22\%). The ligand was prepared via consecutive condensation reactions, as shown in Scheme 1.3.



### 1.15

Scheme 1.3 The preparation of 1.15. a) $\mathrm{K}_{2} \mathrm{CO}_{3}, 18$-crown- $6, \mathrm{CH}_{3} \mathrm{CN} / \mathrm{H}_{2} \mathrm{O}$, reflux; b) isobutylchloroformate $/ \mathrm{NEt}_{3}, 2$-pyrenylmethylamine $\cdot \mathrm{HCl} / \mathrm{NEt}_{3} \mathrm{CH}_{2} \mathrm{Cl}_{2}$, rt.

The anthracene appended phosphines $\mathbf{1 . 1 6}{ }^{77}$ and $\mathbf{1 . 7}{ }^{79,84}$ were prepared by Zhang et al. in good yield ( 73 and $54 \%$ respectively), via the aminolysis of the appropriate secondary amines with $\mathrm{Ph}_{2} \mathrm{PCl}$ (1 equiv. 1.16 and 2 equiv. 1.7) (Equation 1.5). In both cases $\mathrm{NEt}_{3}$ was used to scavenge HCl from the reaction mixture. ${ }^{77,79,84}$


Equation 1.5

Further work by Zhang and co-workers ${ }^{65}$ described the preparation of the ditertiary phosphine 1.17. The ligand was synthesised by Mannich based condensation of the appropriate secondary amine with $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, prepared in-situ from $\mathrm{PHPh}_{2}$ and $\left(\mathrm{CH}_{2} \mathrm{O}\right)_{\mathrm{n}}$ (Equation 1.6).


Equation 1.6
Moreover Wolf et al. ${ }^{83}$ recently prepared the pyrene appended monophosphine ether 1.18, in good yield (81\%), by reaction of 4-bromobutylpyrene with deprotonated $2-$ diphenylphosphinophenol (Equation 1.7).


The coordination chemistry of tertiary phosphines bearing anthracenyl and pyrenyl groups is varied, due to the diverse range of phosphines available. Monophosphines for example, have been found to readily stabilise a variety of transition metal centres of varying oxidation states and coordination numbers, through the formation of new P-M bonds. ${ }^{76,77,80,81,83,86,88}$ For example, Muller et al. reported a diverse family of anthracenyl monophosphine $\mathrm{Au}(\mathrm{I})$ and $\mathrm{Pt}(\mathrm{II})$ complexes that display this simple monodentate $\mathrm{P}-\mathrm{M}$ coordination mode. ${ }^{88}$ One example from this series is the two coordinate $\mathrm{Au}(\mathrm{I})$ complex $\mathbf{1 . 1 9}$, which was prepared in good yield (72\%) by reaction of $\mathbf{1 . 1 0}$ with an equimolar amount of $\mathrm{Au}\left(\mathrm{SMe}_{2}\right) \mathrm{Cl}$ (Equation 1.8).

1.10

1.19

Equation 1.8

More functionalised monophosphines bearing anthracenyl and pyrenyl groups have also been found to coordinate in a P-monodentate manner. ${ }^{75,77}$ For example, Zhang et al. ${ }^{77}$ recently found that the two-coordinate gold complex $\mathbf{1 . 2 0}$ could be readily prepared (yield $81 \%$ ) by reaction of $\mathrm{Au}\left(\mathrm{SMe}_{2}\right) \mathrm{Cl}$ with an equimolar amount of $\mathbf{1 . 1 6}$, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (Equation 1.9).

1.16

1.20

Equation 1.9

In contrast, Jeon et al ${ }^{76}$ and Wolf et al. ${ }^{81,83}$ both recently reported the functionalised monophosphines $\mathbf{1 . 1 5}$ and $\mathbf{1 . 1 8}$ to coordinate transition metal centres in a hemilabile cis $-\mathrm{P}, \mathrm{X}[\mathrm{X}=\mathrm{S}(\mathbf{1 . 1 5})$ or $\mathrm{O}(\mathbf{1 . 1 8})]$ manner. In the case of $\mathbf{1 . 1 5}$, Jeon et al ${ }^{76}$ reported that reaction of two equivalents of the monophosphine with half an equivalent of $[\mathrm{Rh}(\mathrm{nbd}) \mathrm{Cl}]_{2}(\mathrm{nbd}=$ norbornadiene $)$, or one equivalent of $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{PF}_{6}$, yielded the symmetrical cis-M-P,P,S,S complexes $\mathbf{1 . 2 1}$ and $\mathbf{1 . 2 2}$ in excellent yield ( $96 \%$ in both cases) (Figure 1.5). ${ }^{76}$


1.22

Figure 1.5

The hemilabile nature of $\mathbf{1 . 1 5}$ within both complexes $\mathbf{1 . 2 1}$ and $\mathbf{1 . 2 2}$ was confirmed by displacement of the thio-ether sulfur atoms of $\mathbf{1 . 1 5}$ with $\mathrm{CO}(1.23)$ or $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ (1.24), to afford the monodentate $P, P$ complexes $\mathbf{1 . 2 3}$ and 1.24 in excellent yield (100 and $92 \%$ respectively) (Figure 1.6). In the case of the fluorescent $\mathrm{Cu}(\mathrm{I})$ complexes $\mathbf{1 . 2 2}$ and 1.24, the change in coordination mode had a significant effect upon the luminescent properties. ${ }^{76}$

1.23
1.24

Figure 1.6

Similarly, Wolf et al. reported the bidentate-P,O ruthenium halide complexes $\mathbf{1 . 2 5}$ $\mathbf{1 . 2 7}$ of the phosphine pyrene ether $\mathbf{1 . 1 8}$ (Scheme 1.4). ${ }^{81,83}$ Complexes $\mathbf{1 . 2 5}$ and $\mathbf{1 . 2 6}$ were prepared, in low yield (38 and $39 \%$ respectively), by reaction of two equivalents of $\mathbf{1 . 1 8}$ with 1 equivalent of $\mathrm{RuX}_{3} \cdot \mathrm{nH}_{2} \mathrm{O}[\mathrm{X}=\mathrm{Cl}(\mathbf{1 . 2 5})$ or $\mathrm{Br}(\mathbf{1 . 2 6})]$. The iodo complex 1.27 was prepared, in excellent yield (94\%), by chloride substitution of $\mathbf{1 . 2 5}$ with NaI .


Scheme 1.4

As was the case with complexes of $\mathbf{1 . 1 5}$, the hemilabile nature of $\mathbf{1 . 1 8}$ was highlighted by a further reaction. In all three cases, exposure of $\mathbf{1 . 2 5}$ - $\mathbf{1 . 2 7}$ (in $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ to $\mathrm{CO}(1 \mathrm{~atm})$ resulted in displacement of the weakly coordinated ether oxygen of $\mathbf{1 . 1 8}$ by CO , to form the $t t-\mathrm{RuX}_{2}(\mathrm{CO})_{2}(\mathbf{1 . 1 8})_{2}$ complexes $\mathbf{1 . 2 8} \mathbf{- 1 . 3 0}$ (Scheme 1.5). These kinetic products were thought to isomerise, upon removal of the

CO atmosphere, to form the thermodynamic products cct- $\mathrm{RuX}_{2}(\mathrm{CO})_{2}(\mathbf{1 . 1 8})_{2}(\mathbf{1 . 3 1}-$ 1.33) (Scheme 1.5). ${ }^{81,83}$ This change in coordination mode, upon exposure to CO, in all three cases had a significant effect upon the luminescent properties of the pyrene moieties (vide infra).


In contrast to mono-tertiary phosphines, ditertiary phosphines bearing anthracenyl and pyrenyl groups have been found to routinely chelate or bridge transition metals in a trans-P,P manner. ${ }^{65,78,79,84,85,89}$ For example, the anthracene bridged ditertiary phosphine $\mathbf{1 . 1 2}$ was found to react with an equimolar amount of $\mathrm{AgClO}_{4}$ to afford the trans-spanned $\mathrm{Ag}(\mathrm{I})$ complex 1.34, in good yield $74 \%$ (Equation 1.10). ${ }^{79}$ The transspanning nature of $\mathbf{1 . 1 2}$ was confirmed by single crystal X-ray analysis, which shows the bite angle of $\mathbf{1 . 1 2}$ to be only $2^{\circ}$ less than the ideal angle for that of a trans disposition of groups. ${ }^{79}$


Equation 1.10

Xu et al. also reported the diamino analogue $\mathbf{1 . 7}$ of $\mathbf{1 . 1 2}$ to behave in a similar transspanning arrangement upon reaction with $\mathrm{Cu}(\mathrm{I}), \mathrm{Ag}(\mathrm{I})$ and $\mathrm{Au}(\mathrm{I})$ to afford the twoand three-coordinate complexes $\mathbf{1 . 3 5} \mathbf{- 1 . 3 7}$ (Scheme 1.6). ${ }^{79,84}$ However in these cases, the trans-disposition of phosphorus atoms was not close to the idealised angle for a trans-disposition of groups following single crystal X-ray analysis [bite angle $153.97^{\circ} \mathbf{1 . 3 5}, 169.90^{\circ} \mathbf{1 . 3 6}$ and $\left.171.60^{\circ} 1.37\right]$. Complexes $\mathbf{1 . 3 5}$ and 1.36 were prepared, in good yield ( $75 \%$ in both cases), by reaction of 1.7 with an equimolar amount of $\left[\mathrm{Cu}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{ClO}_{4}(\mathbf{1 . 3 5})$ or $\mathrm{AgClO}_{4}$ (1.36). The three-coordinate $\mathrm{Au}(\mathrm{I})$ complex 1.37, was prepared in excellent yield (92\%) by reaction of 1.7 with an equimolar amount of $\mathrm{Au}\left(\mathrm{SMe}_{2}\right) \mathrm{Cl}$. Furthermore in the case of $\mathbf{1 . 3 5}$ and $\mathbf{1 . 3 6}$, a rare $\eta^{6}$-interaction was also observed between the anthracenyl group and the metal centre, which was thought to have an effect upon the luminescent properties of these complexes.


Scheme 1.6

Interestingly Zhang et al. ${ }^{65}$ found that incorporation of an additional carbon between the N and P atoms of $\mathbf{1 . 7}$, to give $\mathbf{1 . 1 7}$, had a significant effect upon the coordination chemistry. Compound $\mathbf{1 . 1 7}$ afforded three new examples of rare bimetallocyclophane complexes 1.38 - 1.40, in good yield $>90 \%$, by reaction with $\left[\mathrm{M}_{\left.\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{4}\right] \mathrm{ClO}_{4}[\mathrm{M}}\right.$ $=\mathrm{Cu}(\mathrm{I})$ or $\mathrm{Ag}(\mathrm{I})]$ or $\mathrm{Au}\left(\mathrm{SMe}_{2}\right) \mathrm{Cl}$, in a 1:1 stoichiometry (Equation 1.11).


It has been suggested that the preparation of these rare dimeric complexes is driven by intermolecular $\pi \cdots \pi$ stacking between the neighbouring anthracene units of coordinated ligands. The occurrence of this $\pi \cdots \pi$ stacking interaction was supported by single crystal X-ray analysis of $\mathbf{1 . 3 8}$, which showed a distance of $3.6 \AA$ between the neighbouring anthracene rings [c.f. interlayer separation within graphite, 3.45 Å]. ${ }^{92}$

Similar work by Holliday et al. ${ }^{85}$ also allowed for the preparation of a bimetallocycle 1.43 through the coordination of an anthracenyl ditertiary phosphine. Complex 1.43 was prepared in two steps (Scheme 1.7); firstly the "condensed" rhodium complex 1.42 was prepared in excellent yield $(>99 \%)$ by reaction of $\mathbf{1 . 4 1}$ with $\left[\mathrm{RhCl}(\cot )_{2}\right]_{2}$. Once prepared, $\mathbf{1 . 4 2}$ was reacted with $\mathrm{CH}_{3} \mathrm{CN}$, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, to afford $\mathbf{1 . 4 3}$ in a quantitative yield due to the efficient displacement of the ether oxygen atom by $\mathrm{CH}_{3} \mathrm{CN}$ in 1.41.


The preparation of ditertiary phosphines, such as $\mathbf{1 . 1 2}$ and 1.17 , capable of coordinating transition metal centres in a trans $-\mathrm{P}-\mathrm{M}-\mathrm{P}$ manner are of particular interest since they frequently show high activity for many catalytic processes. ${ }^{3}$ This activity is thought to result from the ability of such phosphines to form key reaction intermediates within a catalytic cycle, for a low energy debt, due to their inherent flexibility and wide range of available $\mathrm{P}-\mathrm{M}-\mathrm{P}$ bite angles. ${ }^{3,93,94}$ Some of the most noteworthy and recent examples of trans-spanning ditertiary phosphine are shown in Figure 1.7. Transphos is considered to be the first example of a ditertiary phosphine that was specifically designed to trans-span transition metal centres, and was reported in the 1970 's by Venanzi et al. ${ }^{3,95,96}$ The rigid phenanthrene backbone of Transphos was thought to be responsible for the ligand's trans-coordinating nature, particularly in square planar complexes with $\operatorname{Pt}(\mathrm{II})$ and $\mathrm{Pd}(\mathrm{II})$. Complexes of Transphos were comprehensively studied during the 1970 - 1980's as hydroformylation, hydrogenation and oligomeristion catalysis, with some success. ${ }^{95}$ Since then a number of other "iconic" ditertiary phosphines capable of transspanning metal centres have been reported, including SPANphos, ${ }^{97-100}$ Xantphos. ${ }^{101-}$ ${ }^{107} \mathrm{BisBi},{ }^{3,93,108}$ and Trap. ${ }^{109-113}$



BISBI


Trap

Figure 1.7 Some examples of trans-chelating diphosphine ligands.

### 1.2.1 Luminescent Properties of Anthracenyl and Pyrenyl Tertiary Phosphines

The need to selectively detect and monitor small molecules and ions continues to attract a great deal of interest from a variety of disciplines including; chemistry, biology, clinical biology and environmental science. ${ }^{14-120}$ This wide ranging curiosity, undoubtedly stems from the involvement of such species in essential biological, environmental and industrial processes, and is driven by the endeavours of scientists to control and understand these processes further. For example, a means of selectively monitoring small biologically relevant molecules, such as ATP (adenosine triphosphate), could lead to a greater understanding of the mechanisms that make a cell work ${ }^{114,115,121,122}$ whilst the ability to quickly and accurately measure the levels of $\mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Ca}^{2+}$ and $\mathrm{Mg}^{2+}$ within a sample of blood at the scene of an accident, could save lives, as tailored intravenous serums could be prepared prior to the casualties arrival at hospital. ${ }^{14,115}$ Although there are currently numerous analytical methods available that can routinely detect cations, anions and small molecules, such as: flame photometry, neutron activation analysis, mass spectroscopy, NMR, etc. ${ }^{119}$ The majority of these methods are expensive and require
technical expertise to maintain, run, and interpret, as well as often being completely remote from the environment of interest (not capable of real time / in-situ monitoring). It has therefore been desirable to develop alternatives to these more familiar analysis methods. ${ }^{114,116,123}$ Intriguingly, devices based around specifically designed molecules that provide a particular response in the presence of a target analyte, have been shown to offer distinctive advantages in terms of sensitivity, selectivity, response time and cost, over their more traditional counterparts ${ }^{81,114,119,123}$ and these specifically designed molecules have been termed chemosensors since Czarnik's initial use of the term in 1993. ${ }^{124,125}$

The basic schematic design of a chemosensor is depicted in Figure 1.8, and can be summarised into three components; ${ }^{116-120}$
i) A binding site - responsible for selectively coordinating / binding the target analyte.
ii) Signalling moiety or transducer - responsible for converting coordination events at the binding site, at the molecular level, into measurable properties that can be monitored on the macroscopic level.
iii) A linker - usually an alkyl, aryl or peptide group that connect the two aforementioned subunits, however this group is not essential.


Figure 1.8 Schematic illustration of a molecular sensor.

One common chemosensor design strategy is to employ polyaromatic groups as the signalling moiety, thereby tailoring the recognition response of the chemosensor
towards variations in absorbance or fluorescence; such moieties are termed fluorophores. Two widely used fluorophores are anthracene ${ }^{66-69,71,126-128}$ and pyrene, ${ }^{70-73,129,130}$ due to their naturally high quantum yields ( $\varphi$, number of photons emitted / number of photons absorbed), ease of derivatisation and commercial availability. As a result, several of the previously discussed phosphine complexes bearing anthracenyl and pyrenyl groups display chemosensory properties.

The $\mathrm{Cu}(\mathrm{I})$ complexes $\mathbf{1 . 2 2}$ and $\mathbf{1 . 2 4}$ of the pyrene appended hemilabile phosphine 1.15, have been shown to display fluorescence-sensitive binding properties towards various halides (Figure 1.9). ${ }^{76}$ In the absence of any halide ions the fluorescent emission spectra of $\mathbf{1 . 2 2}$ and $\mathbf{1 . 2 4}$ both revealed strong excimer emissions at $\lambda_{\max } 475$ $\mathrm{nm}\left(\lambda_{\text {ex }} 345 \mathrm{~nm}\right.$ ). The intensity of the excimer emission was found to be slightly larger for $\mathbf{1 . 2 4}$, compared to $\mathbf{1 . 2 2}$; an effect attributed to stronger interactions between the neighbouring pyrene fluorophores within $\mathbf{1 . 2 4}$, due to its "more-open" structure. ${ }^{76}$ Interestingly both $\mathbf{1 . 2 2}$ and $\mathbf{1 . 2 4}$ displayed a marked change in fluorescent emission upon addition of $\mathrm{Cl}^{-}, \mathrm{Br}^{-}$or $\mathrm{I}^{-}$, with a significant enhancement of the excimer emission at $\lambda_{\max } 475 \mathrm{~nm}$, following the addition of an equimolar amount of halide. This effect was also attributed to an enhancement of the $\pi \cdots \pi$ stacking between neighbouring pyrene group within both complexes. The enhancement was thought to be due to the formation of a chelate complex involving two amide to halide hydrogen bonds (Figure 1.9).


Figure 1.9 Complex 1.24 depicted in its proposed enhanced excimer emitting state, upon halide anion binding $\left(\mathrm{X}=\mathrm{Cl}^{-}, \mathrm{Br}^{-}\right.$or $\left.\mathrm{I}^{-}\right)$.

The occurrence of this binding configuration was supported by ${ }^{1} \mathrm{H}$ NMR titration, which showed $\delta(\mathrm{NH})$ to shift by $c a .2 .5 \mathrm{ppm}$ upfield as a function of increasing $\left.\left[\mathrm{Cl}^{1}\right]\right]^{76}$ Fascinatingly the addition of further equivalents of halide, past this equivalence point, only served to steadily decrease the excimer emissions of $\mathbf{1 . 2 2}$ and 1.24, until they were completely diminished after the addition of 100 equivalents. This decrease in intensity was suggested to be due to the additional anions disrupting the perceived hydrogen bond complex by the formation of individual amide-halide hydrogen bonds. As a result, $\mathbf{1 . 2 2}$ and $\mathbf{1 . 2 4}$ both represent new chemosensors capable of concentration dependent detection of halide anions via variation in excimer emission. ${ }^{76}$

The ruthenium(II) complexes $\mathbf{1 . 2 5} \mathbf{- 1 . 2 7}$ (Scheme 1.8), have also been shown to display luminescent recognition properties, in this instance towards CO. ${ }^{81,83}$ As previously state, exposure of $\mathbf{1 . 2 5} \mathbf{- 1 . 2 7}$ to CO was thought to yield the thermodynamic products $\mathbf{1 . 3 1} \mathbf{- 1 . 3 3}$. These various ruthenium complexes were found to have different fluorescent properties, thereby allowing the observed change in luminescence to be used to detect CO. For example, the ruthenium(II) chloride complex 1.25, gave a weak monomeric pyrene emission at $c a . \lambda_{\max } 375 \mathrm{~nm}$ (in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution, $\lambda_{\text {ex }} 350 \mathrm{~nm}$ ); presumably due to CT (charge transfer) between the fluorophores and the $\mathrm{Ru}(\mathrm{II})$ metal centre.

1.31 - 1.33

Scheme 1.8

Upon exposure of $\mathbf{1 . 2 5}$ (in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) to $\mathrm{CO}(1 \mathrm{~atm})$, Wolf and co-workers observed the emergence of a strong excimer emission at $c a . \lambda_{\max } 480 \mathrm{~nm}$, coupled with significantly quenching of the monomeric emission at $c a . \lambda_{\max } 375 \mathrm{~nm}$ and a dramatic visible colour change (raspberry-red to a greenish yellow solution). This drastic change in both absorbance and emission was suggested to be caused by displacement of the weakly coordinated ether oxygen of the hemilabile ligand $\mathbf{1 . 1 8}$ by CO , to form the complexes $t t t-\mathrm{RuX}_{2}(\mathrm{CO})_{2}(\mathbf{1 . 1 8})_{2} \mathbf{1 . 2 8} \mathbf{- 1 . 3 0}$. These kinetic products were thought to isomerise further to the excimer emitting thermodynamic products $\mathbf{1 . 3 1} \mathbf{- 1 . 3 3} .^{81,83}$ Whilst the isomerisation mechanism responsible for this OFF-ON excimer emission is currently unknown, Wolf suggests that the process involves dissociation of CO from the kinetic products $\mathbf{1 . 2 8} \mathbf{- 1 . 3 0}$, with the resulting five-coordinate intermediate being stabilised through the $\pi \cdots \pi$ stacking of the neighbouring pyrene groups, which in turn leads to the observed excimer emission in $\mathbf{1 . 3 1} \mathbf{- 1 . 3 3}$. Nevertheless, these findings show that $\mathbf{1 . 2 5} \mathbf{- 1 . 2 8}$ can act as an effective fluorescent sensor for CO. ${ }^{81,83}$

The bimetallocyclophanes $\mathbf{1 . 3 8}$ and $\mathbf{1 . 4 3}$ (Figure 1.10) are two rare examples of novel anthracenyl ditertiary phosphine complexes that display solution-based chemosensor behaviour towards small molecules, in this instance towards aromatic diisocyanides. ${ }^{65}$ As mentioned, the preparation of these large dimeric complexes was suggested to be driven by intermolecular $\pi \cdots \pi$ stacking between the neighbouring anthracene units of the neighbouring ligands upon coordination. These intramolecular interactions were evident in the fluorescent emission spectra of $\mathbf{1 . 3 8}$ and 1.43, which contained characteristic excimer emission at $\lambda_{\max } 435$ and 442 nm respectively (in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions). ${ }^{65,85}$

1.38

1.43

Figure 1.10

In the case of 1.38, fluorescence was found to be significantly enhanced following the addition of 1,4 -benzenediacetonitrile, with a maximum increase in excimer emission being observed upon addition of two equivalents of diisocyanide. This fluorescent enhancement was thought to be caused by incorporation of the second 1,4-benzenediacetonitrile molecule into the centre of the macrocyclic cavity in 1.38. ${ }^{65}$ Scheme 1.9 depicts the suggested enhancement process where initially copolymer 1.38a is formed via substitution of the perchlorate counterions with the cyano groups of the first 1,4-benzeneacetonitrile molecule, followed by formation of the highly fluorescent copolymer 1.38b, upon addition of a second equivalent of 1,4benzeneacetonitrile.



Scheme 1.9
A similar fluorescent enhancement was also observed when an equimolar amount 9,10-anthracenediisocyanide was added to a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{CH}_{3} \mathrm{CN}$ (100:1) solution of 1.43. In this case, a non-polymeric triple layered metallocyclophane was formed, which in turn yielded an enhanced excimer emission at $\lambda_{\max } 466 \mathrm{~nm} .{ }^{85}$ Interestingly the addition of monoisocyanides, alkyl diisocyanides and 1,4-benzeneacetonitrile (in the case of $\mathbf{1 . 4 3}$ ) to a solution of the respective metallocyclophane failed to produce any similar enhancements in excimer emission. This suggests that the photophysical changes observed were selective towards the aromatic diisocyanides studied. ${ }^{65,85}$

The anthracenyl diaminophosphine 1.7 (Scheme 1.10) is another example of a phosphine whose coordination complexes have been used to detect small molecules. ${ }^{79,84}$ As previously stated, $\mathbf{1 . 7}$ was readily prepared by reaction of $9,10-$ ( $N$-propylaminomethyl)anthracene with two equivalents of $\mathrm{Ph}_{2} \mathrm{PCl}$. Once prepared, fluorescent emission spectroscopy revealed $\mathbf{1 . 7}$ to produce a fluorescent monomeric anthracene emission at $\lambda_{\max } 438 \mathrm{~nm}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution $\left(\lambda_{\text {ex }} 362 \mathrm{~nm}\right.$ ). ${ }^{84}$ Upon reaction
of 1.7 with $\mathrm{AgClO}_{4}$ the very weakly-emissive complex 1.36 was prepared; its nonemissive behaviour being attributed to fluorescence quenching caused by CT between the anthracenyl fluorophore and the metal centre. Interestingly the fluorescent properties of the chromophore were subsequently restored by ligand substitution of the $\eta^{6}$-anthracenyl group of complex $\mathbf{1 . 3 6}$ with one equivalent of phosphine $\left(\mathrm{PR}_{3}\right)$. The degree of the restored fluorescence was found to be related to the cone angle of the newly coordinating phosphine, with the smallest cone angle producing the greatest enhancement; $\mathbf{1 . 3 8}>\mathbf{1 . 3 9}>\mathbf{1 . 4 0}$ (Scheme 1.11). This On/Off Off/On fluorescent behaviour of ligand $\mathbf{1 . 7}$ and its silver complexes, was termed a "molecular light switch effect" and was suggested to be exploited two-fold; firstly as a means of selectively probing for phosphines and secondly for the detection of silver ions. ${ }^{84}$


$\underset{+\mathrm{PR}_{3}}{ }$

1.38, $\mathrm{PR}_{3}=\mathrm{PBu}_{3}$
1.39, $\mathrm{PR}_{3}=\mathrm{HPPh}_{2}$
1.40, $\mathrm{PR}_{3}=\mathrm{PPh}_{3}$


Wavelength, nm.

Scheme 1.10 The preparation of $\mathbf{1 . 3 8} \mathbf{- 1 . 4 0}$ (left) and the fluorescence emission spectra of 1.7, 1.36, and 1.38-1.40 (right).

Compound $\mathbf{1 . 1 6}$ (Scheme 1.11) is the final example of an anthracenyl-phosphine whose coordination can be exploited in order to detect small molecules and ions. ${ }^{77}$ In
a similar manner to 1.7 , the monophosphine was prepared by aminolysis of $9-(N-$ propylaminomethyl)anthracene with one equivalent of $\mathrm{Ph}_{2} \mathrm{PCl}$, and emitted a strong monomeric anthracenyl emission centred around $\lambda_{\mathrm{em}} 415 \mathrm{~nm}$, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution. The reaction of $\mathbf{1 . 1 6}$ with an equimolar amount of $\mathrm{Au}\left(\mathrm{SMe}_{2}\right) \mathrm{Cl}$ yielded the twocoordinate gold(I) chloride complex $\mathbf{1 . 2 0}$ (Scheme 1.11), which displayed a significantly enhanced fluorescence of the monomeric emission. This enhancement was suggested to be due to an inhibition of a PET (Photoinduced Electron Transfer) process present between the anthracene unit and the phosphorus atom, upon coordination of the gold(I) centre.


Sceme1.11

Subsequent treatment of $\mathbf{1 . 2 0}$ with $\mathrm{AgClO}_{4}$ and reaction with acetonitrile, pyridine or triphenylphosphine sulfide afforded the novel $\mathrm{Au}(\mathrm{I}) \eta^{2}$-anthracene complexes 1.41 1.44 (Scheme 1.11). The fluorescent emissions of $\mathbf{1 . 4 1} \mathbf{- 1 . 4 4}$ were all found to be significantly weak, by comparison with $\mathbf{1 . 2 0}$ or $\mathbf{1 . 1 6}$, owing to the formation of a CT process between the $\mathrm{Au}(\mathrm{I})^{+}$and the anthracene fluorophore. Interestingly, when solutions of 1.41 and 1.44 were treated with an equimolar amount of $\mathrm{PPh}_{3}$, the intensity of the emission centred around $\lambda_{\text {em }} 415 \mathrm{~nm}$, was significantly increased, suggesting inhibition of the CT process. As a result $\mathbf{1 . 1 6}$ could be used as a
chemosensor towards the detection of $\mathrm{Au}(\mathrm{I})$ ion, whilst 1.41 and $\mathbf{1 . 4 4}$ could be used to indicate the presence of molecules, such as $\mathrm{PPh}_{3} .{ }^{77}$

### 1.3 Ferrocenyl Tertiary Phosphines

The ferrocenyl group $\left[\mathrm{Fc}=\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{Fe}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{4}\right)\right]$ continues to play an important role in the design of new ligands, particularly those containing phosphorus atoms. ${ }^{46,131-133}$ One plausible reason for this success, is the ease with which the cyclopentadienyl rings of the Fc moiety can be functionalised with phosphorus containing substituents. As a result, ferrocene and its derivatives have been routinely used as building blocks in the preparation of an array of functionalised phosphines, ${ }^{134-140}$ diphosphines, ${ }^{141-145,145,146}$ polyphosphines, ${ }^{147-149}$ and chiral ${ }^{150-153}$ or macrocyclic ${ }^{154}$ phosphorus ligands (Figure 1.11). To date, bis(diphenylphosphino)ferrocene (dppf) possibly remains the most iconic example of a phosphorus(III) based ligand containing the Fc moiety, and its coordination chemistry ${ }^{43-46,155}$ and catalytic ${ }^{16,17,36,156}$ properties have been extensively studied.

1.45
1.46

1.47

1.48

Figure 1.11 Examples of ferrocenyl phosphines.

As would be expected, due to the diversity of reported ferrocenyl phosphines, many synthetic strategies towards such organometallic ligands have been developed. ${ }^{5,131,133}$ One synthetic strategy that is commonly employed during the preparation of ferrocenyl phosphines with a $\mathrm{Fc}-\mathrm{P}$ connectivity is the phosphorylation of the cyclopentadienyl groups via treatment with an organometallic base e.g. ${ }^{n} \mathrm{BuLi}$ followed by reaction of the resulting salt with a halophosphine. This strategy has routinely allowed for the preparation of both symmetrical ${ }^{5,157-161}$ and
unsymmetrical ${ }^{133,147,151,152,162}$ mono- and poly-phosphines. Song et al. ${ }^{161}$ use this methodology to good effect to prepare the symmetrical, chiral ditertiary phosphine 1.49 (Equation 1.12).


Equation 1.12

Another method of preparing ferrocenyl phosphines with a $\mathrm{Fc}-\mathrm{P}$ connectivity is to react adequately derivatised cyclopentadienyl salts with an iron(II) halide. For example, the ditertiary phosphine $\mathbf{1 . 5 0}$ was prepared by Broussier and co-workers in moderate yield (46\%), by reaction of $\mathbf{1 . 5 1}$ with half an equivalent of $\mathrm{FeCl}_{2}$ (Equation $1.13) .{ }^{5}$


Equation 1.13

In contrast, ferrocenyl phosphines that do not have a $\mathrm{Fc}-\mathrm{P}$ connectivity, such as the diphosphine 1.52 (Equation 1.14), have been routinely prepared via common organic reactions between phosphines and appropriately derivativised ferrocenyl compounds e.g. peptide coupling ${ }^{14,136,139,140}$ and condensation reactions. ${ }^{57,163}$ For example, 1.52 (Equation 1.14) was prepared via the condensation of the acid chloride, 1,1bis(chlorocarbonyl)ferrocene, with two equivalents of the known aminophosphine, 3-aminopropyldiphenylphosphine. ${ }^{163}$

1.52 Equation 1.14

The considerable interest in ferrocenyl phosphines is, however, not just due to synthetic curiosity. Many of these organometallic compounds have been shown to possess interesting coordination ${ }^{46,57,135,141,144,154,164}$ and catalytic properties. ${ }^{133,137,143,151,152,161}$ The coordination chemistry of ferrocenyl phosphines is diverse, with many compounds being shown to be capable of coordinating a huge variety of transition metal centres of varying oxidation state and coordination number. In particular, ferrocenyl monophosphines have been routinely shown to stabilise a variety of transition metal centres with coordination numbers of 2 to $6,{ }^{135,159,164,165}$ whilst ferrocenyl di- and poly-phosphines have frequently been shown to bridge ${ }^{14,43,46,57,144}$ or chelate ${ }^{14,57,141,142,149,153,154,161,163,166,167}$ transition metal centres (Figure 1.12). This versatility is presumably due to the array of ferrocenyl monoand poly-phosphines available, and the ability of the ferrocenyl group to readily change its conformation in order to match the steric demands of the surrounding environment. ${ }^{46}$


Figure 1.12 Examples of coordination compounds of ferrocenyl phosphines.

Two ferrocenyl ditertiary phosphines that have recently been reported to display interesting coordination chemistry are $\mathbf{1 . 5 3}^{153}$ and $\mathbf{1 . 4 5}^{14}$ (Figure 1.13), as both compounds were found to be capable of trans-spanning various transition metal
centres. Compound 1.53, and its previously reported derivatives, ${ }^{109,110}$ are of particular significance as they represent the only examples of chiral ditertiary phosphines that are known to be capable of trans-spanning transition metal centres. This has relevance in asymmetric catalysis. ${ }^{111-113,153}$

1.53

1.45

Figure 1.13 Trans-spanning ditertiary ferrocenyl phosphines.

In particular, the reaction of $\mathbf{1 . 4 5}$ with $\mathrm{PdCl}_{2}(\mathrm{cod})$ afforded a trans-palladium(II) dichloride complex with a bite angle only $8^{\circ}$ less than the idealised bite angle for the trans disposition of groups as determined by single crystal $\mathrm{X}-$ ray analysis ( $\mathrm{P}-\mathrm{Pd}-\mathrm{P}$ $\left.171.9^{\circ}\right) .{ }^{14}$ Analysis of the molecular structure of trans $-\operatorname{PdBr}_{2}(\mathbf{1 . 5 3})$ and trans$\operatorname{RhCl}(\mathrm{CO})\{\mathbf{1 . 5 3}\}$, revealed comparatively smaller bite angles ( $\mathrm{P}-\mathrm{M}-\mathrm{P} 163.6$ and $161.1^{\circ}$ respectively). ${ }^{110}$

As previously discussed (Section 1.2), ditertiary phosphines capable of transspanning transition metal centres, such as $\mathbf{1 . 4 5}$ and $\mathbf{1 . 5 3}$, have significant catalytic potential due to their ability to access a large range of bite angles for a low energy debt. ${ }^{93}$ Consequentially, the catalytic properties of $\mathbf{1 . 4 5}$ and $\mathbf{1 . 5 3}$ have been investigated. ${ }^{14,111-113,153}$ Recently, $\mathbf{1 . 5 3}$ has been shown to capable of catalysing the asymmetric hydrogenation for various $N-, 2-$ or 3 -substituted indoles, to a high enantiomerselectivity due to the "chiral pocket" created during the catalytic cycle. ${ }^{153}$ The diphosphine was showed to be particularly effective in the conversion of $\mathrm{N}-$ tosylate ( $\mathrm{Ts}=\mathrm{CH}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{SO}_{2}-$ ) protected 3-methylindole, with the corresponding indoline being generated to a high enantiomeric excess (ee 98\%) and yield (up to 98\% conversion) (Equation 1.15).


Equation 1.15

The diphosphine $\mathbf{1 . 4 5}$ has also been shown to be a good catalyst, in this case for the Suzuki-Miyaura cross coupling of phenylboronic acid to 4-substituted aryl bromides (Equation 1.16). ${ }^{14}$ The phosphine proved to be particularly effective at the cross coupling of aryl bromides bearing $-\mathrm{NO}_{2}$ and $-\mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ groups, with the biphenyl product being prepared quantitatively in both cases.



Equation 1.16 The Suzuki-Miyaura cross coupling of aryl bromides and phenylboronic acid $\left[\mathrm{Y}=-\mathrm{NO}_{2},-\mathrm{C}(\mathrm{O}) \mathrm{CH}_{3},-\mathrm{OCH}_{3}\right.$ and $\left.-\mathrm{CH}_{3}\right] .{ }^{14}$

In addition to the trans-spanning phosphines $\mathbf{1 . 4 5}$ and $\mathbf{1 . 5 3},{ }^{14,109,110,153}$ many other organic transformations have been shown to be catalysed by coordination complexes containing non trans-spanning ferrocenyl phosphines ${ }^{5,133}$ such as hydrogenation, ${ }^{45,146,152,153}$ hydroformylation, ${ }^{168}$ cyanation, ${ }^{169,170}$ amination, ${ }^{171,172}$ cyclopropanation ${ }^{161}$ and ethylene oligomerisation, ${ }^{137}$ in addition to various $\mathrm{C}-\mathrm{C}$ bond forming reactions. ${ }^{5,5,136,140,143}$ For example, the ditertiary ferrocenyl phosphine $\mathbf{1 . 4 7}$ (Equation 1.17) was recently shown to catalyse the asymmetric hydrogenation of various alkenes and ketones in excellent selectivity (ee up to 99.7\%) (Equation 1.17). ${ }^{152}$


Equation 1.17

### 1.3.1 Electrochemical Properties of Ferrocenyl Tertiary Phosphines

In addition to the catalytic and coordination properties of ferrocenyl phosphines, these organometallic compounds also attract much attention due to their redox active metal centre $\left[\mathrm{Fc} \leftrightarrow\left[\mathrm{Fe}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\right]^{+}\right.$or ferrocenium ion $\left.\left(\mathrm{Fc}^{+}\right)\right]$, which allows for the study of electronic communication for the development of new electronic materials and devices. ${ }^{57,135,173-175}$ For example, the Fc moiety is ideal as a transducer within chemosensor design (see Section 1.2.1), as it allows coordination responses at the binding site to be tailored towards changes in the electrochemical properties of the compound. ${ }^{176,177,177-182}$ Some recent examples of non-phosphorus containing electrochemical sensors are shown in Figure 1.14. ${ }^{177,177-182}$ Compound 1.56 (Figure 1.14), for example, is one of a series of chiral ferrocenyl ureas ( $\mathbf{1 . 5 4} \mathbf{- 1 . 5 7}$, Figure 1.14) that have recently been shown to be a highly efficient electrochemical chemosensor for chiral carboxylate ions. ${ }^{178}$ In the absence of carboxylate, the cyclic voltammograms of $\mathbf{1 . 5 4}-\mathbf{1 . 5 7}$ were found to produce reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox waves [half wave potentials ( $\mathrm{E}_{1 / 2}$ ) ranging between 0.545 to $0.505 \mathrm{~V}, \mathrm{E}_{1 / 2}=\mathrm{E}_{\mathrm{pa}}+\mathrm{E}_{\mathrm{pc}} / 2$ )], in dry $\mathrm{CH}_{3} \mathrm{CN}$ solutions. However, the addition of an equimolar amount of carboxylate caused a significant cathodic shift in the redox waves of $\mathbf{1 . 5 4}-\mathbf{1 . 5 7}$ i.e. wave moved to lower voltages. This cathodic shift in $\mathrm{E}_{1 / 2}$, was attributed to the coordination of the various carboxylate anions to $\mathbf{1 . 5 4} \mathbf{- 1 . 5 7}$ via complementary hydrogen bonding, an effect which was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy $[c a . \Delta \delta(\mathrm{N} H)+4 \mathrm{ppm}]$. In particular, compound $\mathbf{1 . 5 6}$ stood out from the rest of the series of $\mathbf{1 . 5 4} \mathbf{- 1 . 5 7}$, as it was shown to be able to effectively distinguishing between opposite enantiomers of $N$-benzenesulfonyl proline. This ability was thought to be due to variations in binding constants between $\mathbf{1 . 5 6}$ and the two proline enantiomers, leading to a
significant difference in the observed electrochemical potentials i.e. the stronger the binding constant the greater the cathodic shift. ${ }^{178}$


Figure 1.14

In contrast, compound $\mathbf{1 . 5 8}$ (Figure 1.14) was found to be a selective electrochemical chemosensor for $\mathrm{Cu}(\mathrm{II})$ ions. ${ }^{179}$ In the absence of any transition metal ions, the cyclic voltammogram for 1.58, was found to produce a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox wave at $\mathrm{E}_{1 / 2}+0.254 \mathrm{~V}$, in aqueous solution. Addition of $\mathrm{Ni}(\mathrm{II}), \mathrm{Cu}(\mathrm{II}), \mathrm{Zn}(\mathrm{II}), \mathrm{Cd}(\mathrm{II})$ and $\mathrm{Pb}(\mathrm{II})$ cause a significant anodic shift (shifts to higher voltages) relative to the original $\mathrm{E}_{1 / 2}$ of $\mathbf{1 . 5 8}\left[\mathrm{E}_{1 / 2} \mathrm{Ni}(\mathrm{II})+0.152, \mathrm{Cu}(\mathrm{II})+0.218, \mathrm{Zn}(\mathrm{II})+0.111, \mathrm{Cd}(\mathrm{II})+0.110\right.$ and $\mathrm{Pb}(\mathrm{II})+0.268 \mathrm{~V}]$. This anodic shift was suggested to be due to the coordination of the respective cations at the nitrogen atoms of $\mathbf{1 . 5 8}$. ${ }^{179}$ When $\mathrm{Ni}(\mathrm{II}), \mathrm{Cu}(\mathrm{II}), \mathrm{Zn}(\mathrm{II})$, $\mathrm{Cd}(\mathrm{II})$ and $\mathrm{Pd}($ II $)$ [or only $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Cu}($ II $)$ or Cu (II) and $\mathrm{Pd}($ II $)$ ] were added to solutions of $\mathbf{1 . 5 8}$, the resulting redox potential was found to be approximately equal to that induced by $\mathrm{Cu}(\mathrm{II})$ alone $\left[\mathrm{E}_{1 / 2} 0.472 \mathrm{~V}\right]$, thereby suggesting that $\mathbf{1 . 5 8}$ was capable of selectively detecting $\mathrm{Cu}(\mathrm{II})$ over the other cations studied. ${ }^{179}$

Interestingly, only a handful of ferrocenyl phosphine-based compounds capable of acting as chemosensors have been reported, ${ }^{163,175,176}$ and the phosphines in question
are displayed in Figure 1.15. The occurrence of so few examples of this type of chemosensor is somewhat surprising, given the general importance of ferrocenyl phosphines within catalysis and coordination chemistry and suggests that there is significant potential to generate new examples of such compounds.

dppf

1.52

Figure 1.15 Ferrocenyl phosphines capable of acting as electrochemical sensors.

Gholivand ${ }^{175}$ provided the first of these rare examples, through the preparation of a new Zr ion sensitive PVC (poly vinyl-chloride) electrode coating system, which contained the ferrocenyl ditertiary phosphine dppf as the electrochemically active component. The dppf used in this new electrode coating system was prepared via a known literature method, ${ }^{183}$ involving treatment of a lithiated solution of ferrocene with two equivalents of chlorodiphenylphosphine. The electrode coating was prepared by dissolution of dppf, PVC, plasticiser and various additives in THF, followed by evaporation of the solvent, to yield an oily concentrate which was coated onto Pyrex or Teflon tubes. The dried coated tubes were subsequently internally filled with electrolyte and conditioned for 1 d , before the electrical responses of the electrodes towards various aqueous solutions of metal ions was tested. In the majority of cases, the introduction of cations [Cu(II), $\mathrm{Ni}(\mathrm{II}), \mathrm{Cr}(\mathrm{II}), \mathrm{Mn}(\mathrm{II}), \mathrm{Hg}(\mathrm{II})$, $\mathrm{Al}(\mathrm{III}), \mathrm{Co}(\mathrm{II}), \mathrm{Pb}(\mathrm{II}), \mathrm{Cd}(\mathrm{II}), \mathrm{Zn}(\mathrm{II}), \mathrm{Ce}(\mathrm{II}), \mathrm{Y}$ (III) and $\mathrm{Pd}(\mathrm{II})]$ to the dppf coating caused a cathodic shift in the $\mathrm{E}_{1 / 2}$ of the immobilized dppf molecules (values ranged between ca. $\Delta \mathrm{E}_{1 / 2}-0.025$ to $\left.-0.120 \mathrm{~V}\right) .{ }^{175}$ However, by far the most dramatic response was observed upon addition of Zr ions to the electrode system, which revealed a significant shift of $c a . \Delta \mathrm{E}_{1 / 2}-0.350 \mathrm{~V}$ at high Zr concentrations $(0.1$ moldm ${ }^{-3}$ ). This selective response of the dppf electrode towards zirconium ions was proposed to be due to the strong tendency of the immobilised dppf molecules to bind Zr ions. This change in electrical potential, was also found to be concentration
dependent (linear range $1 \times 10^{-1}$ to $1 \times 10^{-7} \mathrm{moldm}^{-3}$ of cation) and allowed the dppfelectrode to be successfully used to determine the concentration of zirconium ions in tap water and standard metal alloys, to an accuracy of $\pm 0.004 \mathrm{M}$. ${ }^{175}$

The bis(phosphine) amide linked ferrocene $\mathbf{1 . 5 2}$ and its transition metal coordination complexes ( $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9 )}$ ) provide the only other examples of phosphine-based ferrocenyl compounds capable of electrosensitive recognition (Figure 1.16). ${ }^{163,176}$

$\mathrm{M}=\mathrm{Mo} 1.66$ $\mathrm{M}=\mathrm{Cr} \quad 1.67$

1.68

1.69

Figure 1.16

As previously noted, compound $\mathbf{1 . 5 2}$ was prepared via condensation of the acid chloride, 1, $1^{\prime}-b i s(c h l o r o c a r b o n y l) f e r r o c e n e, ~ w i t h ~ t w o ~ e q u i v a l e n t s ~ o f ~ 3-~$ aminopropyldiphenylphosphine. ${ }^{163}$ Whilst the coordination complexes 1.66 - 1.69 were prepared either by ligand displacement ( $\mathbf{1 . 6 6}, 1.67$ and 1.69 ) or dimer cleavage (1.68) reactions, involving 1.52 and the respective transition metal precursors. ${ }^{163}$ The electrochemical properties of $\mathbf{1 . 5 2}$ and $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9}$ were all investigated by cyclic voltammetry. Compound $\mathbf{1 . 5 2}$ displayed a single irreversible oxidation potential ( $\mathrm{E}_{\mathrm{pa}}$ ) at $\mathrm{E}_{\mathrm{pa}} 0.440 \mathrm{~V}$ (relative to the $\mathrm{E}_{1 / 2}$ of ferrocene), which was attributed to the ferrocenyl group within the ligand. The irreversible nature of the Fe centre within
1.52 was suggested to be due to a stabilising interaction between the lone pairs of the phosphorus atoms and the positively charged ferrocenium moiety. ${ }^{163,184}$ In contrast, the cyclic voltammograms of $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9}$ all contained reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couples in addition to those of the coordinated metals. ${ }^{163}$ Furthermore, the $\mathrm{E}_{\mathrm{pa}}$ values of 1.66 - $\mathbf{1 . 6 9}$ were found to be significantly anodically shifted (shifts to higher voltages) with respect to that of $\mathbf{1 . 5 2}$. The chemosensory properties of $\mathbf{1 . 5 2}$ and $\mathbf{1 . 6 6}$ - $\mathbf{1 . 6 9}$ were investigated by the addition of $\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{H}_{2} \mathrm{PO}_{4}^{-}$and $\mathrm{HSO}_{4}^{-}$to $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{CH}_{3} \mathrm{CN}$ (1:1) solutions of $\mathbf{1 . 5 2}$ and $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9}$. All five compounds displayed a significant cathodic shift in their Fe oxidation potential ( $\mathrm{E}_{\mathrm{pa}}$ shifted to lower voltages) upon the introduction of the respective anions. This effect was suggested to be due to the formation of two intermolecular hydrogen bonds between the amide hydrogen atoms of $\mathbf{1 . 5 2}$ and $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9}$ and the respective anion, an effect that was confirmed by ${ }^{1} \mathrm{H}$ NMR titration studies. These intermolecular interactions were suggested to allow the bound anions to effectively stabilise the positively charged ferrocenium moieties of $\mathbf{1 . 5 2}$ and $\mathbf{1 . 6 6} \mathbf{- 1 . 6 9}$, through donation of electron density. This donation of charge enhanced the oxidation process, as less energy (or voltage) was required to oxidise $\mathrm{Fe}(\mathrm{II})$ to Fe (III), hence the cathodic shift. This effect (cathodic shift, move to lower voltages) was found to be particularly significant in the case of $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$. As a consequence of these findings, it is apparent that $\mathbf{1 . 5 2}$ and 1.66 - $\mathbf{1 . 6 9}$ could be used to electrochemically detect the presence of anions within organic solutions, through variations in the electrochemical potential of the ferrocenyl redox couple. In contrast, the free ligand $\mathbf{1 . 5 2}$ could also be used to determine the presence of transition metals via phosphorus coordination.

### 1.4 Thesis Aim

Whilst their have been many functionalised tertiary phosphines bearing polyaromatic or ferrocenyl groups reported over the years, comparatively few examples have been prepared via Mannich condensation reactions. As a result, the aim of this research is to investigate the scope of this reaction to prepare new examples of such tertiary phosphines, and to explore their coordination chemistry and physical properties.

## Chapter 2

The Synthesis, Characterisation and Coordination Chemistry of Novel Tertiary Phosphines Bearing Polyaromatic Groups

### 2.1 Introduction

The incorporation of polyaromatic groups, such as anthracene and pyrene, into the design of new molecules has long been used as a means of imparting interesting properties upon the resulting compounds, with phosphines bearing such groups displaying notable catalytic, ${ }^{89}$ coordination ${ }^{74,75,79}$ and luminescent properties. ${ }^{65,77,78,82}$ The versatility of these medium sized polyaromatic groups (anthracene and pyrene) within phosphine synthesis can be readily illustrated by some of the diverse compounds previously reported in the literature. In these cases the aromatic groups are employed as either substituents directly bonded to phosphorus, ${ }^{74,75,82,87}$ a rigid backbone for accessing mono- and di-phosphines ${ }^{65,77,78}$ or as a substituent indirectly bound to phosphorus through an alkyl or aryl tether (Figure 2.1). ${ }^{80,89}$


Figure 2.1 The versatility of anthracene and pyrene groups within phosphine synthesis. ${ }^{65,80,87}$

As discussed in Chapter 1, one area of significant research involving compounds bearing anthracene and pyrene moieties has been aimed towards the development of molecular devices capable of detecting small molecules and ions (Section 1.2.1). Such molecular species are important as they play a fundamental role in several chemical, biological and environmental processes. ${ }^{116,118,119}$ Surprisingly, the design of pyrenyl and anthracenyl bearing molecules capable of this chemosensory behaviour has seldom involved a phosphorus donor atom, presumably due to the ease of incorporation of hard donors, such as nitrogen and oxygen, and the susceptibility
of phosphorus(III) to oxidation. However recent work by Wolf and co-workers has shown that ruthenium(II) complexes, containing a coordinated phosphine pyrene ether, can be used to detect carbon monoxide. ${ }^{81,83}$ This suggests that phosphine ligands, and particularly their coordination complexes, maybe a neglected source of new chemosensory devices. To this end, this chapter describes the preparation of a series of new tertiary phosphines based upon the known cation chemosensors (Figure 2.2 ), ${ }^{128,130,185}$ with the aim of preparing new examples of phosphine based molecular devices via simple chemical modification. The coordination chemistry of these new tertiary phosphines towards $\mathrm{Pt}(\mathrm{II}), \mathrm{Pd}(\mathrm{II}), \mathrm{Ni}(\mathrm{II}), \mathrm{Ru}(\mathrm{II}), \mathrm{Pd}(\mathrm{I}), \mathrm{Rh}(\mathrm{I}), \mathrm{Au}(\mathrm{I})$ and $\operatorname{Mo}(0)$ is described, in addition to the luminescent properties of selected non complexed ligands and their coordination compounds. Finally, a preliminary study into the chemosensory behaviour of four $\mathrm{Pt}(\mathrm{II})$ complexes, towards a series of readily available metal cations, is also discussed.


Figure 2.2 Cation chemosensors.

### 2.2 Preparation and Characterisation of the Ditertiary Phosphines 2.1-2.4

It has been demonstrated that phosphorus based Mannich condensation reactions are an extremely flexible procedure for preparing functionalised phosphines. ${ }^{1,21,23,58,186}$ These procedures routinely involve reaction of a primary or secondary amine with a tertiary phosphine synthon, such as $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}^{21,23}$ To this end, the new ditertiary phosphines 2.1 - 2.4 were prepared, in good yield ( $72-90 \%$ ), by double condensation of $\left\{\mathrm{RCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}\left(\mathrm{R}=\mathrm{Ph}, \mathrm{C}_{10} \mathrm{H}_{7}, \mathrm{C}_{14} \mathrm{H}_{9}\right.$ and $\left.\mathrm{C}_{16} \mathrm{H}_{9}\right)$ with 2 equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ in MeOH at reflux (Equation 2.1). The known secondary amines, $\left\{\mathrm{RCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$, were prepared prior to this condensation reaction by the reductive amination of the respective aromatic aldehyde ( 2 equiv.) with ethylene diamine ( 1 equiv.) (yields ranged between $96-100 \%$ ). ${ }^{128,187}$


Equation 2.1
Compounds 2.2-2.4 were deposited from solution during the course of the reaction, allowing the phosphines to be isolated in high purity (by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR) and yield (range 72 - 90\%). In contrast, $\mathbf{2 . 1}$ did not crystallise and was frequently obtained instead as a viscous oil following complete removal of the solvent. The purity of 2.1, within this isolated oil was, however, considered sufficient to be used directly in coordination studies [purity $90 \%$ (2.1) by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR]. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of 2.1-2.4 (in freeze-thawed $\mathrm{CDCl}_{3}$ ) all exhibited a new phosphorus singlet at $c a$. $\delta(\mathrm{P})-28.0 \mathrm{ppm}$ (Table 2.1), some 18 ppm upfield to that of the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material $\left[\delta(\mathrm{P})-10.0 \mathrm{ppm}\right.$, in $\left.\mathrm{CDCl}_{3}\right]$. All four ditertiary phosphines showed evidence
of aerobic oxidation over the course of several hours, when $\mathrm{CDCl}_{3}$ solutions were left to stand. Careful monitoring of $\mathrm{CDCl}_{3}$ solutions of $\mathbf{2 . 1}$ - $\mathbf{2 . 4}$ over a period of three days, by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, revealed the gradual disappearance of the singlets at $c a . \delta(\mathrm{P})-28.0 \mathrm{ppm}$ and the emergence of new resonances, presumably relating to the respective monoxides and dioxides of $\mathbf{2 . 1} \mathbf{- 2 . 4}[\delta(\mathrm{P}) 13.2-39.7$ $\mathrm{ppm}] .{ }^{188,189}$ This susceptibility to aerobic oxidation may be an important consideration during any investigation of the luminescent properties of $\mathbf{2 . 1} \mathbf{- 2 . 4}$, as the phosphorus(III) and phosphorus(V) species may have different luminescent properties (vide infra). All of the ditertiary phosphines were found to be stable in the solid state. In the case of $\mathbf{2 . 3}$ no oxidation was observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in freeze-thawed $\mathrm{CDCl}_{3}$ ) following exposure of the solid to air for two months.

The ${ }^{1} \mathrm{H}$ NMR spectra (in freeze-thawed $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 1}$ - $\mathbf{2 . 4}$ revealed three characteristic methylene resonances, of equal integral, between $\delta\left(\mathrm{CH}_{2}\right) 2.7-4.4 \mathrm{ppm}$ (Table 2.1). Two of these resonances appeared as singlets and were assigned to the analogous hydrogen atoms within the respective parent amines by comparison with literature values, ${ }^{130,185,187}$ whilst the newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated as a characteristic doublet between $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 3.1-3.4 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 3.2-3.6\right.$ Hz ) (Table 2.1). ${ }^{22,23}$ Furthermore, the absence of a $v_{\mathrm{NH}}$ stretch in the infrared spectra of $\mathbf{2 . 1}$ - $\mathbf{2 . 4}$ confirmed the ternary nature of both nitrogen atoms within the newly formed ditertiary phosphines.

Table 2.1 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ and ${ }^{1} \mathrm{H} \operatorname{NMR}[\delta(\mathrm{H})$ in ppm and $(J)$ in Hz$]$ for 2.1 - 2.4. ${ }^{\text {a }}$

|  | $\delta(\mathrm{P})$ | $\delta\left(\mathrm{NCH}_{2}\right)$ | $\delta\left(\mathrm{RCH}_{2} \mathrm{~N}\right)$ | $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ | ${ }^{2} J_{\mathrm{PH}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{2 . 1}^{\mathrm{b}}$ | -27.8 | 3.64 | 2.71 | 3.21 | 3.6 |
| $\mathbf{2 . 2}$ | -28.2 | 4.00 | 2.78 | 3.36 | 3.6 |
| $\mathbf{2 . 3}$ | -28.1 | 4.41 | 2.77 | 3.11 | 3.2 |
| $\mathbf{2 . 4}$ | -27.7 | 4.23 | 2.85 | 3.26 | 3.2 |
| In freeze-thawed $\mathrm{CDCl}_{3}$ solution. |  |  |  |  |  |
| ${ }^{\mathrm{b}}$ Product found to be $90 \%$ pure by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR using freeze-thawed $\mathrm{CDCl}_{3}$. |  |  |  |  |  |

The fluorescent emission spectra of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ (Figure 2.3) have also been recorded, and are shown along side the emission spectra of their parent amines.


Figure 2.3 Emission spectra of $\left\{\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} / 2.3$ (left) and $\left\{\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} / 2.4$ (right), in dry THF solutions containing analyte ( $5 \mu \mathrm{M}$ ), (slit widths 0.4 mm ). $\lambda_{\text {ex }}$ anthracene derivatives $=370 \mathrm{~nm}$, $\lambda_{\text {ex }}$ pyrene derivatives $=$ 344 nm .

The fluorescent emission spectra of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ both exhibited typical monomer emission bands relating to the respective fluorophores, ${ }^{77,79-81}$ with little change in $\lambda_{\max }$ compared to the emissions of their respective parent amines (Figure 2.3, Table 2.2). ${ }^{116,119,128,187}$ Weak excimer emissions were observed for the parent amines (ca. $\lambda_{\mathrm{em}} 500$ and 440 nm respectively), whilst $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ afforded no excimer emissions at the concentration studied $(5 \mu \mathrm{M})$, suggesting that the introduction of the $\mathrm{CH}_{2} \mathrm{PPh}_{2}$ moieties sterically hinders the formation of excimers. The quantum yield ( $\Phi$, photons emitted / photons absorbed) of $\mathbf{2 . 4}$ was found to be significantly weaker than that of its parent amine, a change that is thought to be due to the incorporation of the $\mathrm{CH}_{2} \mathrm{PPh}_{2}$ moieties (Figure 2.3, Table 2.2). One tentative suggestion for this quenching effect, upon incorporation of the $\mathrm{CH}_{2} \mathrm{PPh}_{2}$ moieties (particularly in the case of 2.4), is an enhancement of the photoinduced electron transfer (PET) process known to occur within similar amino anthracenyl and pyrenyl systems. ${ }^{129,190,191}$

Table 2.2 $\lambda_{\text {max }}(\mathrm{nm})$ and $\Phi$ data for 2.3, 2.4 and their parent amines.

|  | $\lambda_{\max }$ | $\Phi$ |
| :--- | :---: | :---: |
| $\left\{\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$ | $391,414,439,466$ | 0.04 |
| $\mathbf{2 . 3}$ | $393,415,440,469$ | 0.03 |
| $\left\{\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$ | $376,387,396,416$ | 0.82 |
| $\mathbf{2 . 4}$ | $376,387,396,416$ | 0.19 |

$\lambda_{\text {ex }}$ anthracene derivatives $=370 \mathrm{~nm}, \lambda_{\text {ex }}$ pyrene derivatives $=344 \mathrm{~nm}$.

This process leads to the reformation of the ground state of the fluorophore's via a non-radiative decay pathway involving electron transfer from the HOMO of an electron donor (usually an amino group) to the HOMO of an excited fluorophore (Figure 2.4). ${ }^{190}$ It is therefore reasonable to speculate that modification of the amino group may affect the PET process in some manner, in this case enhancing it.


Figure 2.4 PET process involving the HOMO and LUMO of the fluorophores and an external molecular orbital (normally a nitrogen lone pair).

It is unclear why this proposed PET enhancement is not as significant for 2.3, compared to 2.4, suggesting that any change in the PET process is specific to the pyrene fluorophores. ${ }^{192}$ The enhancement of PET for $\mathbf{2 . 4}$ may be a product of better orbital overlap or enhanced intermolecular quenching, however further work is needed to support these suggestions.

The molecular structure of $\mathbf{2 . 4}$ has also been determined by single crystal X-ray diffraction (Section 2.2.1).

### 2.2.1 The Molecular Structure of 2.4

Colourless crystalline plates suitable for single crystal X-ray diffraction were obtained by layering MeOH onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 2.4. The molecular structure of $\mathbf{2 . 4}$ was determined by single crystal X-ray diffraction (Figure 2.5), selected bond lengths and angles are given in Table 2.3.


Figure 2.5 The solid solution of $\mathbf{2 . 4}$ and its oxide $\mathbf{2 . 6}$ [minor component oxide freely refined to $19.77(3) \%$ occupancy, highlighted by dashed bond]. All hydrogen atoms, except $H(2)$ and $H\left(2^{\prime}\right)$, have been omitted for clarity. Symmetry operator for equivalent atoms, ${ }^{\prime}=-\mathrm{x}+2,-\mathrm{y}+1,-\mathrm{z}$.

The molecular structure of 2.4 shows the phosphine lies on a crystallographic inversion centre located at the mid-point of the ethylenediamine backbone. As a consequence, only half of a molecule of $\mathbf{2 . 4}$ and a MeOH molecule of crystallisation
were found within the asymmetric unit. The molecular structure of $\mathbf{2 . 4}$ also revealed the phosphorus atom, $\mathrm{P}(1)$, to be partially oxidised to give a "solid solution" containing 2.4 and its oxide (2.6) [occupancy of minor component oxide freely refined to $19.77(3) \%$ ]. When present, the phosphorus(V) atom was found to adopt a distorted tetrahedral arrangement [C-P-O angles ranged between 111.50(3) $\left.120.50(3)^{\circ}\right]$, whilst the phosphorus(III) atom was found to adopt a distorted trigonal pyramidal geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles [ $\mathrm{C}-\mathrm{P}-\mathrm{C}$ ranged between $100.01(8)-102.49(8)^{\circ}$ (Table 2.3)]. The nitrogen atom, $\mathrm{N}(1)$, was also found to adopt a distorted trigonal pyramidal geometry [sum of component angles $=$ $331^{\circ}$ ]. In the case of the minor component oxide $\mathbf{2 . 6}$, the $\mathrm{P}=\mathrm{O}$ bond length was found to be $1.331(6) \AA$ which, following a search of the CSD (Cambridge Structural Database), was found to be short with respect to $\mathrm{O}=\mathrm{PPh}_{3}\left[\mathrm{O}=\mathrm{PPh}_{3} 1.492 \AA\right] .{ }^{193}$ This short $\mathrm{P}=\mathrm{O}$ bond is probably associated with the occorance of $\mathbf{2 . 6}$ as a minor disorder component. The assignment of $\mathbf{2 . 6}$ was however supported by electron difference mapping and intermolecular bonding (vide infra). When present, the oxygen atom of the $\mathrm{P}=\mathrm{O}$ moiety was also found to form an intermolecular hydrogen bond to the neighbouring MeOH of crystallisation $[\mathrm{O}(1)-\mathrm{O}(2) 2.775(8) \AA, \mathrm{O}(1) \cdots \mathrm{H}(2) 1.94 \AA$, $\left.\mathrm{O}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{O}(1) 171^{\circ}\right]$ (Figure 2.5). Further analysis of the intermolecular packing revealed two $\pi \cdots \cdot \pi$ interactions between neighbouring molecules of 2.4, or 2.6. These involved, a phenyl group on one face [shortest separation $=3.32 \AA$, mean separation $=3.62 \AA$ ] and another pyrene group on the opposite face [shortest separation $=3.45$ $\AA$, mean separation $=3.59 \AA$, c.f. graphite $3.45 \AA$ layer separation] (Figure 2.6). The mean plane of the phenyl group was found to be tilted ( $c a .3 .5^{\circ}$ ) with respect to the neighbouring pyrene group, whilst the two pyrene groups were found to be coplanar.


Figure 2.6 Packing plot for the solid solution of 2.4 and 2.6. Intermolecular $\pi \cdots \pi$ interactions highlighted by the dashed red box.

Table 2.3 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for the solid solution of $\mathbf{2 . 4}$ and 2.6.

| $\mathrm{P}(1)-\mathrm{O}(1)$ | $1.3310(6)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(1)$ | $111.50(3)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8356(18)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | $120.50(3)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.8294(17)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $117.80(3)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.8479(18)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(1)$ | $102.49(8)$ |
| $\mathrm{C}(13)-\mathrm{N}(1)$ | $1.467(2)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $100.01(8)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.472(2)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13) 101.72(8)$ |  |
| $\mathrm{C}(14)-\mathrm{C}\left(14^{\prime}\right)$ | $1.517(3)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1) 110.65(11)$ |  |
| $\mathrm{N}(1)-\mathrm{C}(15)$ | $1.479(2)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14) 110.66(13)$ |  |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.510(2)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(15) 109.21(13)$ |  |
|  |  | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(15) 111.34(13)$ |  |
|  |  | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}\left(14^{\prime}\right) 111.52(17)$ |  |
|  | $\mathrm{N}(1)-\mathrm{C}(15)-\mathrm{C}(16) 112.99(13)$ |  |  |
| Symmetry operation for equivalent atoms, ${ }^{\prime}=-\mathrm{x}+2,-\mathrm{y}+1,-\mathrm{z}$. |  |  |  |

### 2.3 The Chemical Oxidation of 2.3 and 2.4

Following the observed susceptibility of $\mathbf{2 . 1} \mathbf{- 2 . 4}$ to aerobic oxidation in $\mathrm{CDCl}_{3}$ (by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR, Section 2.2) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions (Section 2.2.1), samples of the diphosphine oxides 2.5 and 2.6 were deliberately prepared, in good yield, by treatment of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ (in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) with hydrogen peroxide at ambient temperature (Equation 2.2). In contrast to $\mathbf{2 . 3}$ and $\mathbf{2 . 4} \mathbf{2} \mathbf{2} \mathbf{6}$ was found to be insoluble in common deuterated solvents precluding any NMR measurement, whilst 2.5 was found to be readily soluble only in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 2.5 showed a singlet resonance at $\delta(\mathrm{P}) 26.7 \mathrm{ppm}$, some 40 ppm downfield to that of 2.3, indicating both phosphorus atoms had been oxidised. ${ }^{188,189}$ The ${ }^{1}$ H NMR spectrum [in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ ] of 2.5 contained the anticipated resonances relating to the oxidised diphosphine, with little change in $\delta\left(\mathrm{CH}_{2}\right)$ being observed by comparison with the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 . 3}$.


2.5

2.6

Equation 2.2

The infrared spectra of $\mathbf{2 . 5}$ and $\mathbf{2 . 6}$ both showed characteristically strong $\mathrm{P}=\mathrm{O}$ absorption bands at $v_{\mathrm{P}=\mathrm{O}} 1171$ and $1188 \mathrm{~cm}^{-1}$ respectively. ${ }^{188,189,194}$ The preparation of $\mathbf{2 . 5}$ was further confirmed by single crystal X-ray diffraction (Section 2.3.1).

The fluorescent emission spectra of $\mathbf{2 . 5}$ and $\mathbf{2 . 6}$ (in dry THF) revealed typical monomer emission bands relating to the respective fluorophores by comparison with 2.3 and $\mathbf{2 . 4}$ (Figure 2.7 and Table 2.4). The emissions were, however, found to be
significantly weaker than their diphosphine counterparts. This is presumably due to quenching of the excited state of the respective fluorophore by the newly formed $\mathrm{CH}_{2} \mathrm{P}(\mathrm{O}) \mathrm{Ph}_{2}$ groups. Unfortunately, the origins of such a nonradiative decay process were not apparent following a search of the literature. However, the occurrence of a PET or charge transfer (CT) process should not be ruled out. ${ }^{190}$ The involvement of the $-\mathrm{CH}_{2} \mathrm{P}(\mathrm{O}) \mathrm{Ph}_{2}$ groups in some form of nonradiative decay process was however supported by consecutive fluorescent emission spectra of 2.3 (and 2.4), taken over a period of three hours, which revealed significantly weakened emissions following 1 - 3 h of exposure to air; an effect presumably due to the progressive oxidation of the tertiary phosphine groups within $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ over time (Figure 2.7). This partial oxidation, is also in agreement with the time resolved ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy study previously discussed (Section 2.2).


Figure 2.7 Fluorescence emission spectrum of $\mathbf{2 . 5}$ and the time resolved emission spectra for 2.3 over 3h (in THF); concentration: $5 \mu \mathrm{M}$, $\lambda_{\text {ex }} 370 \mathrm{~nm}$, slit width: 0.4 mm , samples degassed with nitrogen prior to recording emission spectra, samples left to stand in air between measurements.

Table 2.4 $\lambda_{\max }(\mathrm{nm})$ and $\Phi$ data for $2.3-\mathbf{2 . 6}$.

| Compound $^{\text {a,b }}$ | $\lambda_{\text {max }}$ | $\Phi$ |
| :--- | :---: | :---: |
| $\mathbf{2 . 3}^{\mathrm{a}}$ | $393,415,440$ | 0.03 |
| $\mathbf{2 . 5}^{\mathrm{a}}$ | $398,415,437$ | 0.01 |
| $\mathbf{2 . 4}^{\mathrm{b}}$ | $376,387,396,416$ | 0.19 |
| $\frac{\mathbf{2 . 6}^{\mathrm{b}}}{} \quad{ }^{\mathrm{a}} \boldsymbol{\lambda}_{\mathrm{ex}}=370 \mathrm{~nm},{ }^{\mathrm{b}} \lambda_{\text {ex }}=344 \mathrm{~nm}$. | $376,387,396,415$ | 0.05 |

This reduction in fluorescence upon oxidation is some cause for concern, as any potential fluorescence based applications involving the free phosphines would be significantly affected. Coordination of the phosphorus lone pair should offer a means of protection against aerobic oxidation, ${ }^{81,83}$ whilst also allowing $2.1 \mathbf{- 2 . 4}$ to be used as ligands toward the preparation of new phosphorus containing molecular devices. ${ }^{77,84,195}$

### 2.3.1 The Molecular Structure of $\mathbf{2 . 5}$

The molecular structure of $\mathbf{2 . 5}$ was determined from colourless crystalline blocks obtained from a $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ solution of 2.5 (Figure 2.8), selected bond lengths and angles are given in Table 2.5.


Figure 2.8 Molecular structure of 2.5. All hydrogen atoms and $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ molecules of crystallisation have been removed for clarity. Symmetry operator for equivalent atoms ' $=-\mathrm{x},-\mathrm{y}+2,-\mathrm{z}+1$.

The molecular structure of $\mathbf{2 . 5}$ showed the diphosphine oxide to adopt an "open" conformation in the solid state, similar to that displayed by the previously discussed solid solution of $\mathbf{2 . 4}$ and $\mathbf{2 . 6}$ (Section 2.2.1) [ $\mathrm{P}(1) \cdots \mathrm{P}\left(1^{\prime}\right) c a .8 .517$ (2.5) and 8.196 (2.6) $\AA$ ]. The asymmetric unit was found to contain half a molecule of $\mathbf{2 . 5}$ and one and a half molecules of $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ of crystallisation. The phosphorus atom was found to adopt a distorted tetrahedral geometry, as indicated by the relevant $\mathrm{O}-\mathrm{P}-\mathrm{C}$ angles [ $\mathrm{O}-\mathrm{P}-\mathrm{C}$ ranged between $112.27(7)-114.92(7)^{\circ}$ ]. The nitrogen atom adopted a distorted trigonal pyramidal geometry [sum of component angles $=331^{\circ}$ ]. The $\mathrm{P}=\mathrm{O}$ bond length $[\mathrm{P}=\mathrm{O}, 1.4912(11) \AA$ ] was found to compare well with other $\mathrm{P}=\mathrm{O}$ bond
lengths found during a more detailed search of the CSD [74 hits, mean $\mathrm{P}=\mathrm{O} 1.485 \AA$, range of values 1.426 to $1.523 \AA$, c.f. $\mathrm{O}=\mathrm{PPh}_{3} 1.492 \AA$ ]. No inter or intramolecular interactions of note were observed in the molecular structure of 2.5.

Table 2.5 Selected bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ for $\mathbf{2 . 5}$.

| $\mathrm{P}(1)-\mathrm{O}(1)$ | $1.4912(11)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(1)$ | $112.27(7)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8119(15)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | $112.47(7)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.7966(16)$ | $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $114.92(7)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.8217(16)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(1)$ | $106.46(7)$ |
| $\mathrm{C}(13)-\mathrm{N}(1)$ | $1.4632(19)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $100.95(7)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.474(2)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13)$ | $108.89(8)$ |
| $\mathrm{C}(14)-\mathrm{C}\left(14^{\prime}\right)$ | $1.517(3)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $117.35(11)$ |
| $\mathrm{N}(1)-\mathrm{C}(15)$ | $1.475(2)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $109.82(12)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.513(2)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(15)$ | $110.53(13)$ |
|  |  | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(15)$ | $110.35(12)$ |
|  |  | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}\left(14^{\prime}\right)$ | $110.71(17)$ |
|  |  | $\mathrm{N}(1)-\mathrm{C}(15)-\mathrm{C}(16)$ | $112.21(13)$ |

Symmetry operation for equivalent atoms, ${ }^{\prime}=-x,-y+2,-z+1$.

### 2.4 The Coordination Chemistry of 2.1-2.4 to divalent group 10 metals

The coordination chemistry of $\mathbf{2 . 1} \mathbf{- 2 . 4}$ was initially investigated by reaction with a series of readily available Group 10 metal dichlorides, $\mathrm{MCl}_{2}(\operatorname{cod})(\mathrm{M}=\mathrm{Pt}$ or Pd$)$ and $\mathrm{NiCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (Equation 2.3). Ligand displacement of cod from $\mathrm{PtCl}_{2}$ (cod) by an equimolar amount of $\mathbf{2 . 1} \mathbf{- 2 . 4}$, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at ambient temperature, gave the platinum(II) complexes $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$ in reasonable to good yield (range 43 - 87\%) (Equation 2.3).


$\mathrm{R}=$

2.7
$\mathrm{M}=\mathrm{Pd}$
2.11

2.8
2.12

2.9
2.13
2.15

2.14

Equation 2.3

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$ all exhibited a new phosphorus singlet resonance between $\delta(\mathrm{P})-1.3$ to -3.8 ppm (Table 2.6), some 25 ppm downfield from that observed for the free ligands. The new phosphorus resonances were all flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites $\left[{ }^{1} J_{\mathrm{PtP}} 3593-3633 \mathrm{~Hz}\right.$. The characteristically large ${ }^{1} J_{\text {PtP }}$ coupling constant suggests that the platinum(II) dichloride complexes adopt a cis conformation in solution, this was also verified in the solid state by X-ray crystallography. ${ }^{58,186,196}$

Table 2.6 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR [ $\delta$ in ppm, $J$ in Hz ] and FT-IR data $\left(\mathrm{cm}^{-1}\right)$ for 2.7-2.10.

|  | $\delta(\mathrm{P})$ | ${ }^{1} J_{\mathrm{PtP}}$ | $\delta\left(\mathrm{PCH}_{2}\right)$ | ${ }^{3} J_{\mathrm{PtH}}$ | $\delta\left(\mathrm{CH}_{2}\right)$ | $v_{\mathrm{PtCl}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{2 . 7}$ | -1.3 | 3633 | 4.02 | 39.2 | $3.52,3.35$ | 316,290 |
| $\mathbf{2 . 8}$ | -3.6 | 3606 | 4.10 | 40.8 | $3.94,3.97$ | 317,292 |
| $\mathbf{2 . 9}$ | -2.7 | 3593 | 4.11 | 37.6 | $4.26,3.92$ | 318,294 |
| $\mathbf{2 . 1 0}$ | -3.8 | 3620 | 4.11 | 36.0 | $3.99,3.95$ | 316,292 |

The ${ }^{1} \mathrm{H}$ NMR spectra of 2.7-2.10 all contained the anticipated resonances relating to the coordinated ligands (Table 2.6). However, in all four cases, the characteristic $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ resonance appeared as a singlet flanked by broad equidistant satellites $\left[\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 4.02-4.11 \mathrm{ppm}\right]$. This splitting pattern is consistent with platinum(II)
coordination and can be explained as follows; the equidistant satellites are assigned to a ${ }^{3} J_{\mathrm{PtH}}$ coupling [ ${ }^{3} J_{\mathrm{PtH}} 36.0-40.8 \mathrm{~Hz}$ ] whilst the ${ }^{2} J_{\mathrm{PH}}$ couplings, previously observed in the ${ }^{1} \mathrm{H}$ NMR spectra of the free ligands $\left[\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 3.11-3.36 \mathrm{ppm},{ }^{2} J_{\mathrm{PH}}\right.$ $3.2-3.6 \mathrm{~Hz}$, were unresolved when recorded on a Bruker DPX-400 FT spectrometer.

The FT-IR spectra of 2.7-2.10 displayed two characteristic $\nu_{\text {PtCl }}$ absorptions bands between $290-318 \mathrm{~cm}^{-1}$, which is in agreement with values previously reported for cis-platinum(II) dichloride complexes of diphosphines. ${ }^{1,58,186,196}$ The positive ion FAB mass spectroscopy results for $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$ also revealed the expected molecular
 2.10); 867, 967, 1067 and $1115[\mathrm{M}-\mathrm{Cl}]^{+}(2.7$ - 2.10) $\}$. Moreover the elemental analysis results for $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$ were also found to be satisfactory (see Experimental Section). The molecular structures of $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$ have also been determined by single crystal X-Ray diffraction (Section 2.4.1).

In contrast to the platinum chemistry, reaction of $\mathbf{2 . 1} \mathbf{- 2 . 4}$ with an equimolar amount of $\mathrm{PdCl}_{2}(\mathrm{cod})$ in dichloromethane gave impure samples of $\mathbf{2 . 1 1} \mathbf{- 2 . 1 4}$, by solution ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{2 . 1 1} \mathbf{- 2 . 1 4}$ revealed the presence of several major phosphorus-containing species downfield of those of the free ligands $[\delta(\mathrm{P}) 4.2-30.4 \mathrm{ppm}]$. The major species were tentatively assigned to either the cis or trans-isomers of $\mathrm{PdCl}_{2}(\mathbf{2 . 1}$ - 2.4) (possibly monomeric or polymeric). ${ }^{57}$ Further inspection of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the isolated solids, revealed two further doublets at significant downfield shifts [ca. $\delta(\mathrm{P}) 159.0$ and 79.0 $\left.\mathrm{ppm},{ }^{2} J_{\mathrm{PP}} 16 \mathrm{~Hz}\right]$. This, in conjunction with the observation of a new doublet at $\delta\left(\mathrm{CH}_{2}\right) 3.41 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 6.8 \mathrm{~Hz}\right)$ in the ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{2 . 1 1}-\mathbf{2 . 1 4}$, and the time resolved ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy studies discussed for the analogous ferrocenyl complex 3.7 (Section 3.4.1), led us to speculate that $\mathbf{2 . 1 1}$ - $\mathbf{2 . 1 4}$ undergo slow decomposition to give the five membered chelate complex $\mathrm{PdCl}_{2}\left(\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OPPh}\right)_{2}$ by elimination of some, as of yet unidentified, arylamine byproduct(s). ${ }^{57}$ Support for the nonsymmetric nature of this coordinated bidentate phosphorus(III) ligand comes from previous studies with $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OPPh}_{2}$ and, ${ }^{197}$ more recently $\mathrm{RR}^{\prime} \mathrm{POCH}_{2} \mathrm{P}\left(\mathrm{CH}_{2} \mathrm{OH}\right)_{2}\left(\mathrm{R}, \mathrm{R}^{\prime}=\mathrm{Ph}, \mathrm{Cy}\right),{ }^{198}$ which show good agreement with the $\delta(\mathrm{P})$ and ${ }^{2} J_{\mathrm{PP}}$ coupling constants observed. Further characterisation of 2.11-2.14
was hampered by this decomposition process, with numerous attempts to purify the crude material or to prepare crystals suitable for X-ray diffraction proving fruitless.

The synthesis of $\mathbf{2 . 1 5}$ (Equation 2.3) was conducted in a similar manner to that described by Pringle et al., during the investigation of the coordination chemistry of the trans-spanning ditertiary phosphine $o-\mathrm{C}_{6} \mathrm{H}_{4}\left\{\mathrm{CH}_{2} \mathrm{P}\left(\mathrm{C}_{8} \mathrm{H}_{14}\right)\right\} 2$, ${ }^{93}$ with $\mathrm{H}_{2} \mathrm{O}$ being displaced from the nickel centre by reflux with an equimolar amount of 2.3. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 1 5}$ contained a new singlet at $\delta(\mathrm{P}) 15.3 \mathrm{ppm}$, some 43 ppm downfield to that of $\mathbf{2 . 3}$. The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 . 1 5}$ contained the characteristic resonances associated with the coordinated ligand, when compared with the ${ }^{1} \mathrm{H}$ NMR spectrum of 2.3. The $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ resonance of $\mathbf{2 . 1 5}$ was, however, notably different to that observed for $2.3\left[\Delta \delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 1.08 \mathrm{ppm}, \Delta^{2} J_{\mathrm{PH}} 1.2 \mathrm{~Hz}\right]$, presumably due to coordination. Furthermore the elemental analysis result for $\mathbf{2 . 1 5}$ showed good agreement with the formula $\mathbf{2 . 1 5} \cdot 1.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$. Unfortunately, attempts to obtain crystals suitable for X-ray crystallography, to confirm the exact identity of this particular structural isomer, proved fruitless.

### 2.4.1 Molecular structures of 2.7-2.10

Colourless crystals suitable for X-ray crystallography were grown by either layering hexane (2.7) or $\mathrm{MeOH}(\mathbf{2} .8)$ onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of the respective complexes or by slow vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{2 . 9}$ and 2.10. The molecular structures of $\mathbf{2 . 7}$ and $\mathbf{2 . 1 0}$ were determined in the home laboratory, whilst the molecular structure of $\mathbf{2 . 8}$ was determined from reflection data collected by the EPSRC National Crystallography Service (both using a $\mathrm{MoK}_{\alpha}$ radiation source). The molecular structure of $\mathbf{2 . 9}$ was determined using synchrotron radiation due to the small size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ). Selected bond lengths and angles are given in Tables 2.7a and 2.7b.


Figure 2.9 The molecular structure of 2.10. All hydrogen atoms except $\mathrm{H}(26 \mathrm{~A})$ and $H(26 B)$ have been removed for clarity.

Figure 2.9 shows $\mathbf{2 . 1 0}$ as a typical example of this family of platinum(II) complexes (2.7-2.10). Each complex adopted a pseudo square planar geometry with respect to the platinum(II) centre $\left[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2) 169.33(2)-172.51(4)^{\circ}\right.$ and $\mathrm{P}(2)-\mathrm{Pt}(1)-$ $\left.\mathrm{Cl}(1) 168.42(2)-172.27(4)^{\circ}\right]$, with 2.1 - $\mathbf{2 . 4}$ coordinating the metal via both phosphorus atoms to form a nine-membered cis-chelate ring [bite angle range: $\mathrm{P}(1)-$ $\left.\operatorname{Pt}(1)-\mathrm{P}(2) 94.87(10)-99.04(4)^{\circ}\right]$. The phosphorus donor atoms were all found to adopt a distorted tetrahedral geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Pt}$ angles [C-P-Pt ranged between $\left.105.59(10)-121.81(14)^{\circ}\right]$, whilst the nitrogen atoms adopted a distorted trigonal pyramidal arrangement [sum of component angles for $\mathrm{N}(1)$ and $\mathrm{N}(2)=332^{\circ}, 343^{\circ}(\mathbf{2} .7), 328^{\circ}, 349^{\circ}(\mathbf{2 . 8}), 331^{\circ}, 345^{\circ}(\mathbf{2 . 9})$ and $331^{\circ}, 344^{\circ}$ (2.10), see Tables 2.7 a and 2.7 b ].

All four complexes were found to contain one intramolecular $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A}) \cdots \mathrm{Pt}(1)$ interaction $[\mathrm{C}(26) \cdots \operatorname{Pt}(1) 3.428-3.718 \AA, \mathrm{H}(26 \mathrm{~A}) \cdots \operatorname{Pt}(1) 2.51-2.81 \AA, \mathrm{C}(26)-$ $\left.\mathrm{H}(26 \mathrm{~A}) \cdots \mathrm{Pt}(1) 152.5-153.5^{\circ}\right]$, similar to that observed for the analogous platinum(II) dichloride complex 3.4 (Section 3.3.1) and in other medium ring sized
palladium(II) and platinum(II) complexes. ${ }^{199,200}$ This $\mathrm{C}(26)-\mathrm{H}(26 \mathrm{~A}) \cdots \mathrm{Pt}(1)$ interaction is thought to assist the $\operatorname{PtP}_{2} \mathrm{C}_{4} \mathrm{~N}_{2}$ ring to adopt a more constrained conformation than may be otherwise expected (Figure 2.10). This axial interaction between the $\mathrm{C}_{\text {sp } 3}-\mathrm{H}$ of the coordinated ligand backbone and the platinum(II) centre is not significantly mirrored in the ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{2 . 7} \mathbf{- 2 . 1 0}$, in which there is no evidence for any ${ }^{1} J_{\mathrm{PtH}}$ coupling nor notable shift in $\delta\left(\mathrm{CH}_{2}\right)\left[c a . \Delta \delta\left(\mathrm{CH}_{2}\right) 0.3 \mathrm{ppm}\right]$.


Figure 2.10 The $\operatorname{PtP}_{2} \mathrm{C}_{4} \mathrm{~N}_{2}$ ring conformation adopted by 2.7 - 2.10. All hydrogen atoms, except $\mathrm{H}(26 \mathrm{~A})$ and $\mathrm{H}(26 \mathrm{~B})$, and $\mathrm{C}_{6} \mathrm{H}_{5}$ moieties have been removed for clarity.

Further analysis of the molecular structure of $\mathbf{2 . 1 0}$ revealed a head-to-tail intermolecular packing arrangement, where one of the pyrene groups of $\mathbf{2 . 1 0}$ is involved in a combination of both, slipped $\pi \cdots \pi$ stacking [mean separation $=3.69 \AA$, minimum separation $=3.49 \AA$, c.f. graphite layer separation, $3.45 \AA]^{92}$ and four $\mathrm{C}(29)-\mathrm{H}(29 \mathrm{X}) \cdots \mathrm{C}_{6} \mathrm{H}_{3} \quad \pi \cdots$ acceptor interactions $[\mathrm{C}(29) \cdots \mathrm{Ar} 3.865-3.918 \AA$, $\left.\mathrm{H}(29 \mathrm{X}) \cdots \operatorname{Ar} 2.88-2.93 \AA, \mathrm{C}(29)-\mathrm{H}(29 \mathrm{X}) \cdots \operatorname{Ar} 115-152^{\circ}, \mathrm{X}=\mathrm{A}-\mathrm{D}\right]$, with a neighbouring molecule of $\mathbf{2 . 1 0}$ (Figure 2.11).



Figure 2.11 Intermolecular packing between neighbouring molecules of $\mathbf{2 . 1 0}$ in the solid state (left) and similar anti-parallel stacking between neighbouring benzyl groups (right).

Following a search of the literature, similar packing interactions have been analysed by Ciunik and Jarosz, ${ }^{201}$ who found anti-parallel benzyl groups to form diads (Figure 2.11, right) [mean separation $c a .3 .4-3.7 \AA, \mathrm{C}-\mathrm{H} \cdots \mathrm{Ph} c a .2 .5-3.0 \AA, \mathrm{C}-\mathrm{H} \cdots \mathrm{Ph} c a$. $\left.120-160^{\circ}\right]$. No similar intermolecular packing arrangements were observed in the molecular structures of $\mathbf{2 . 7} \mathbf{- 2 . 9}$, suggesting that the pyrene groups of $\mathbf{2 . 1 0}$ are the primary influence upon this novel type of solid state packing. Furthermore, following a search of the CSD, only five additional examples of nine-membered cis-chelate complexes have been previously reported, ${ }^{202-205}$ none of which were found to contain a square planar platinum(II) centre. As a result, complexes 2.7-2.10 are considered to be rare examples containing this ring system.
Table 2.7a Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2.7 - 2.10.

|  | $\mathbf{2 . 7}$ | $\mathbf{2 . 8}$ | $\mathbf{2 . 9}$ | $\mathbf{2 . 1 0}$ |  | $\mathbf{2 . 7}$ | $\mathbf{2 . 8}$ | $\mathbf{2 . 9}$ | $\mathbf{2 . 1 0}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3497(11)$ | $2.3489(9)$ | $2.358(3)$ | $2.3604(5)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $85.34(4)$ | $88.64(4)$ | $85.33(10)$ | $85.21(2)$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.3478(11)$ | $2.3473(11)$ | $2.345(2)$ | $2.3398(6)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $91.26(4)$ | $85.14(4)$ | $93.15(10)$ | $91.90(2)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.2564(10)$ | $2.2855(10)$ | $2.255(3)$ | $2.2472(5)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $96.55(4)$ | $99.04(4)$ | $94.87(10)$ | $95.985(19)$ |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.2480(10)$ | $2.2855(10)$ | $2.254(3)$ | $2.2435(5)$ | $\mathrm{Cl}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $87.92(4)$ | $87.32(4)$ | $87.06(10)$ | $88.54(2)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.820(4)$ | $1.811(5)$ | $1.814(11)$ | $1.826(2)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $169.68(4)$ | $172.51(4)$ | $171.76(10)$ | $169.33(2)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.831(4)$ | $1.830(4)$ | $1.827(10)$ | $1.824(2)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $171.50(4)$ | $172.27(4)$ | $170.68(10)$ | $168.24(2)$ |
| $\mathrm{P}(1)-\mathrm{C}(25)$ | $1.846(4)$ | $1.858(4)$ | $1.848(9)$ | $1.837(2)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{H}(26 \mathrm{~A})$ | 80 | 69 | 84 | 83 |
| $\mathrm{C}(25)-\mathrm{N}(1)$ | $1.462(5)$ | $1.448(5)$ | $1.457(12)$ | $1.462(3)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{H}(26 \mathrm{~A})$ | 73 | 69 | 76 | 74 |
| $\mathrm{~N}(1)-\mathrm{C}(26)$ | $1.483(5)$ | $1.486(6)$ | $1.493(11)$ | $1.480(3)$ | $\mathrm{Cl}(2)-\mathrm{Pt}(1)-\mathrm{H}(26 \mathrm{~A})$ | 115 | 118 | 107 | 114 |
| $\mathrm{~N}(1)-\mathrm{C}(29)$ | $1.485(5)$ | $1.484(5)$ | $1.497(12)$ | $1.490(3)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{H}(26 \mathrm{~A})$ | 92 | 114 | 87 | 86 |
| $\mathrm{C}(26)-\mathrm{C}(27)$ | $1.530(6)$ | $1.511(6)$ | $1.519(14)$ | $1.518(3)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $119.54(13)$ | $110.53(13)$ | $120.6(3)$ | $121.66(7)$ |
| $\mathrm{C}(27)-\mathrm{N}(2)$ | $1.459(5)$ | $1.439(8)$ | $1.477(13)$ | $1.473(3)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $112.53(14)$ | $115.07(14)$ | $112.7(4)$ | $112.07(7)$ |
| $\mathrm{N}(2)-\mathrm{C}(\mathrm{X})^{\mathrm{a}}$ | $1.472(5)$ | $1.498(7)$ | $1.472(13)$ | $1.471(3)$ | $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(25)$ | $113.10(14)$ | $120.09(14)$ | $113.1(3)$ | $105.59(10)$ |
| $\mathrm{N}(2)-\mathrm{C}(28)$ | $1.468(5)$ | $1.455(7)$ | $1.450(12)$ | $1.462(3)$ | $\mathrm{P}(1)-\mathrm{C}(25)-\mathrm{N}(1)$ | $113.1(3)$ | $115.2(3)$ | $113.4(7)$ | $113.05(14)$ |

[^0]Table 2.7b Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2.7 - $\mathbf{2 . 1 0}$.

|  | 2.7 | 2.8 | 2.9 | 2.10 |  | 2.7 | 2.8 | 2.9 | 2.10 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(2)-\mathrm{C}(13)$ | 1.811(4) | 1.832(4) | 1.812(10) | 1.827(2) | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(26)$ | 113.7(3) | 108.5(3) | 114.9(8) | 113.04(16) |
| $\mathrm{P}(2)-\mathrm{C}(19)$ | 1.824(4) | $1.828(5)$ | $1.846(10)$ | 1.810(2) | $\mathrm{C}(29)-\mathrm{N}(1)-\mathrm{C}(26)$ | 108.2(3) | 108.2(3) | 105.6(7) | 108.25(16) |
| $\mathrm{C}(28)-\mathrm{P}(2)$ | 1.864(4) | 1.894(4) | $1.869(10)$ | 1.870(2) | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(29)$ | 110.1(3) | 111.0(3) | 110.0(8) | 109.59(16) |
| $\operatorname{Pt}(1) \cdots \mathrm{H}(26 \mathrm{~A})$ | 2.64 | 2.81 | 2.51 | 2.62 | $\mathrm{N}(1)-\mathrm{C}(26)-\mathrm{C}(27)$ | 111.2(3) | 115.3(4) | 111.6(8) | 112.41(17) |
|  |  |  |  |  | $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{N}(2)$ | 112.1(3) | 115.4(5) | 116.2(8) | 114.44(17) |
|  |  |  |  |  | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(28)$ | 115.6(3) | 121.8(4) | 116.2(8) | 117.27(17) |
|  |  |  |  |  | $\mathrm{C}(28)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X})^{\mathrm{a}}$ | 113.8(3) | 117.3(4) | 115.5(8) | 114.08(16) |
|  |  |  |  |  | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X})^{\mathrm{a}}$ | 113.9(3) | 109.9(5) | 113.4(8) | 113.11(16) |
|  |  |  |  |  | $\mathrm{N}(2)-\mathrm{C}(28)-\mathrm{P}(2)$ | 108.3(3) | 122.4(4) | 111.8(7) | 109.24(14) |
|  |  |  |  |  | $\mathrm{C}(28)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 114.30(14) | 121.81(14) | 111.5(4) | 111.28(7) |
|  |  |  |  |  | $\mathrm{C}(19)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 116.65(14) | $112.20(17)$ | 115.3(4) | 115.16(7) |
|  |  |  |  |  | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 113.13(15) | 112.22(17) | 114.7(4) | 115.50(7) |

[^1]
### 2.4.2 The Coordination Chemistry of 2.2 - 2.4 to Palladium(II) and Rhodium(I)

The coordination chemistry of $\mathbf{2 . 2} \mathbf{- 2 . 4}$ was explored further by treatment with $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\mathrm{cod})$ (1 equiv.) and $\left\{\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}(0.5$ equiv.), to afford the complexes $\mathbf{2 . 1 6} \mathbf{- 2 . 1 9}$ (Equation 2.4). The trans disposition of $\mathbf{2 . 1 6}$ - $\mathbf{2 . 1 9}$ about the palladium(I) and rhodium(I) centres is of particular interest, as ligands capable of trans-spanning transition metal centres are thought to have potential catalytic applications due to their ability to readily access the various bite angles, at low strain, needed during the formation of catalytic intermediates. ${ }^{93}$


$\mathrm{M}=\mathrm{Pd}, \mathrm{X}=\mathrm{CH}_{3} 2.16$
$\mathrm{M}=\mathrm{Pd}, \mathrm{X}=\mathrm{CH}_{3} 2.17$
$\mathrm{M}=\mathrm{Pd}, \mathrm{X}=\mathrm{CH}_{3} 2.18$
$\mathrm{M}=\mathrm{Rh}, \mathrm{X}=\mathrm{CO} 2.19$
2.19

Equation 2.4 (i) $\operatorname{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\operatorname{cod})\left(\mathbf{2} .16\right.$ - 2.18); (ii) $0.5\left\{\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}(\mathbf{2} .19)$.

The reactions of 2.2 - $\mathbf{2 . 4}$ with equimolar amounts of $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\mathrm{cod})$, gave impure samples of $\mathbf{2 . 1 6} \mathbf{- 2 . 1 8}$ which, by solution ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, revealed the presence of several phosphorus containing species downfield of those of the free ligands [ $\delta(\mathrm{P}) 8.6-32.9 \mathrm{ppm}]$. The major species in all three cases, resonated as a singlet between $\delta(\mathrm{P}) 13.9-14.3 \mathrm{ppm}$ and accounted for $c a .66 \%$ of the total ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei. These major species, were tentatively assigned to the trans isomer of $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}\left(2.2\right.$ - 2.4) by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the analogous ferrocenyl complex 3.9, $[\delta(\mathrm{P}) 13.0 \mathrm{ppm}, \Delta \delta c a .1 \mathrm{ppm}]$ (Section 3.4.1). ${ }^{57}$ The ${ }^{1} \mathrm{H}$ NMR
spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 1 6} \mathbf{- 2 . 1 8}$ also supported the proposed symmetrical trans- $\mathbf{P}-$ $\operatorname{PdCl}\left(\mathrm{CH}_{3}\right)-\mathrm{P}$ disposition, with the presence of a major new $\mathrm{CH}_{3}$ triplet resonance at $\delta\left(\mathrm{CH}_{3}\right)-0.19$ to $1.21 \mathrm{ppm},\left({ }^{3} J_{\mathrm{PH}}\right.$ ranged between $\left.12.4-14.0 \mathrm{~Hz}\right)$. The preparation, and trans arrangement, of $\mathbf{2 . 1 7}$ was further supported by single crystal X-ray diffraction (Sections 2.4.2.1). The nature of the minor singlets within the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of 2.16 - $\mathbf{2 . 1 8}$ remains uncertain [ $\delta(\mathrm{P}) 8.6$ - 32.9 ppm$]$. However, these resonances may relate to further coordination complexes (monomeric / polymeric) or even the component oxides of the respective ligands [ $\delta(\mathrm{P}) 26.7 \mathrm{ppm}\left(\right.$ in $\left.\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)(\mathbf{2 . 5})\right]$. Further work is clearly required to fully understand these unassigned signals. The preparation of 2.16 - 2.18 was further supported by infrared spectroscopy which displayed a characteristic $v_{\text {PdCl }}$ absorption band between $v_{\text {PdCl }} 261-263 \mathrm{~cm}^{-1} .{ }^{21}$ The positive ion FAB mass spectra of $\mathbf{2 . 1 6}$ and $\mathbf{2 . 1 8}$ also revealed the expected fragmentation patterns $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 857,1005[\mathrm{M}-\mathrm{Cl}]^{+}\right.$(2.16 and 2.18) and $990\left[\mathrm{M}-\mathrm{Cl}-\mathrm{CH}_{3}\right]^{+}$(2.18) \}.

Treatment of $\mathbf{2 . 3}$ with half an equiv. of $\left\{\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}$, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, afforded the new rhodium chlorocarbonyl complex 2.19 via halogen bridge cleavage (Equation 2.4). Unfortunately, whilst 2.19 was prepared in good yield, the complex was found to be insoluble in common deuterated solvents precluding any NMR measurement. As a consequence the preparation of $\mathbf{2 . 1 9}$ could only be confirmed by solid state characterisation methods. Elemental analysis showed good agreement with the formula $\mathbf{2 . 1 9} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ (see Experimental Section) whilst the infrared spectra of $\mathbf{2 . 1 9}$ revealed a characteristic terminal carbonyl absorption band at $v_{\mathrm{CO}} 1969 \mathrm{~cm}^{-1} .{ }^{194,206}$ The coordination mode of $\mathbf{2 . 3}$ about the rhodium centre is therefore unclear. However, comparison of $\mathbf{2 . 1 9}$ with the analogous ferrocenyl complex $\mathbf{3 . 1 0}$ (Section 3.4.2) and the previously discussed trans $-\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}$ analogues (2.16 - 2.18) suggests that 2.19 is likely to be of a trans-disposition (monomeric / polymeric).

### 2.4.2.1 Molecular structure of 2.17

Colourless crystalline plates of $\mathbf{2 . 1 7}$ were grown by slow evaporation of an $\mathrm{Et}_{2} \mathrm{O} /$ $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 2.17. The molecular structure of $\mathbf{2 . 1 7}$ was determined in the home laboratory (Figure 2.12). Selected bond lengths and angles are given in Table 2.8.


Figure 2.12 Molecular structure of 2.17. All hydrogen atoms have been removed for clarity.

The molecular structure of $\mathbf{2 . 1 7}$ shows the asymmetric unit to contain one molecule of the palladium complex. The complex was found to adopt a distorted square planar geometry with respect to the metal centre, with $\mathbf{2 . 3}$ coordinating the metal via both phosphorus atoms to form a nine-membered trans-chelate ring $[\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{P}(2)$ $154.97(2)^{\circ}$ and $\left.\mathrm{C}(59)-\mathrm{Pd}(1)-\mathrm{Cl}(1) 170.25(8)^{\circ}\right]$. The phosphorus atoms were found to adopt a distorted pyramidal geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Pd}$ angles $[\mathrm{C}-\mathrm{P}-$

Pd ranged between $107.59(9)^{\circ}$ and $124.22(9)^{\circ}$, Table 2.8]. The nitrogen atoms, $\mathrm{N}(1)$ and $\mathrm{N}(2)$, both adopted a distorted trigonal pyramidal geometry [sum of component angles $=$ $337^{\circ}$ and $336^{\circ}$ respectively]. No inter or intramolecular interactions of note were observed.

Following a search of the CSD, 2.17 was found to represent the first crystallographically characterised nine-membered trans-chelate complex of palladium. Further comparison with similar complexes reported in the CSD database, highlighted the constraining effect of the $\mathrm{P}_{2} \mathrm{C}_{4} \mathrm{~N}_{2}$ backbone, with the $\mathrm{P}-\mathrm{Pd}-\mathrm{P}$ angle within the unconstrained dimonophosphine complexes 2A and 2B (Figure 2.13), being significantly closer to the idealised angle for a trans disposition of groups, than the bite angle found within 2.17 $\left[\mathrm{P}-\mathrm{Pd}-\mathrm{P}\right.$ angle $=177.49(2)^{\circ} \mathbf{( 2 A )}, 177.59(2)^{\circ} \mathbf{( 2 B )}$ and $\left.154.97(2)^{\circ}(\mathbf{2 . 1 7})\right] .{ }^{207}$


2A


2B

Figure 2.13 Trans-bis(triphenylphosphine)chloro(methyl)palladium(II) (2A) and transbis(triphenylphosphine)chloro(chloromethyl)palladium(II) (2B).

Table 2.8 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2.17.

| $\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | 2.4148(7) | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | 96.52(3) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pd}(1)-\mathrm{C}(59)$ | 2.066(3) | $\mathrm{C}(59)-\mathrm{Pd}(1)-\mathrm{P}(1)$ | 90.23(8) |
| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | 2.3303(7) | $\mathrm{C}(59)-\mathrm{Pd}(1)-\mathrm{P}(2)$ | 89.54(8) |
| $\mathrm{Pd}(1)-\mathrm{P}(2)$ | 2.3077(7) | $\mathrm{P}(2)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | 87.31(3) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.817(3) | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{P}(2)$ | 154.97(2) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.835(3) | $\mathrm{C}(59)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | 170.25(8) |
| $\mathrm{P}(1)-\mathrm{C}(25)$ | 1.854(3) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pd}(1)$ | 117.59(9) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | 1.469(3) | $C(7)-P(1)-P d(1)$ | 124.22(9) |
| $\mathrm{N}(1)-\mathrm{C}(26)$ | 1.460(3) | $\mathrm{C}(25)-\mathrm{P}(1)-\mathrm{Pd}(1)$ | 107.59(9) |
| $\mathrm{N}(1)-\mathrm{C}(29)$ | 1.477(3) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | 101.79(12) |
| $\mathrm{C}(26)-\mathrm{C}(27)$ | 1.528(4) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(25)$ | 105.81(12) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.488(3) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(25)$ | 96.77(12) |
| $\mathrm{N}(2)-\mathrm{C}(28)$ | 1.456(3) | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{P}(1)$ | 118.39(18) |
| $\mathrm{N}(2)-\mathrm{C}(44)$ | 1.484(3) | $\mathrm{C}(26)-\mathrm{N}(1)-\mathrm{C}(25)$ | 116.3(2) |
| $\mathrm{P}(2)-\mathrm{C}(13)$ | 1.823(3) | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(29)$ | 110.8(2) |
| $\mathrm{P}(2)-\mathrm{C}(19)$ | 1.823(3) | $\mathrm{C}(26)-\mathrm{N}(1)-\mathrm{C}(29)$ | 112.4(2) |
| $\mathrm{P}(2)-\mathrm{C}(28)$ | 1.870(3) | $\mathrm{N}(1)-\mathrm{C}(26)-\mathrm{C}(27)$ | 116.3(2) |
|  |  | $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(26)$ | 108.9(2) |
|  |  | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(28)$ | 114.0(2) |
|  |  | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(44)$ | 111.2(2) |
|  |  | $\mathrm{C}(28)-\mathrm{N}(2)-\mathrm{C}(44)$ | 110.6(2) |
|  |  | $\mathrm{N}(2)-\mathrm{C}(28)-\mathrm{P}(2)$ | 114.95 (17) |
|  |  | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{C}(28)$ | 104.05(12) |
|  |  | $\mathrm{C}(19)-\mathrm{P}(2)-\mathrm{C}(28)$ | 103.07(12) |
|  |  | $\mathrm{C}(28)-\mathrm{P}(2)-\mathrm{Pd}(1)$ | 111.13(9) |
|  |  | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{C}(19)$ | 102.71(12) |
|  |  | $\mathrm{C}(19)-\mathrm{P}(2)-\mathrm{Pd}(1)$ | 116.05(10) |
|  |  | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{Pd}(1)$ | 118.11(9) |

### 2.4.3 The Ruthenium(II), Gold(I) and Molybdenum(0) coordination chemistry of 2.3

Treatment of 2.3 with $\{\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2}$ (1 equiv.) and $\mathrm{AuCl}($ tht $)$ ( 2 equiv.), in dichloromethane at ambient temperature, gave the bimetallic complexes 2.20 and 2.21 in good yield (97 and $87 \%$ respectively) (Scheme 2.1). In both cases 2.20 and 2.21 were found to be insoluble in common deuterated solvents precluding any NMR measurement. As a consequence the bimetallic nature of the complexes was alluded to by elemental analysis, which showed good agreement with the proposed empirical formulae (see Experimental Section). The infrared spectrum of 2.21 was also found to contain a characteristic $\mathrm{Au}-\mathrm{Cl}$ absorption band at $v_{\mathrm{AuCl}} 331 \mathrm{~cm}^{-1} .{ }^{23}$


Scheme 2.1 (i) $\{\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2}$ or $2 \mathrm{AuCl}($ tht $)$; (ii) $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd})$, under nitrogen, reflux. Solvent; $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

In contrast, treatment of 2.3 with an equimolar amount of $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd})$ afforded the $\mathrm{CDCl}_{3}$ soluble octahedral complex 2.22, in good yield (Scheme 2.1). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 2 2}$ revealed a new singlet resonance at $\delta(\mathrm{P}) 19.1 \mathrm{ppm}$. The proposed cis conformation of $\mathbf{2 . 2 2}$ was not apparent from the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum, as both the cis and trans conformers of $\operatorname{Mo}(\mathrm{CO})_{4}(\mathbf{2} .3)$ are symmetrical about the metal centre. The infrared spectrum of $\mathbf{2 . 2 2}$ also failed to reveal the exact stereochemistry, with only two broad terminal $v_{\mathrm{CO}}$ absorption bands being observed [ $v_{\mathrm{CO}} 2017$ and 1893 $\left.\mathrm{cm}^{-1}\right] . .^{203,208}$ The preparation of the proposed cis isomer of $\mathbf{2 . 2 2}$ was however confirmed by X-ray crystallography, which showed $\mathbf{2 . 3}$ to coordinate the metal centre via both
phosphorus atoms to form a nine-membered cis-chelate complex (Section 2.4.3.1). However, this cis arrangement must be treated with caution, when referring to the bulk sample of 2.22, due to the nature of single crystal X-ray diffraction. Nevertheless, the preparation of a new molybdenum tetracarbonyl complex was further supported by elemental analysis, which agreed with the formula $\mathbf{2 . 2 2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$, and by the positive ion FAB mass spectrum which displayed the anticipated parent ion and fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1045[\mathrm{M}]^{+}, 989[\mathrm{M}-2 \mathrm{CO}]^{+}\right.$.

### 2.4.3.1 Molecular structure of $\mathbf{2 . 2 2}$

Colourless crystalline slabs of $\mathbf{2 . 2 2}$ suitable for X-ray crystallography were grown by layering MeOH onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{2 . 2 2}$. The molecular structure of $\mathbf{2 . 2 2}$ was determined from reflection data collected by the EPSRC National Crystallography Service (Figure 2.14). Selected bond lengths and angles are given in Table 2.9.


Figure 2.14 Molecular structure of 2.22. All hydrogen atoms and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solvent molecules have been removed for clarity.

The molecular structure of $\mathbf{2 . 2 2}$ showed the asymmetric unit to consist of one molecule of $\mathbf{2 . 2 2}$ and two dichloromethane molecules of crystallisation. The complex was found to adopt a distorted octahedral geometry with respect to the molybdenum centre [ $\mathrm{C}(60)-$ $\mathrm{Mo}(1)-\mathrm{P}(1) \quad 174.14(6)^{\circ}, \quad \mathrm{C}(62)-\mathrm{Mo}(1)-\mathrm{P}(2) \quad 174.22(7)^{\circ}$ and $\mathrm{C}(59)-\mathrm{Mo}(1)-\mathrm{C}(61)$ $172.49(9)^{\circ}$ (Table 2.9)] with $\mathbf{2 . 3}$ coordinating the metal via both phosphorus atoms, to
form a nine-membered cis-chelate ring [bite angle, $\mathrm{P}(1)-\mathrm{Mo}(1)-\mathrm{P}(2) 96.549(17)^{\circ}$ ]. The Mo-P and Mo-C bond lengths (Table 2.9) were found to compare well with previously reported molybdenum tetracarbonyl diphosphine complexes, ${ }^{202,203}$ with the carbonyl bond lengths appearing to be unaffected by the close proximity of the two dichloromethane molecules of crystallisation. The phosphorus atoms were found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Mo}$ angles [C-P-Mo ranged between; 106.86(6) - $\left.124.42(7)^{\circ}\right]$. The nitrogen atoms were found to adopt a distorted pyramidal geometry [sum of component angles for $\mathrm{N}(1), \mathrm{N}(2)=340$, $331^{\circ}$ respectively]. No inter- or intramolecular packing, of note, was observed.

A search of the CSD revealed only four analogous molybdenum diphosphine cis-chelate complexes have been previously reported (Figure 2.15), ${ }^{202-204}$ suggesting that $\mathbf{2 . 2 2}$ is a rare example of such an intermediate size diphosphine chelate.




Figure 2.15 Known nine-membered cis-chelate complexes. ${ }^{\text {202-204 }}$

The molecular structure of cis- $\mathrm{Mo}(\mathrm{CO})_{4}\left[\left\{\mathrm{CH}_{3} \mathrm{~N}^{( }\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}\right]$ (Figure 2.15, left) $)^{202}$ offered the most closely analogous example to $\mathbf{2 . 2 2}$. Unfortunately only limited comparison between the reported $\mathrm{Mo}^{\cdots} \mathrm{N}$ separations of cis$\mathrm{Mo}(\mathrm{CO})_{4}\left[\left\{\mathrm{CH}_{3} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}\right]$ and 2.22 was achieved, due to a lack of atomic coordinate data within the CSD archive [ $\mathrm{Mo}{ }^{\cdots} \cdot \mathrm{N} ; 3.92,4.44^{202}$ and 4.57, 4.45 (2.22) $\AA$ ]. Nevertheless this limited comparison revealed the respective chelate rings to be different in conformation, with cis $-\mathrm{Mo}(\mathrm{CO})_{4}\left[\left\{\mathrm{CH}_{3} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}\right]$ adopting a more twisted
ethylenediamine backbone with respect to the molybdenum centre. Moreover in both cases, no coordination of the molybdenum centre by the nitrogen atoms of the ethylenediamine moiety is observed. ${ }^{202}$ Grim et al. also highlight the fact that the preparation of intermediate sized chelate ring structures such as $\mathbf{2 . 2 2}$ may be difficult, due to the instability caused by the inherent flexibility within such compounds. ${ }^{202}$ Such comments further emphasise the rarity of $\mathbf{2 . 2 2}$ and any analogous nine-membered chelate complexes discussed herein.

Table 2.9 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{2 . 2 2}$.

| $\mathrm{Mo}(1)-\mathrm{P}(1)$ | 2.5516(6) | $\mathrm{C}(59)-\mathrm{Mo}(1)-\mathrm{P}(1) 94.75(6)$ |
| :---: | :---: | :---: |
| $\mathrm{Mo}(1)-\mathrm{P}(2)$ | $2.5700(5)$ | $\mathrm{C}(60)-\mathrm{Mo}(1)-\mathrm{P}(1)$ 174.14(6) |
| $\mathrm{Mo}(1)-\mathrm{C}(59)$ | 2.032(2) | $\mathrm{C}(61)-\mathrm{Mo}(1)-\mathrm{P}(1) 92.58(7)$ |
| $\mathrm{Mo}(1)-\mathrm{C}(60)$ | 1.998 (2) | $\mathrm{C}(62)-\mathrm{Mo}(1)-\mathrm{P}(1) 86.62(7)$ |
| $\mathrm{Mo}(1)-\mathrm{C}(61)$ | 2.047(2) | $\mathrm{P}(1)-\mathrm{Mo}(1)-\mathrm{P}(2) 96.549(17)$ |
| $\mathrm{Mo}(1)-\mathrm{C}(62)$ | 1.990 (2) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Mo}(1) 117.98(7)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.836(2) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Mo}(1) 109.60(7)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.840(2) | $\mathrm{C}(25)-\mathrm{P}(1)-\mathrm{Mo}(1) 123.54$ (7) |
| $\mathrm{P}(1)-\mathrm{C}(25)$ | 1.857(2) | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(26) 115.16$ (16) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | 1.459(3) | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(29)$ 112.16(16) |
| $\mathrm{N}(1)-\mathrm{C}(26)$ | 1.461(3) | $\mathrm{C}(26)-\mathrm{N}(1)-\mathrm{C}(29) 113.12$ (15) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.478 (3) | $\mathrm{N}(1)-\mathrm{C}(26)-\mathrm{C}(27) 117.88$ (19) |
| $\mathrm{N}(2)-\mathrm{C}(28)$ | 1.474 (3) | $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(26) 112.89$ (16) |
| $\mathrm{C}(26)-\mathrm{C}(27)$ | $1.525(3)$ | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(28) 110.24(16)$ |
| $\mathrm{P}(2)-\mathrm{C}(19)$ | 1.833(2) | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(44) 111.62(16)$ |
| $\mathrm{P}(2)-\mathrm{C}(28)$ | 1.865(2) | $\mathrm{C}(28)-\mathrm{N}(2)-\mathrm{C}(44) 109.20$ (15) |
|  |  | $\mathrm{N}(2)-\mathrm{C}(28)-\mathrm{P}(2) 115.63$ (14) |
|  |  | $\mathrm{C}(13)-\mathrm{P}(2)-\mathrm{Mo}(1) 106.86$ (6) |
|  |  | $\mathrm{C}(19)-\mathrm{P}(2)-\mathrm{Mo}(1) 118.56$ (7) |
|  |  | $\mathrm{C}(28)-\mathrm{P}(2)-\mathrm{Mo}(1) 124.42$ (7) |

### 2.5 Luminescent Properties of Coordination Compounds of 2.3 and 2.4

In order to evaluate how coordination of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ affects their fluorescent properties, the fluorescent emission spectra of the THF soluble complexes, 2.9, 2.17, 2.19, 2.22 and $\mathbf{2 . 1 0}$ were recorded. The results are summarised in Table 2.10.

Table $2.10 \lambda_{\max }(\mathrm{nm})$ and $\Phi$ data for the phosphines $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$, and the coordination complexes 2.9, 2.17, 2.19, 2.22 and 2.10.

| Compound | $\lambda_{\text {max }}$ | $\Phi$ |
| :---: | :---: | :---: |
| $\mathbf{2 . 3}^{\mathrm{a}}$ | $393,415,440$ | 0.03 |
| $\mathbf{2 . 9}^{\mathrm{a}}$ | $394,416,442$ | 0.01 |
| $\mathbf{2 . 1 7}^{\mathrm{a}}$ | $392,415,438$ | 0.01 |
| $\mathbf{2 . 1 9}^{\mathrm{a}}$ | $392,416,441$ | 0.01 |
| $\mathbf{2 . 2 2}^{\mathrm{a}}$ | $393,415,442$ | 0.01 |
| $\mathbf{2 . 4}^{\mathrm{b}}$ | $376,387,396,416$ | 0.19 |
| $\mathbf{2 . 1 0}^{\mathrm{b}}$ | $376,387,396,418$ | 0.05 |
| ${ }^{\mathrm{a}} \boldsymbol{\lambda}_{\mathrm{ex}}=370 \mathrm{~nm},{ }^{\mathrm{b}} \boldsymbol{\lambda}_{\text {ex }}=344 \mathrm{~nm}$ |  |  |

The emission spectra of the complexes in Table 2.10 all revealed a characteristic monomer emission relating to the respective fluorophores, ${ }^{77,79-81,116}$ with little change in $\lambda_{\text {max }}$ being observed relative to the free ligands. In contrast, the emission intensities (Ф) of all the complexes studied were found to be significantly diminished, compared to $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ (Table 2.10). This reduction in fluorescent emission, upon coordination, is presumably due to a charge transfer process between the respective fluorophores and the d-orbitals of the coordinated metal. ${ }^{77,78,81,195}$ The observation that the pyrenyl and anthracenyl monomer emissions are not completely quenched by this charge transfer process also suggests that, either the difference in energy between the d-orbitals of the coordinated metal and those of the fluorophore singlet state is not sufficient to allow complete quenching, or that the fluorophore is not close enough to the metal centre to be significantly quenched. ${ }^{81,209}$


Figure 2.16 The fluorescence emission spectra of 2.3, 2.5, 2.9, 2.17, 2.19 and 2.22, in THF; concentration: $5 \mu \mathrm{M}, \lambda_{\mathrm{ex}} 370 \mathrm{~nm}$, slit width: 0.4 mm .

Interestingly this reduction in emission intensity ( $\Phi$ ), upon coordination of $\mathbf{2 . 3}$ and 2.4, is similar to that observed upon the oxidation of the respective phosphines [ $\Phi 0.01$ (2.5) and 0.05 (2.6)] (Figure 2.16). This highlights, that whilst coordination prevents aerobic oxidation of the phosphorus atoms, and the associated "enhanced" PET quenching process previously discussed (Section 2.2), the excited state of the fluorophore is still significantly affected. Nevertheless, pyrenyl and anthracenyl bearing molecular devices that start in a monomer quenched state and progress into a more fluorescent state, are common within the literature, ${ }^{116,118,119}$ and as a result 2.9, 2.17, 2.19, $\mathbf{2 . 2 2}$ and $\mathbf{2 . 1 0}$ may also behave in a similar manner, upon addition of an analyte.

No excimer emissions were observed for any of the complexes studied. This suggests that any changes in conformation upon coordination of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ were insufficient to cause any "OFF-ON" excimer emission, similar to that observed within other pendant arm bearing ligands upon coordination. ${ }^{81,83,210}$ This observation is in agreement with the
single crystal X-ray diffraction data previously discussed, which shows only weak intermolecular $\pi \cdots \pi$ stacking, in the case of $\mathbf{2 . 1 0}$, in the solid state structure. The pursuit of phosphines that are capable of this OFF-ON excimer formation upon coordination or introduction of an analyte, may be important towards the preparation of new chemosensors based upon 2.3 and $\mathbf{2 . 4}$, due to their naturally weak monomer emission upon oxidation or coordination. One potential reason for the absence of an excimer emission upon coordination of $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$, is the restraining effects caused by the ethylene diamine backbone, which is evident from the previously discussed X-ray diffraction data (Section 2.4.3.1). Therefore one means of promoting excimer formation within coordination compounds similar to those discussed above, maybe to break the ethylene diamine backbone within $\mathbf{2 . 3}$ and 2.4, and prepare bis-monophosphine complexes, where the fluorophores potentially have significantly more conformational freedom (Section 2.6).

### 2.6 Preparation and Characterisation of 2.23-2.25

To this end, the methodology used to prepare 2.1 - 2.4 was utilised to prepare the analogous monophosphines 2.23 - $\mathbf{2 . 2 5}$ (Scheme 2.2).


In the case of $\mathbf{2 . 2 3}$, the desired tertiary phosphine deposited during the course of the reaction allowing the ligand to be isolated in a high purity, by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy ( $96 \%$ by integral) and in reasonable yield ( $67 \%$ ). In contrast, 2.24 and 2.25 did not crystallise during the reaction of their parent amines with $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$. In the case of $\mathbf{2 . 2 4}$, complete evaporation of the solvent after stirring for three days at ambient
temperature repeatedly yielded a viscous oil which was thought to be sufficiently pure, by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy ( $81 \%$ by integration) to be used directly in coordination and luminescent studies. Attempts to prepare $\mathbf{2 . 2 5}$ at ambient temperature failed, with only the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material being observed by in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy under the same reaction conditions. Further efforts to prepare $\mathbf{2 . 2 5}$ using harsher reaction conditions also proved inadequate, with the extreme case being a 5 d reflux of an equimolar solution of $\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{Ph}$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, which afforded 2.25 with a purity of $4 \%$ by in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy $[\delta(\mathrm{P})-25.1 \mathrm{ppm}, 4 \%$ by integration], by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}[\Delta \delta(\mathrm{P}) c a .3$ $\mathrm{ppm}]$. The repeatedly low yields of $\mathbf{2 . 2 5}$, for the above, were attributed to delocalisation of the parent amine lone pair into the neighbouring phenyl ring, thereby significantly reducing its availability to be involved in the desired condensation process.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ (in freeze-thawed $\mathrm{CDCl}_{3}$ ) both revealed new phosphorus singlet resonances at $\delta(\mathrm{P})-27.6$ and -27.7 ppm respectively, some 18 ppm upfield to that observed for the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. Furthermore, both phosphines appeared to show evidence of aerobic oxidation over the course of several hours, when $\mathrm{CDCl}_{3}$ solutions were left to stand, with the formation of presumably oxide resonances at $c a . \delta(\mathrm{P}) 32 \mathrm{ppm} .{ }^{188,189}$ The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ contained the anticipated $\delta\left(\mathrm{CH}_{2}\right)$ and $\delta\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ resonances previously observed in the ${ }^{1} \mathrm{H}$ NMR spectra of the parent amines. The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ moieties resonated as characteristic doublets at $\delta(\mathrm{H}) 3.35$ and 3.34 ppm respectively, $\left({ }^{2} J_{\mathrm{PH}} 2.8\right.$ and 3.6 $\mathrm{Hz}){ }^{22,23}$ Comparison between the $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ and ${ }^{2} J_{\mathrm{PH}}$ values of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ with those of their ditertiary phosphine analogues ( $\mathbf{2} \mathbf{3}$ and 2.4), revealed relatively little change (ca. $\Delta \delta 0.2 \mathrm{ppm}, c a . \Delta^{2} J_{\mathrm{PH}} 0.4 \mathrm{~Hz}$ ) (Section 2.2). Furthermore, the absence of a significant $v_{\mathrm{NH}}$ absorption band in the infrared spectrum of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ supported the ternary nature of the phosphine nitrogen atoms. The positive ion FAB mass spectroscopy results for $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ also gave the anticipated molecular fragments $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: $\mathrm{m} / \mathrm{z} 432[\mathrm{M}]^{+}$(2.23) and $456[\mathrm{M}-\mathrm{H}]^{+}$(2.24).

The fluorescent emission spectra of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ both exhibited typical monomer emission bands relating to their respective fluorophores, ${ }^{77,79-81}$ with little change in $\lambda_{\max }$ being observed relative to the emissions of 2.3, 2.4 and the parent amines (Figure 2.17 and Table 2.11).


Figure 2.17 Emission spectra of $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3} / \mathbf{2 . 2 3}$ (left) and $\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3} / 2.24$ (right), in dry THF solutions containing analyte ( $5 \mu \mathrm{M}$ ), slit widths 0.4 mm . $\lambda_{\text {ex }}$ anthracene derivatives $=370 \mathrm{~nm}, \lambda_{\text {ex }}$ pyrene derivatives $=344$ nm.

Table $2.11 \lambda_{\text {max }}(\mathrm{nm})$ and $\Phi$ data for 2.3, 2.4, 2.23, 2.24 and the parent amines of the monophosphines.

| Compound | $\lambda_{\max }$ | $\Phi$ |
| :--- | :---: | :---: |
| $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3}{ }^{\text {a }}$ | $393,415,440$ | 0.97 |
| $\mathbf{2 . 2 3}^{\mathrm{a}}$ | $394,415,439$ | 0.11 |
| $\mathbf{2 . 3}^{\mathrm{a}}$ | $393,415,440$ | 0.03 |
| $\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3}{ }^{\mathrm{b}}$ | $376,387,395,416$ | 1.08 |
| $\mathbf{2 . 2 4}^{\mathrm{b}}$ | $376,387,396,416$ | 0.46 |
| $\mathbf{2 . 4}^{\mathrm{b}}$ | $376,387,396,416$ | 0.19 |
| ${ }^{\mathrm{a}} \boldsymbol{\lambda}_{\text {ex }}$ anthracene derivatives $=370 \mathrm{~nm},{ }^{\mathrm{b}} \lambda_{\text {ex }}$ pyrene derivatives $=344 \mathrm{~nm}$. |  |  |

The emissions of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ were found to be weaker than those observed for the parent amines (Table 2.11, Figure 2.17), which is in agreement with the suggested PET quenching process previously observed for $\mathbf{2 . 3}$ and 2.4. ${ }^{190}$ The intensity of the emissions of 2.23 and 2.24 were, however, found to be significantly greater than those of their ditertiary phosphine counterparts (Table 2.11). No excimer emissions were observed for $\mathbf{2 . 2 3}$ or $\mathbf{2 . 2 4}$ at the concentrations studied.

### 2.7.1 Platinum(II) Coordination Chemistry of 2.23 and 2.24

The coordination chemistry of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ was briefly explored by treatment of two equiv. of the respective monophosphines with one equiv. of $\mathrm{PtCl}_{2}(\operatorname{cod})$, to afford the dichloroplatinum complexes 2.26 and 2.27 (Equation 2.5).


Equation 2.5

In contrast to the analogous diphosphine coordination chemistry (2.3 and 2.4, Section 2.4), both 2.23 and 2.24 were found to afford impure samples of $\mathbf{2 . 2 6}$ and 2.27 , by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. In the case of 2.26, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) revealed a new singlet resonance flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites at $\delta(\mathrm{P}) 2.6 \mathrm{ppm}$ $\left({ }^{1} J_{\text {PtP }} 3636 \mathrm{~Hz}, 88 \%\right.$ pure by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR integration), in addition to several minor ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active species between $\delta(\mathrm{P})-0.5$ to 9.1 ppm . Similarly the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of 2.27 , revealed a new singlet resonance flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites at $\delta(\mathrm{P}) 3.7 \mathrm{ppm}\left({ }^{1} J_{\mathrm{PtP}} 3628 \mathrm{~Hz}, 64 \%\right.$ pure by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR integration),
in addition to a minor species which resonated between $\delta(\mathrm{P})-9.7$ to 19.3 ppm . In both instances, these major resonances were assigned to the desired platinum dichloride complexes (2.26 and 2.27) by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the analogous diphosphine complexes 2.9 and $\mathbf{2 . 1 0}\left[c a . \Delta \delta(\mathrm{P}) 6.4 \mathrm{ppm}, c a . \Delta^{1} J_{\mathrm{PtP}} 26\right.$ $\mathrm{Hz}] .{ }^{58,186,196}$ Further inspection of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ suggested that the observed impurities related to aerobic oxidation products of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ or various new mixed phosphine platinum complexes of $\mathbf{2 . 2 3} / \mathbf{2 . 2 4}, \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ and $\mathrm{PHPh}_{2}$ (all of which were observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{2 . 2 3}$ and 2.24). As a result, the minor species observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 2.27, which resonated as two doublets flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites $[\delta(\mathrm{P}) 1.3$ and 7.7 ppm , ${ }^{2} J_{\mathrm{PP}} 13.0 \mathrm{~Hz}$, ${ }^{1} J_{\mathrm{PtP}} 3764$ and 3565 Hz respectively], was assigned to the unsymmetrical cis-platinum dichloride 2.27A complex [(cis$\mathrm{PtCl}_{2}\left\{\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2} \mathrm{CH}_{3}\right\}\left\{\mathrm{Ph}_{2} \mathrm{PR}\right.$ ), $\mathrm{R}=\mathrm{H}$ or $\mathrm{CH}_{2} \mathrm{OH}$ (Figure 2.18) due to the characteristically large ${ }^{1} J_{\mathrm{PtP}}$ and ${ }^{2} J_{\mathrm{PP}}$ splitting pattern. ${ }^{58,186,196}$

2.27A

Figure 2.18 Suggested minor species observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 2.27.

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ were assigned by comparison with the ${ }^{1} \mathrm{H}$ NMR spectra of 2.23 and 2.24 and showed the anticipated resonances relating to the coordinated ligands, with little change in $\delta(\mathrm{H})$. The characteristic $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ doublets, previously observed in the ${ }^{1} \mathrm{H}$ NMR spectra of the free ligands, did however resonate as broad singlets within the ${ }^{1} \mathrm{H}$ NMR spectra of 2.26 and 2.27 , presumably due to
coordination. Furthermore the positive ion FAB mass spectra of $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ both revealed the expected fragmentation patterns $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1097\right.$ (2.26) and 1145 (2.27) $\left.[\mathrm{M}-\mathrm{Cl}]^{+}\right\}$. Attempts to recrystallise $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ from the crude solids obtained, using a variety of organic solvents, proved unsuccessful. The purity of $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ was however thought to be sufficient enough to provide insight into the luminescent properties of the platinum dichloride complexes (Section 2.8).

### 2.7.2 Gold(I) Coordination Chemistry of 2.23 and 2.24

The coordination chemistry of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ was explored further by reaction with an equimolar amount of $\mathrm{AuCl}(\mathrm{tht})$ at ambient temperature, to afford 2.28 and 2.29 in reasonable yield (69 and 63\% respectively) (Equation 2.6).

2.23 or 2.24


2.28 or $\mathbf{2 . 2 9}$

$$
\mathrm{R}=\mathrm{C}_{14} \mathrm{H}_{9}(2.23 \text { and } 2.28), \mathrm{C}_{16} \mathrm{H}_{9}(2.24 \text { and } 2.29)
$$

Equation 2.6

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{2} .28$ and $\mathbf{2 . 2 9}$ exhibit a new phosphorus singlet resonance at $\delta(\mathrm{P}) 18.9$ and 18.5 ppm respectively, some 45 ppm downfield to those of 2.23 and $2.24\left[\delta(P)-27.6\right.$ and -27.7 ppm respectively]. The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of 2.28 and 2.29 contained the anticipated resonances relating to the coordinated ligand, with little change in $\delta(\mathrm{H})$ being observed compared to $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$. The characteristic $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ doublet, previously observed in the ${ }^{1} \mathrm{H}$ NMR spectra of the free ligands, resonated as broad singlets in both cases, presumably due to coordination. Furthermore, the positive ion FAB mass spectra of 2.28 and 2.29 both contained the expected molecular fragments $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 630\right.$ and $654[\mathrm{M}-\mathrm{Cl}]^{+}$respectively $\}$. The
elemental analysis results for $\mathbf{2 . 2 8}$ and $\mathbf{2 . 2 9}$ were also found to be satisfactory, agreeing with the formulae ( $\mathbf{2} .28$ or $\mathbf{2 . 2 9}$ ) $\cdot 0.25 \mathrm{C}_{6} \mathrm{H}_{14}$ (see Experimental Section).

### 2.8 Luminescent Properties of the Coordination Compounds of 2.23 and 2.24

The fluorescent emission spectra of 2.23, 2.24 and their respective platinum (2.26 and 2.27) and gold ( $\mathbf{2 . 2 8}$ and 2.29) complexes are given in Figure 2.19.


Figure 2.19 Emission spectra of 2.23, $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 8}$ (left), and 2.24, 2.27 and $\mathbf{2 . 2 9}$ (right), in dry THF solutions ( $5 \mu \mathrm{M}$ ), slit widths 0.4 mm . $\lambda_{\text {ex }}$ anthracene derivatives $=$ $370 \mathrm{~nm}, \lambda_{\text {ex }}$ pyrene derivatives $=344 \mathrm{~nm}$.

The emission spectra of $\mathbf{2 . 2 3}, \mathbf{2 . 2 4}, \mathbf{2 . 2 6} \mathbf{- 2 . 2 9}$ all revealed characteristic monomer emissions relating to the respective fluorophores, ${ }^{77,79-81}$ with little change in $\lambda_{\max }$ compared to the emissions of the respective ligands (Figure 2.19, Table 2.12). No excimer emissions were observed at the concentration studied ( $5 \mu \mathrm{M}$ ). The emissions of 2.26, 2.27 and $\mathbf{2 . 2 9}$ were found to be significantly diminished compared with the free ligands, presumably due to a charge transfer between the respective fluorophores and the coordinated metal (Table 2.19, Figure 2.12), ${ }^{77,78,81,195}$ which is in agreement with previous diphosphine coordination chemistry (Section 2.5). In contrast, complex $\mathbf{2 . 2 8}$
gave an enhanced emission relative to $\mathbf{2 . 2 3}$ (Table 2.19, Figure 2.12). This increase in emission strength was attributed to the inhibition of the PET process previously observed in the free ligand, owing to phosphorus coordination to the gold atom, and is in agreement with a similar monophosphine gold chloride complex described by Zhang et al. ${ }^{77}$

Table $2.12 \lambda_{\text {max }}(\mathrm{nm})$ and $\Phi$ data for 2.23, 2.24, 2.26 - 2.29 in dry THF solutions containing analyte $(5 \mu \mathrm{M})$, slit widths 0.4 mm . $\lambda_{\text {ex }}$ anthracene derivatives $=370 \mathrm{~nm}, \lambda_{\text {ex }}$ pyrene derivatives $=344 \mathrm{~nm}$.

| Compound | $\lambda_{\max }$ | $\Phi$ |
| :--- | :---: | :---: |
| $\mathbf{2 . 2 3}^{\text {a }}$ | $394,415,439$ | 0.05 |
| $\mathbf{2 . 2 6}^{\text {a }}$ | $394,415,440$ | 0.01 |
| $\mathbf{2 . 2 8}^{\text {a }}$ | $393,415,439$ | 0.05 |
| $\mathbf{2 . 2 4}^{\text {b }}$ | $376,387,396,416$ | 0.23 |
| $\mathbf{2 . 2 7}^{\text {b }}$ | $376,387,396,417$ | 0.15 |
| $\mathbf{2 . 2 9}^{\mathrm{b}}$ | $376,387,396,416$ | 0.09 |
| ${ }^{\mathrm{a}} \boldsymbol{\lambda}_{\text {ex }}=370 \mathrm{~nm},{ }^{\mathrm{b}} \boldsymbol{\lambda}_{\mathrm{ex}}=344 \mathrm{~nm}$ |  |  |

### 2.9 Preliminary Study into the Chemosensory Behaviour of 2.3, 2.4, 2.23 and 2.24

In order to obtain insight into the potential use of 2.3, 2.4, 2.23 and $\mathbf{2 . 2 4}$ as ligands for phosphine based molecular devices, the chemosensory behaviour of the platinum complexes 2.9, 2.10, $\mathbf{2 . 2 6}$ and $\mathbf{2 . 2 7}$ towards a series of readily available metal cations $\left(\mathrm{Li}^{+}, \mathrm{K}^{+}, \mathrm{Na}^{+}, \mathrm{Ag}^{+}, \mathrm{Ba}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Cu}^{2+}, \mathrm{Ni}^{2+}, \mathrm{Co}^{2+}\right.$ and $\mathrm{Fe}^{3+}$ ) were briefly investigated.

Initially, a qualitative-screening approach was used to very-crudely assess the binding properties of 2.9, 2.10, 2.26 and 2.27 towards these metal cations, due to the known chromatic response of some pyrenyl and anthracenyl chemosensors toward various ions, ${ }^{82,130}$ and the limited time available in the laboratory. To this end, saturated
solutions of perchlorate salts of $\mathrm{Li}^{+}, \mathrm{K}^{+}, \mathrm{Na}^{+}, \mathrm{Ag}^{+}, \mathrm{Ba}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Cu}^{2+}, \mathrm{Ni}^{2+}, \mathrm{Co}^{2+}$ and $\mathrm{Fe}^{3+}$ (in dry THF) were added dropwise to pale yellow solutions of 2.9, 2.10, 2.26 and 2.27 (in dry THF, ca. 1 mM ), and any visual responses noted. Interestingly, the only significant response observed was upon addition of $\mathrm{Fe}\left(\mathrm{ClO}_{4}\right)_{3}$ to 2.27 , which afforded a pale green fluorescence, presumably due to some form of recognition response between 2.27 and $\mathrm{Fe}^{3+}$. As a result the luminescent properties of $\mathbf{2 . 2 7}$ were explored further, in order to gain some insight into the source of this change in fluorescence, whilst 2.9, 2.10 and 2.26 were left for future study. The fluorescent emission spectrum of $\mathbf{2 . 2 7}$ was therefore recorded in the absence and presence of increasing amounts of $\mathrm{Fe}^{3+}$ (Figure 2.20).


Figure 2.20 Fluorescent emission spectra, and normalised fluorescent emission spectra (insert top right) of $\mathbf{2 . 2 7}$ following the progressive addition of $\mathrm{Fe}\left(\mathrm{ClO}_{4}\right)_{3}$ in dry THF solutions; concentration of $2.27(5 \mu \mathrm{M}), \lambda_{\mathrm{ex}} 344 \mathrm{~nm}$.

The emission spectrum of 2.27 alone gave rise to the previously observed pyrene monomer fluorescence at $c a .376 \mathrm{~nm},{ }^{76,80,81}$ whilst the addition of $\mathrm{Fe}^{3+}$ caused a marked change in the emission of the complex, with substantial quenching of the monomer emission accompanied by the emergence of a broad structureless emission at 556 nm (Figure 2.20). This change in emission was attributed to the formation a new excimer emitting complex of $\mathbf{2 . 2 7}$ upon addition of $\mathrm{Fe}^{3+},{ }^{116,211}$ and is in agreement with the pale green fluorescence observed during the qualitative testing of 2.27; $\lambda_{\text {(green) }} c a .520-570$ $\mathrm{nm} .{ }^{212}$

The formation of an excimer emitting complex, in this manner, is normally associated with a change in the conformation of a "chemosensor" upon association of a target analtye; particularly by chemosensors bearing anthracene and pyrene fluorophores. ${ }^{73,116,211}$ The continuous decline in the pyrene monomer emission, and the seeming ratiometric growth of the excimer emission, upon addition of up to 1.25 equiv. of $\mathrm{Fe}\left(\mathrm{ClO}_{4}\right)_{3}$, also suggests that the excimer emitting complex maybe of a $1: 1 \mathbf{2} \mathbf{2 . 2 7}: \mathrm{Fe}^{3+}$ stoichiometry. ${ }^{211}$ One tentative suggestion towards the nature of such a complex, is 2.27B (Figure 2.21), where the lone pairs of the ternary nitrogen atoms of $\mathbf{2 . 2 7}$ coordinate $\mathrm{Fe}^{3+}$ to form an eight-membered bimetallocycle, which in turn induces the anticipated conformational change within 2.27, leading to formation of an intramolecular excimer. The occurrence of a complex such as 2.27B may also explain why no visual response was observed for $\mathbf{2 . 9}$ and $\mathbf{2 . 1 0}$ upon addition of various metal cations studied during the qualitative testing; as the ethylene diamine linker between the two respective pyrenyl (2.9) and anthracenyl (2.10) groups may sterically hinder coordination by the nitrogen atoms, whilst also inhibiting the fluorophores from adopting an excimer emitting conformation.


Figure 2.21 Suggested monomer (left) and excimer (right) emitting conformations of 2.27, observed by fluorescent emission spectroscopy.

The binding properties of $\mathbf{2 . 2 7}$ towards other readily available metal cations were briefly investigated by fluorescent emission spectroscopy, in an attempt to determine if the formation of an excimer emitting complex of $\mathbf{2 . 2 7}$ was specific to just ferric ions. Interestingly, addition of $\mathrm{Na}^{+}$and $\mathrm{Cu}^{2+}$ to THF solutions of $\mathbf{2 . 2 7}$ resulted in a marked enhancement of the pyrene monomer emission and no excimer emission (Figures 2.22).


Figure 2.22 Fluorescent emission spectra of $\mathbf{2 . 2 7}$ following the progressive addition of $\mathrm{M}\left(\mathrm{ClO}_{4}\right)_{\mathrm{x}}$, in dry THF solutions; $\mathrm{M}=\mathrm{Na}^{+}$and $\mathrm{Cu}^{2+}$ (insert, top right), $\mathrm{x}=1(\mathrm{Na})$ and 2 $(\mathrm{Cu})$, concentration of $2.27(5 \mu \mathrm{M}), \lambda_{\mathrm{ex}} 344 \mathrm{~nm}$.

In the case of $\mathrm{Na}^{+}$, this enhancement appeared to be ratiometric, with the monomer emission increasing in intensity up to the addition of an equimolar amount of $\mathrm{NaClO}_{4}$ (Figure 2.22), suggesting that the resulting fluorescent enhanced complex maybe of a 1:1 2.27: $\mathrm{Na}^{+}$stoichiometry. However, in the case of $\mathrm{Cu}^{2+}$, the maximum enhancement of the monomer emission was reached following the addition of only 0.1 equiv. of $\mathrm{Cu}\left(\mathrm{ClO}_{4}\right)_{2}$ (Figure 2.22, insert).

In both cases, this fluorescent enhancement was attributed to an inhibition of the photoinduced electron transfer (PET) process, previously credited to the quenching of the monomer emission of the free ligand (2.24) (Section 2.6, Figure 2.17 left). ${ }^{189,190}$ This type of fluorescent enhancement, upon coordination of a target ion, is a common
phenomenon exploited within chemosensor design, ${ }^{116,118,119,189,190,209}$ and is thought to result from an increase in the redox potential of the nitrogen atom upon coordination to the respective cations. This, in turn, lowers the energy of the nitrogen HOMO below that of the fluorophore HOMO, therefore preventing any PET process from taking place (Figure 2.23, right). ${ }^{190}$ Hence fluorescent intensity is enhanced upon coordination of $\mathrm{Na}^{+}$ or $\mathrm{Cu}^{2+}$, by the nitrogen lone pairs of $\mathbf{2 . 2 4}$, as radiative decay becomes more likely.


Figure 2.23 Mechanism of fluorescence enhancement upon cation coordination.

Further work is clearly required to fully understand the true binding mechanism of $\mathbf{2 . 2 7}$ to $\mathrm{Fe}^{3+}, \mathrm{Na}^{+}$and $\mathrm{Cu}^{2+}$, as well as the selectivity and binding strength of 2.27 towards these, and other metal cations. However this preliminary work does show that the emission of $\mathbf{2 . 2 7}$ can be significantly affected by the presence of metal cations, in THF solution, with both variation of the PET process and the formation of excimer emitting complexes of 2.27 being observed. ${ }^{73,189,190,211}$

### 2.10 Preparation and Characterisation of 2.30

Following on from the preparation, diverse coordination chemistry and interesting luminescent properties of the mono and ditertary phosphines discussed thus far, preliminary efforts to prepare less sterically restricted diphosphines based on the general formula $\left\{\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2} \mathrm{X}$ (where $\mathrm{R}=$ aryl group, $\mathrm{X}=$ backbone variation) were made, in an attempt to prepare further coordination compounds with interesting luminescent properties. To this end the known secondary amine,
$\left\{\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}$ was reacted with two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ at reflux for 3 d (Equation 2.7).

2.30

Equation 2.7
Unfortunately $\mathbf{2 . 3 0}$ did not crystallise during the course of the reaction, in contrast to the ethylenediamine analogue 2.4. However, following the complete removal of the solvent, a viscous oil was repeatedly isolated. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the isolated oil (in freeze-thawed $\mathrm{CDCl}_{3}$ ) exhibited a new phosphorus singlet resonance at $\delta(\mathrm{P})-28.1 \mathrm{ppm}$ (purity $83 \%$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR), which was assigned to $\mathbf{2 . 3 0}$ by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathbf{2 . 4}[\delta(\mathrm{P})-27.7 \mathrm{ppm}, \Delta \delta(\mathrm{P}) 0.4 \mathrm{ppm}]$. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum also revealed the reaction to be incomplete, with the remaining $17 \%$ of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei assigned to the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. The incomplete nature of the reaction was also evident in the ${ }^{1} \mathrm{H}$ NMR spectrum (in freezethawed $\mathrm{CDCl}_{3}$ ) of the isolated material, which showed unreacted amine and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$. Assignment of the characteristic $\mathrm{CH}_{2}$ resonances of $\mathbf{2 . 3 0}$ was however possible by comparison with the ${ }^{1} \mathrm{H}$ NMR spectrum of the parent amine and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ (see Experimental Section). The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms were found to resonate as a characteristic doublet at $\delta(\mathrm{H}) 3.24 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 4.0 \mathrm{~Hz}\right),{ }^{22,23}$ which compared well with the same hydrogen atoms in $\mathbf{2 . 1}-\mathbf{2 . 4}\left[{ }^{2} J_{\mathrm{PH}} 3.2-3.6 \mathrm{~Hz}\right]$. Further characterisation proved inconclusive.

### 2.11 Conclusion

In summary, a range of new tertiary phosphines with polyaromatic appendages have been prepared, characterised and coordinated to several transition metal centres. The coordination chemistry of $\mathbf{2 . 1}$ - $\mathbf{2 . 4}$ was extensively studied and revealed this family of ditertary phosphines to be capable of bridging two transition metal centres as well as forming new examples of rare, nine-membered cis and trans chelate complexes. Variation of the chemistry used to prepare 2.1-2.4 also allowed the synthesis of two analogous monophosphines $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$ and the diphosphine 2.30. The luminescent properties of selected compounds have also been discussed, in addition to preliminary studies into the cation sensing abilities of the platinum complexes 2.9, 2.10, 2.26 and 2.27. Further study into the luminescent properties of all the tertiary phosphines and coordination compounds reported in this Chapter is required. However, this preliminary work does show promise towards the preparation of new phosphine based molecular devices, as the fluorescent emission of $\mathbf{2 . 2 7}$ is significantly affected by the presence of metal cations, with both variation of PET and the formation of excimer emitting complexes being observed.

## Chapter 3

The Synthesis, Characterisation and Coordination Chemistry of Novel Ferrocenyl Phosphines

### 3.1 Introduction

The ferrocenyl ( Fc ) group continues to play a fundamental role in the design of new mono- and poly-phosphorus containing ligands and some of their transition metal complexes have been studied as homogenous catalysts. ${ }^{46,131-133}$ The Fc group can be employed either as a substituent bonded to phosphorus ${ }^{134}$ or alternatively as a backbone for accessing primary and secondary phosphines, ${ }^{164}$ di- and poly-phosphines, ${ }^{149,208}$ nonsymmetric ligands ${ }^{137,140,162,213}$ and chiral systems. ${ }^{146,151,166,214}$ To date, 1,10bis(diphenylphosphino)ferrocene (dppf) (Figure 3.1) possibly remains the most iconic example of a phosphorus(III) based ligand containing the Fc moiety. ${ }^{43-45,155,156}$ Furthermore the ferrocenyl group continues to attract much attention because of its redox active metal centre, thereby allowing studies of electronic communication for the development of new electronic materials and devices. ${ }^{215-217}$

dppf

1.46

1.56

Figure 3.1 The versatility of the ferrocenyl group.
Recently Tucker and co-workers ${ }^{178}$ have shown how ferrocenyl modified ureas (Figure 3.1, right) can be used as electrochemical sensors for chiral carboxylates. Surprisingly phosphines bearing ferrocenyl groups have been seldom investigated for such a "sensory" role. ${ }^{163,175}$ To this end, modification of the general ligand design discussed in the previous chapter to include a ferrocenyl groups at the R position, $\left\{\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}$, may afford new examples of novel phosphines possessing similar electrochemical properties, whilst providing further examples of this new class of novel ditertiary phosphine.

### 3.2 Preparation and Characterisation of 3.1-3.3

The new ditertiary phosphines $\mathbf{3 . 1}$ - $\mathbf{3 . 3}$ were prepared via the double Mannich-base condensation of the known bis secondary amine ${ }^{218}\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$ with two equiv. of the relevant tertiary phosphine synthon, $\mathrm{RPCH}_{2} \mathrm{OH}\left(\mathrm{RP}=\mathrm{Ph}_{2} \mathrm{P}, \mathrm{Cy}_{2} \mathrm{P}\right.$ or $\mathrm{AdP}=$ 1,3,5,7,-tetramethyl-2,4,8-trioxa-6-phospha-adamantane) (Equation 3.1).


$$
\begin{array}{ll}
\mathrm{PR}=\mathrm{PPh}_{2} & \mathbf{3 . 1} \\
\mathrm{PR}=\mathrm{PCy}_{2} & \mathbf{3 . 2} \\
\mathrm{PR}=\mathrm{PAd} & \mathbf{3 . 3}
\end{array}
$$

Equation 3.1
All three new phosphines precipitated during the course of the reaction, allowing the ligands to be isolated to a high purity (by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR), whilst yields varied across the series (yields ranged between $34-72 \%$ ). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1}$ 3.3 all exhibited a characteristic phosphorus singlet upfield to that of the $\mathrm{PRCH}_{2} \mathrm{OH}$ starting material (Table 3.1). ${ }^{21,58,186}$ The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1}$ and $\mathbf{3 . 2}$ displayed three distinct $\mathrm{CH}_{2}$ environments of characteristic integral and $\delta\left(\mathrm{CH}_{2}\right)$, by comparison with the analogous polyaromatic phosphines 2.1-2.4. In the case of 3.1, the newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated as a characteristic doublet $\left[\delta\left(\mathrm{PCH}_{2}\right)\right.$ $3.11 \mathrm{ppm},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}$ whilst the same hydrogens appeared as a broad singlet in the spectrum of $\mathbf{3 . 2}\left[\delta\left(\mathrm{PCH}_{2}\right) 2.49 \mathrm{ppm}\right]$ (Table 3.1).

Table 3.1 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ and ${ }^{1} \mathrm{H}$ NMR [ $\delta$ in ppm] for $\mathbf{3 . 1}$ - 3.3.

|  | $\delta(\mathrm{P})$ | $\delta\left(\mathrm{CH}_{2} \mathrm{~N}\right)$ | $\delta\left(\mathrm{FcCH}_{2}\right)$ | $\delta\left(\mathrm{PCH}_{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{3 . 1}$ | -27.3 | 3.54 | 2.58 | 3.11 |
| $\mathbf{3 . 2}$ | -18.1 | 3.52 | 2.46 | 2.49 |
| $\mathbf{3 . 3}$ | -42.8 | $3.59,3.42$ | 2.54 | $2.71,2.31$ |

In contrast, the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 . 3}$ contained a series of broad multiplets of similar $\delta(\mathrm{H})$ to the analogous $\mathrm{CH}_{2}$ hydrogen atoms within $\mathbf{3 . 1}$ and $\mathbf{3 . 2}$ [signals ranged between $\delta(\mathrm{H}) 2.28-3.61 \mathrm{ppm}]$. The broad resonances were therefore assigned to the respective $\mathrm{CH}_{2}$ hydrogen atoms within $\mathbf{3 . 3}$ (Table 3.1), with the observed increase in multiplicity being cautiously assigned to a combination of diastereotopic hydrogen atoms, in the case of $\delta\left(\mathrm{CH}_{2} \mathrm{~N}\right)$ and $\delta\left(\mathrm{PCH}_{2}\right)$, and the enantiomeric nature of the phosphaadamantane cages. Previous work by ourselves has shown similar $\mathrm{CH}_{2}$ hydrogen atoms, close to phosphaadamantyl cages, to display this diastereotopic $\mathrm{CH}_{2}$ effect. ${ }^{58}$ Furthermore other research groups have shown compounds containing phosphaadamantyl cages to exist as racemic mixtures of $\alpha$ and $\beta$ enantiomers (Figure 3.2). ${ }^{10,13,219,220}$

$\alpha$

$\beta$

Figure 3.2 Enantiomeric structures of the PAd moiety.

Further work is clearly required to fully characterise the various ${ }^{1} \mathrm{H}$ environments observed in the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 . 3}$, however additional characterisation methods support the synthesis of this phosphine. The absence of a $v_{\mathrm{NH}}$ absorption band from the infrared spectra of 3.1-3.3 further confirmed the ternary nature of the nitrogen atoms within the newly formed ditertiary phosphines, whilst the elemental analysis results for 3.1 - 3.3 were also found to be satisfactory (see Experimental Section). The positive ion FAB mass spectra of $\mathbf{3 . 1}$ and $\mathbf{3 . 2}$ also revealed predictable molecular fragments \{MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}=667\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}$(3.1) and $\left.875[\mathrm{M}-\mathrm{H}]^{+}(\mathbf{3 . 2})\right\}$, and the molecular structures of $\mathbf{3 . 1}$ and $\mathbf{3 . 3}$ have been determined by single crystal X-ray diffraction (Sections 3.2.1 and 3.2.2).

### 3.2.1 Molecular Structure of $\mathbf{3 . 1}$

Orange crystalline blocks suitable for single crystal X-ray diffraction were grown by slow evaporation of a $\mathrm{MeOH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 3.1. The molecular structure was then determined using synchrotron radiation due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature (Figure 3.3). Selected lengths and angles are given in Table 3.2.


Figure 3.3 Molecular structure of 3.1, all hydrogen atoms have been removed for clarity. Symmetry operator for equivalent atoms ' $=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$.

The molecular structure of $\mathbf{3 . 1}$ showed the phosphine to lie across a crystallographic inversion centre located at the mid-point of the ethylenediamine backbone. As a consequence, only half a molecule of $\mathbf{3 . 1}$ was found within the asymmetric unit. Compound 3.1 was found to adopt a significantly open conformation (symmetry imposed), similar to that of the analogous polyaromatic phosphine oxide $\mathbf{2 . 5}$ previously
discussed (Chapter 2, Section 2.3.1), with the phosphorus atoms orientated in an anti conformation with respect to each other $\left[\mathrm{P}(1) \cdots \mathrm{P}\left(1^{\prime}\right) c a .7 .548 \AA, \mathrm{Fe}(1) \cdots \mathrm{Fe}\left(1^{\prime}\right) c a\right.$. $11.181 \AA$, symmetry operator ' $=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1]$. The phosphorus atom adopts a distorted pyramidal geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles (Table 3.2). The nitrogen atom, $\mathrm{N}(1)$, was found to adopt a distorted pyramidal geometry [sum of component angles $\left.=336^{\circ}\right]$. The two $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were found to be eclipsed and essentially coplanar [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(21)=$ $3.4^{\circ}$ ].

Table 3.2 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.1.

| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8324(13)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | $105.06(6)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.8332(13)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $102.09(6)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.8922(12)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13)$ | $97.99(5)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.4573(15)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $115.74(8)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.4721(15)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $110.69(9)$ |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.4653(15)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | $112.97(9)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.4972(17)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | $112.77(9)$ |
| $\mathrm{C}(25)-\mathrm{C}\left(255^{\prime}\right)$ | $1.522(2)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $112.80(9)$ |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | $1.6426(6)$ | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)$ | 3.4 |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | $1.6455(6)$ |  |  |

[^2]
### 3.2.2 Molecular Structure of $\mathbf{3 . 3}$

Orange crystalline tablets suitable for single crystal X-ray diffraction were grown by the slow evaporation of a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 3.3. The molecular structure was determined using synchrotron radiation due to the small crystal dimensions (at least one dimension $<$ 0.05 mm ) and their poorly diffracting nature (Figure 3.4). Selected lengths and angles are given in Table 3.3.


Figure 3.4 Molecular structure of 3.3. All hydrogen atoms have been removed for clarity.

The molecular structure of $\mathbf{3 . 3}$ shows the asymmetric unit to contain one unique molecule of $\mathbf{3 . 3}$, with the two bulky phosphaadamantyl cages adopting an anti conformation with respect to each other (not symmetry imposed) $[\mathrm{P}(1) \cdots \mathrm{P}(2) c a .7 .167$ $\AA, \mathrm{Fe}(1) \cdots \mathrm{Fe}(2) 9.682 \AA]$. The open conformation of $\mathbf{3 . 3}$ is consistent with that previously described for $\mathbf{3 . 1}\left[\mathrm{P}(1) \cdots \mathrm{P}(2) c a .7 .548 \AA, \mathrm{Fe}(1) \cdots \mathrm{Fe}\left(1^{\prime}\right) 11.181 \AA\right]$. The phosphorus atoms within 3.3 were found to adopt a distorted pyramidal arrangement, as
indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles (Table 3.3). The nitrogen atoms were also found to adopt a distorted pyramidal geometry [sum of component angles $=334$ and $331^{\circ}$ respectively]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings within 3.3 were found to be essentially eclipsed [torsional twist about $\mathrm{C}(\mathrm{A}-\mathrm{D})-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(\mathrm{A}-\mathrm{D})=9.3$ and $4.3^{\circ}$ (Table 3.3)] and coplanar, which is consistent with that previously described for $\mathbf{3 . 1}$ [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{C} \mathrm{p}_{\text {cent }}-\mathrm{C}(21)=3.4^{\circ}$ for 3.1] (Table 3.2).

Table 3.3 Selected lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ for 3.3.

| $\mathrm{P}(1)-\mathrm{C}(2)$ | 1.867(2) | $\mathrm{C}(2)-\mathrm{P}(1)-\mathrm{C}(11)$ | 101.93(10) |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(9)$ | 1.877(2) | $\mathrm{C}(9)-\mathrm{P}(1)-\mathrm{C}(11)$ | 100.57(10) |
| $\mathrm{P}(1)-\mathrm{C}(11)$ | 1.858(2) | $\mathrm{C}(2)-\mathrm{P}(1)-\mathrm{C}(9)$ | 92.43(10) |
| $\mathrm{N}(1)-\mathrm{C}(11)$ | 1.470 (3) | $\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{P}(1)$ | 110.88(15) |
| $\mathrm{N}(1)-\mathrm{C}(12)$ | $1.476(2)$ | $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(23)$ | 110.32(16) |
| $\mathrm{N}(1)-\mathrm{C}(23)$ | $1.459(3)$ | $\mathrm{C}(12)-\mathrm{N}(1)-\mathrm{C}(23)$ | 113.25(15) |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | 1.501(3) | $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(12)$ | 110.74(17) |
| $\mathrm{C}(23)-\mathrm{C}(24)$ | 1.522(3) | $\mathrm{N}(1)-\mathrm{C}(12)-\mathrm{C}(13)$ | 114.52(16) |
| $\mathrm{N}(2)-\mathrm{C}(24)$ | 1.460 (3) | $\mathrm{N}(1)-\mathrm{C}(23)-\mathrm{C}(24)$ | 114.47(16) |
| $\mathrm{N}(2)-\mathrm{C}(25)$ | $1.472(3)$ | $\mathrm{N}(2)-\mathrm{C}(24)-\mathrm{C}(23)$ | 114.39(16) |
| $\mathrm{N}(2)-\mathrm{C}(36)$ | $1.468(3)$ | $\mathrm{C}(24)-\mathrm{N}(2)-\mathrm{C}(36)$ | 109.86(17) |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | 1.494(3) | $\mathrm{C}(24)-\mathrm{N}(2)-\mathrm{C}(25)$ | 110.09(16) |
| $\mathrm{P}(2)-\mathrm{C}(36)$ | 1.860(2) | $\mathrm{C}(25)-\mathrm{N}(2)-\mathrm{C}(36)$ | 110.70(18) |
| $\mathrm{P}(2)-\mathrm{C}(38)$ | 1.872(3) | $\mathrm{N}(2)-\mathrm{C}(25)-\mathrm{C}(26)$ | 113.78(17) |
| $\mathrm{P}(2)-\mathrm{C}(45)$ | 1.869(2) | $\mathrm{N}(2)-\mathrm{C}(36)-\mathrm{P}(2)$ | 110.32(15) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | 1.6404(9) | $\mathrm{C}(36)-\mathrm{P}(2)-\mathrm{C}(45)$ | 102.24(11) |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | $1.6476(10)$ | $\mathrm{C}(36)-\mathrm{P}(2)-\mathrm{C}(38)$ | 102.30(11) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ | 1.6484(12) | $\mathrm{C}(38)-\mathrm{P}(2)-\mathrm{C}(45)$ | 92.64(10) |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ | $1.6447(10)$ | $\mathrm{C}(13)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(19)$ | 9.3 |
|  |  | $\mathrm{C}(26)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(32)$ | 4.3 |

[^3]
### 3.3 Platinum(II) Coordination Chemistry of 3.1-3.3

The coordination chemistry of this new family of bimetalloligands (3.1-3.3) was briefly investigated by treatment of each with an equimolar amount of $\mathrm{PtCl}_{2}(\operatorname{cod})$ to afford the four coordinate complexes 3.4-3.6 (Equation 3.2). Yields of the isolated solids varied across the series, with 3.4 isolated in good yield (86\%) whilst $\mathbf{3 . 5}$ and $\mathbf{3 . 6}$ were isolated in relatively poor yields (36 and 39\% respectively).

$\mathrm{PR}=\mathrm{PPh}_{2}$
3 .1
$\mathrm{PR}=\mathrm{PCy}_{2}$
$\mathrm{3.2}$
$\mathrm{PR}=\mathrm{PAd}$
$\mathbf{3 . 3}$
3.4
3.5
3.6

Equation 3.2
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4}$ exhibited a new phosphorus singlet at $\delta(\mathrm{P}) 2.6 \mathrm{ppm}, c a . \delta(\mathrm{P}) 30 \mathrm{ppm}$ downfield from that of the free ligand. The new phosphorus resonance was flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites [ ${ }^{1} J_{\mathrm{PtP}} 3666 \mathrm{~Hz}$ ]. The inference from the characteristically large ${ }^{1} J_{\text {PtP }}$ coupling constant is that the platinum(II) complex adopts a cis conformation in solution. ${ }^{58,93,186,196}$ The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4}$ was also found to contain the anticipated resonances relating to the coordinated ligand, by direct comparison with the ${ }^{1} \mathrm{H}$ NMR spectrum of 3.1.

In contrast the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of the isolated solids gained after treatment of 3.2 and 3.3 with an equimolar amount of $\mathrm{PtCl}_{2}(\operatorname{cod})$, were more complicated than expected. In the case of the reaction between $\mathbf{3 . 3}$ and $\mathrm{PtCl}_{2}(\mathrm{cod})$, the isolated solid revealed several new phosphorus containing species between $\delta(\mathrm{P}) 26.3$ and $-38.2 \mathrm{ppm}\left[\delta(\mathrm{P})-42.8\right.$ (3.3) ppm]. Closer inspection of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum revealed two major species which resonated as singlets flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites, which accounted for $c a .70 \%$ of the total NMR active ${ }^{31} \mathrm{P}$ nuclei $[\delta(\mathrm{P}) 2.9$ ppm, ${ }^{1} J_{\mathrm{PtP}} 3411 \mathrm{~Hz}$ and $-27.5 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3397 \mathrm{~Hz}$, respective ratio $1: 2$ by integration].

The inference from the characteristically large ${ }^{1} J_{\mathrm{PtP}}$ coupling constants, in both cases, is that the majority of the isolated material consisted of two platinum complexes of 3.3, both of which adopt a cis conformation in solution. ${ }^{58,93,186,196}$ The species at $\delta(\mathrm{P}) 2.9$ ppm was assigned to the expected cis-platinum dichloride complex (3.6) (Equation 3.2), by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathbf{3 . 4}\left[\Delta \delta(\mathrm{P}) 0.3 \mathrm{ppm}, \Delta^{1} J_{\mathrm{PtP}} 255 \mathrm{~Hz}\right]$, whilst the remaining species at $\delta(\mathrm{P})-27.5 \mathrm{ppm}$ was cautiously assigned to a [cis,cis$\left\{\mathrm{PtCl}_{2}(\mathbf{3 . 3})\right]_{2}$ dimeric complex of $\mathbf{3 . 3}$ (3.6A, Figure 3.5).

3.3

3.6

3.6A

Figure 3.5 Proposed monomeric (3.6) and dimeric (3.6A) complexes observed by ${ }^{31} \mathrm{P}\{1 \mathrm{H}\}$ NMR spectroscopy (in CDCl3).

Following a search of the literature, there are few examples of large platinumbimetallocyclophanes that are similar to $\mathbf{3 . 6 A} \mathbf{.}^{221-223}$ Of those that are observed, a downfield $\delta(\mathrm{P})$ is common, ${ }^{221-223}$ which is in contrast to the significant upfield $\delta(\mathrm{P})$ suggested to relate to $\mathbf{3 . 6 A}[\delta(\mathrm{P})-27.5 \mathrm{ppm}]$. However the synthesis of $\mathbf{3 . 6 A}$ was supported further by the $\operatorname{Pd}(\mathrm{II})$ and $\operatorname{Rh}(\mathrm{I})$ coordination chemistry of $\mathbf{3 . 1}$, which afforded two further examples of 18 -membered bimetallocyclophanes (Section 3.4.2). The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid ( $\mathbf{3 . 6} / \mathbf{3 . 6 A}$ ) also revealed the anticipated $\mathrm{CH}_{2}$ and ferrocenyl hydrogen atoms as broad resonances, an effect that may be expected if such a mixture of analogous mono and dimeric complexes were to exist $\left[\delta\left(\mathrm{C}_{5} \mathrm{H}_{5}\right.\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{4}\right) 4.13$ - $4.19 ; \delta\left(\mathrm{CH}_{2}\right) 4.03$, 3.70 and 2.96 ppm$]$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid that was gained following treatment of 3.2 with $\mathrm{PtCl}_{2}(\operatorname{cod})$ was also unexpected, with the spectrum revealing several phosphorus containing species between $\delta(\mathrm{P}) 33.5-5.4 \mathrm{ppm}$. The downfield
nature of these resonances, compared to that of $3.2[\delta(\mathrm{P})-18.1 \mathrm{ppm}]$, suggested a change in the electronic properties of the phosphorus atoms within 3.2 (presumably coordination / oxidation), however no platinum satellites were observed. Analysis of the filtrate residue did however reveal two distinct platinum complexes by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ) [ $\left.\delta(\mathrm{P}) 18.8 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3586 \mathrm{~Hz} ; \delta(\mathrm{P}) 17.9 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3402 \mathrm{~Hz}\right]$. The characteristically large ${ }^{1} J_{\mathrm{PtP}}$ coupling constants and downfield nature of the singlets implies that the two platinum complexes adopt a cis conformation in solution (possibly monomeric / dimeric). ${ }^{58,93,186,196}$ Further analysis of the filtrate residue supported the preparation of $\mathbf{3 . 5}$ (monomeric / dimeric) with the elemental analysis result agreeing with the formula, $3.5 \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

Further support for the preparation of $\mathbf{3 . 4} \mathbf{- 3 . 6}$ comes from positive ion FAB mass spectroscopy results which gave the expected fragmentation patterns (monomeric only) $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}=1118[\mathrm{M}]^{+}(\mathbf{3 . 4}), 1071[\mathrm{M}-\mathrm{Cl}]^{+}(\mathbf{3 . 5})\right.$ and $\left.1071[\mathrm{M}-2 \mathrm{Cl}]^{+} \mathbf{( 3 . 6 )}\right\}$. The elemental analysis results of $\mathbf{3 . 4}$ and $\mathbf{3 . 6}$ were also found to be satisfactory (see Experimental Section). The preparation of $\mathbf{3 . 4}$ and $\mathbf{3 . 6}$ was further supported by the FTIR spectra which contained two characteristic $v_{\text {PtCl }}$ absorption bands between $290-318$ $\mathrm{cm}^{-1} .{ }^{58,186,196}$ Observation of the $v_{\mathrm{PtCl}}$ absorption bands within the FT-IR spectrum of $\mathbf{3 . 5}$ (filtrate residue) was not possible due to a lack of a spectrometer with appropriate scan range. The molecular structure of $\mathbf{3 . 4}$ has also been determined by single crystal X-ray diffraction (Sections 3.3.1).

### 3.3.1 Molecular Structure of $\mathbf{3 . 4}$

Yellow crystalline blocks suitable for single crystal X-ray diffraction were grown by the slow evaporation of a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{Et}_{2} \mathrm{O}$ solution of 3.4. The molecular structure was determined (Figure 3.6) with selected lengths and angles given in Table 3.4.


Figure 3.6 Molecular structure of 3.4. All hydrogen atoms, except those on the ethylenediamine backbone, and a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule of crystallisation have been removed for clarity.

The molecular structure of 3.4 shows the asymmetric unit to contain one unique molecule of 3.4 and one disordered molecule of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ [major disorder component 59.2(9)\%]. The platinum(II) dichloride complex was found to adopt a distorted square planar geometry with respect to the metal centre $\left[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2) 166.34(5)^{\circ}, \mathrm{P}(2)-\right.$ $\mathrm{Pt}(1)-\mathrm{Cl}(1) 170.42(5)^{\circ}$, Table 3.4], with 3.1 coordinating to the platinum(II) centre via
both phosphorus atoms to form a nine-membered chelate ring [bite angle, $\mathrm{P}(1)-\mathrm{Pt}(1)-$ $\left.\mathrm{P}(1), 103.05(5)^{\circ}\right]$. The phosphorus atoms were found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{Pt}-\mathrm{P}-\mathrm{C}$ angles (Table 3.4). The nitrogen atoms were found to adopt a distorted pyramidal geometry [sum of component angles $=336$ and $331^{\circ}$ respectively]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were found to be essentially eclipsed and coplanar, as previously observed in the molecular structure of $\mathbf{3 . 1}$ [torsional twist about $\left.\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(21)=1.6^{\circ}, \mathrm{C}(28)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(34)=8.9^{\circ}\right]$. The $\mathrm{Fe}(1) \cdots \mathrm{Fe}(2)$ separation was found to be shorter than that observed in the molecular structure of $\mathbf{3 . 1}[\mathrm{Fe}(1) \cdots \mathrm{Fe}(2) c a .6 .510 \AA$ (3.4) and $11.181 \AA(3.1)]$ and is thought to be a direct consequence of coordination. This change in $\mathrm{Fe}(1) \cdots \mathrm{Fe}(2)$ separation $[\Delta \mathrm{Fe}(1) \cdots \mathrm{Fe}(2) c a .5 \AA]$ could be important when comparing the interaction between iron centres during an investigation of the electrochemical properties of $\mathbf{3 . 4}$ and the free ligand (vide infra).

One feature of the molecular structure of 3.4 that has been observed for analogous platinum(II) dichloride complexes (2.14-2.17) and in other medium ring sized palladium(II) and platinum(II) complexes, ${ }^{199,200}$ is the close contact between $\mathrm{H}(26 \mathrm{~A})$ of the coordinated ligand and the platinum(II) centre $[\mathrm{C}(26) \cdots \mathrm{Pt}(1) 3.477 \AA, \mathrm{H}(26 \mathrm{~A}) \cdots \mathrm{Pt}(1)$ $2.4871 \AA, \operatorname{Pt}(1) \cdots \mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26) 147.6^{\circ}$ ] (Figure 3.6). This axial interaction between the $\mathrm{C}_{\mathrm{sp}}{ }^{3}-\mathrm{H}$ bond of the ligand backbone and the metal centre is not significantly mirrored in the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 . 4}$, in which there is only a small downfield shift $\left[\mathrm{ca} . \delta\left(\mathrm{CH}_{2}\right)\right.$ $0.6 \mathrm{ppm}]$. Upon further inspection of the crystal structure of $\mathbf{3 . 4}$ a slipped intramolecular $\pi \cdots \pi$ interaction between the phenyl rings containing $\mathrm{C}(7)$ and $\mathrm{C}(45)$ was also observed [minimum separation $=3.04 \AA$, c.f. graphite $3.45 \AA .{ }^{92}$ The phenyl ring containing $\mathrm{C}(45)$ is slanted $12.5^{\circ}$, with respect to phenyl ring containing $\left.\mathrm{C}(7)\right]$.

Table 3.4 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.4.

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | 2.2551(15) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 103.05(5) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | 2.2401(14) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 84.71(5) |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3535(14)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 84.29(5) |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.3558(15)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 87.00(5) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.824(6) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 166.34(5) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.819(6) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 170.42 (5) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.871(6) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 113.38(19) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.456(7)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 124.84(19) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.472(7)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 104.4(2) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | 1.484(7) | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 113.3(4) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.504(8) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 110.3(4) |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | $1.509(8)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 112.5(4) |
| $\mathrm{N}(2)-\mathrm{C}(26)$ | $1.485(7)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 113.3(4) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.492(7) | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | 115.1(5) |
| $\mathrm{N}(2)-\mathrm{C}(38)$ | 1.468(7) | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}(26)$ | 114.1(5) |
| $\mathrm{C}(27)-\mathrm{C}(28)$ | $1.485(8)$ | $\mathrm{N}(2)-\mathrm{C}(26)-\mathrm{C}(25)$ | 113.5(4) |
| $\mathrm{P}(2)-\mathrm{C}(38)$ | 1.853(6) | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(27)$ | 109.6(4) |
| $\mathrm{P}(2)-\mathrm{C}(39)$ | 1.829(6) | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(38)$ | 109.5(4) |
| $\mathrm{P}(2)-\mathrm{C}(45)$ | 1.822(6) | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(38)$ | 112.7(4) |
| $\mathrm{Pt}(1)-\mathrm{H}(26 \mathrm{~A})$ | 2.49 | $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(28)$ | 112.2(5) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | 1.6418(28) | $\mathrm{N}(2)-\mathrm{C}(38)-\mathrm{P}(2)$ | 112.8(4) |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | 1.6536(31) | $\mathrm{C}(38)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 107.77(19) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ | 1.6488(26) | $\mathrm{C}(39)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 111.90(18) |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ | 1.6544(29) | $\mathrm{C}(45)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 123.9(2) |
|  |  | $\mathrm{Pt}(1) \cdots \mathrm{H}(26 \mathrm{~A})-\mathrm{C}(26)$ | 148 |
|  |  | $\mathrm{C}(13)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(19)$ | 1.6 |
|  |  | $\mathrm{C}(26)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(32)$ | 8.5 |

$\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24), \mathrm{CpC}_{\text {cent }}=\mathrm{C}(28)$ to $\mathrm{C}(32)$, $\mathrm{CpD}_{\text {cent }}=\mathrm{C}(33)$ to $\mathrm{C}(37)$.

### 3.4 Coordination Chemistry of 3.1

Following on from the successful preparation of 3.4, the coordination chemistry of the new bimetalloligand 3.1 was explored further by reaction with a series of transition metal precursors, in an attempt to gain a greater understanding of the coordination modes available to this type of novel ditertiary phosphine.

### 3.4.1 Palladium(II) and Platinum(II) Coordination Chemistry of 3.1.

The ability of $\mathbf{3 . 1}$ to form further examples of 9 -membered precious metal chelate complexes was explored further by treatment of the bimetalloligand with an equimolar amount of four readily available platinum and palladium precursors; $\mathrm{PdCl}_{2}(\mathrm{cod})$, $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}, \mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\mathrm{cod})$ and $\mathrm{Pt}\left(\mathrm{CH}_{3}\right)_{2}(\operatorname{cod})$ (Scheme 3.1).


Scheme 3.1 (i) $\mathrm{PdCl}_{2}(\operatorname{cod}), \mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ or $\operatorname{Pt}\left(\mathrm{CH}_{3}\right)_{2}(\operatorname{cod})$, (ii) $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\operatorname{cod})$

In contrast to the $\mathrm{PtCl}_{2}$ (cod) chemistry previously discussed, reaction of $\mathbf{3 . 1}$ with an equimolar amount of $\mathrm{PdCl}_{2}(\operatorname{cod})$ or $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ gave an impure sample of $\mathbf{3 . 7}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum revealed the presence of several phosphorus containing species between $\delta(\mathrm{P}) 20.8 \mathrm{ppm}$ and 11.1 ppm, the major species were tentatively assigned to either cis- or trans-isomers of $\mathrm{PdCl}_{2}(\mathbf{3 . 1})$ (possibly monomeric or dimeric) due to their downfield nature compared to that of the free ligand $[\delta(\mathrm{P})-27.3 \mathrm{ppm}(\mathbf{3 . 1})]$. Careful monitoring of $\mathrm{CDCl}_{3}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ or $\mathrm{C}_{6} \mathrm{D}_{6}$ solutions containing an equimolar amount of $\mathbf{3 . 1}$ and $\mathrm{PdCl}_{2}(\operatorname{cod})$ or $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$,
over a period of four days, revealed the gradual disappearance of these signals and the emergence of two new doublets at significant downfield shifts [ $\delta(\mathrm{P}) 159.9 \mathrm{ppm}, 79.1$ $\mathrm{ppm},{ }^{2} J_{\mathrm{PP}} 17 \mathrm{~Hz}$. This in conjunction with the observation of a new doublet at $\delta\left(\mathrm{CH}_{2}\right)$ $3.41 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 6.8 \mathrm{~Hz}\right)$ in the ${ }^{1} \mathrm{H}$ NMR spectrum led us to speculate that $\mathrm{PdCl}_{2}(\mathbf{3 . 1})$ undergoes slow decomposition to give the five-membered chelate complex $\mathrm{PdCl}_{2}\left(\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OPPh}_{2}\right)(\mathbf{3 . 7 A})$ with the elimination of some, as of yet unidentified, ferrocenylamine by-products. Support for the nonsymmetric nature of this coordinated bidentate phosphorus(III) ligand comes from previous studies with $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OPPh}_{2}$ and, ${ }^{197}$ more recently, $\mathrm{RR}^{\prime} \mathrm{POCH}_{2} \mathrm{P}\left(\mathrm{CH}_{2} \mathrm{OH}\right)_{2}\left(\mathrm{R}, \mathrm{R}^{\prime}=\mathrm{Ph}, \mathrm{Cy}\right),{ }^{198}$ which support the characteristic $\delta(\mathrm{P})$ and ${ }^{2} J_{\mathrm{PP}}$ coupling constants observed. The same transformation was also observed for 3.4 upon monitoring of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ and ${ }^{1} \mathrm{H}$ NMR spectra over time, however the rate of decomposition was notably slower as would be expected, owing to the different reactivity between $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ square-planar metal centres. This decomposition effect has also been observed in the previously discussed ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the analogous aryl substituted palladium complexes $\mathbf{2 . 1 1} \mathbf{- 2 . 1 4}$, and appears to be an intrinsic property of this family of palladium dichloride complexes [ $\mathrm{PdCl}_{2}\left\{\mathrm{RCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2}, \mathrm{R}=$ ferrocenyl or aryl group]. Moreover 3.7A has been prepared on a preparative scale following the 4 d ambient temperature reaction of an equimolar $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{3 . 1}$ and $\mathrm{PdCl}_{2}(\operatorname{cod})\left[\delta(\mathrm{P})\right.$ in $\left(\mathrm{CDCl}_{3}\right)$ : 159.9 and 79.9 $\mathrm{ppm},{ }^{2} J_{\mathrm{PP}} 17.0 \mathrm{~Hz} ; \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 542[\mathrm{M}-\mathrm{Cl}]^{+} ; v_{\mathrm{PdCl}} 308$ and $\left.289 \mathrm{~cm}^{-1}\right]$.

In contrast, treatment of $\mathbf{3 . 1}$ with $\operatorname{Pt}\left(\mathrm{CH}_{3}\right)_{2}(\operatorname{cod})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at ambient temperature gave the cis-platinum(II) complex 3.8, in poor yield (33\%), following recrystallisation from hexane (Scheme 3.1). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid exhibited two new phosphorus species with resonances shifted significantly downfield from that of the free ligand at $\delta(\mathrm{P}) 28.3$ and 19.7 ppm respectively. The new singlet at $\delta(\mathrm{P}) 19.7 \mathrm{ppm}$, accounted for $82 \%$ of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei, and was flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites [ ${ }^{1} J_{\mathrm{PtP}} 1866 \mathrm{~Hz}$ ], and was assigned to 3.8. The characteristically small ${ }^{1} J_{\mathrm{PtP}}$ coupling constants supported the proposed cis conformation by comparison with literature examples. ${ }^{224}$ The remaining singlet at $\delta(\mathrm{P}) 28.3 \mathrm{ppm}$, was assigned to the symmetrical phosphine oxide of $\mathbf{3 . 1}$ by comparison with the analogous
aryl substituted diphosphine oxides $\mathbf{2 . 5}[\delta(\mathrm{P}) 26.7 \mathrm{ppm}(\mathbf{2 . 5})]$, previously discussed. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 8}$ was found to contain the anticipated resonances relating to the coordinated ligand in addition to a new $\mathrm{CH}_{3}$ multiplet at $\delta\left(\mathrm{CH}_{3}\right) 0.25 \mathrm{ppm}$ $\left[^{2} J_{\mathrm{PtH}} 69.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{PH}} 13.2 \mathrm{~Hz},{ }^{2} J_{\mathrm{PtH}}\right.$ and $\left.{ }^{3} J_{\mathrm{PH}} 12.8 \mathrm{~Hz}\right]$. Furthermore the positive ion FAB mass spectrum of $\mathbf{3 . 8}$ gave the expected fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: m/z 1062 $\left.\left[\mathrm{M}-\mathrm{CH}_{3}\right]^{+}\right\}$, and the elemental analysis result supported the formulaution $3.8 \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$.

Reaction of 3.1 with $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\operatorname{cod})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ afforded the trans-spanning diphosphine complex 3.9, in reasonable yield (61\%) (Scheme 3.1). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid exhibited a new ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ singlet significantly downfield compared to $\mathbf{3 . 1}$, at $\delta(\mathrm{P}) 13.0 \mathrm{ppm}$. The proposed trans disposition of the complex (monomeric or dimeric) was supported by the characteristic splitting pattern observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum, as a symmetrical P-Pd-P centre is only possible for such a trans-conformation. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 9}$ also supported this trans disposition, with a new $\mathrm{CH}_{3}$ triplet resonance $\left[\delta\left(\mathrm{CH}_{3}\right) 0.00,{ }^{3} J_{\mathrm{PH}} 12\right.$ $\mathrm{Hz}]$, characteristic of a symmetrical trans $-\mathrm{P}-\mathrm{PdCl}\left(\mathrm{CH}_{3}\right)-\mathrm{P}$ environment, being observed in addition to the anticipated resonances relating to the coordinated ligand. Further support for the preparation of $\mathbf{3 . 9}$ came from positive ion FAB mass spectroscopy, which revealed the expected fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 973[\mathrm{M}-\mathrm{Cl}]^{+}\right\}$, in addition to elemental analysis, which agreed with the formula $3.9 \cdot 2.5 \mathrm{H}_{2} \mathrm{O}$. Moreover the FT-IR spectrum of $\mathbf{3 . 9}$ contained a $v_{\text {PdCl }}$ absorption band at $v_{\text {PdCl }} 263 \mathrm{~cm}^{-1} .{ }^{21}$

Interestingly, closer inspection of the FAB mass spectrum of $\mathbf{3 . 9}$ suggested that the complex could be of a trans, trans $-\left[\operatorname{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}\{\mathbf{3 . 1}\}\right]_{2}$ dimeric disposition, rather than its anticipated monomeric form, with the spectrum revealing dimeric fragments $\{\mathrm{FAB}-$ MS: m/z $\left.2018[2 \mathrm{M}]^{+}, 1983[2 \mathrm{M}-\mathrm{Cl}]^{+}\right\}$. Following a search of the literature no nitrogen containing trans,trans $-\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}$ diphosphine complexes have previously been reported, however an analogous alkyl diphosphine dimer has previously been discussed $\left[(\mathrm{dpph}) \mathrm{PdCl}_{2}\right]_{2}$ (dpph = 1,6-bis(diphenylphosphino)hexane). ${ }^{225}$ The isolated solid, 3.9, is therefore considered to be monomeric in nature, due to the lack of reported examples and the unreliability of FAB mass spectroscopy at high molecular weights ( $>1000 \mathrm{~m} / \mathrm{z}$ ).

The dimeric form may also be possible and has been seen in subsequent rhodium coordination chemistry (vide infra). Further analysis of $\mathbf{3 . 9}$ by MALDI mass spectroscopy would be useful in order to accurately determination the dimers high molecular weight.

### 3.4.2 Rhodium(I) Coordination Chemistry of $\mathbf{3 . 1}$

Reaction of $\mathbf{3 . 1}$ with half an equiv. of $\left\{\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ afforded a new example of a trans, trans-diphosphine complex (3.10) (Equation 3.3).


Equation 3.3
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1 0}$ revealed a new doublet significantly downfield to that of the free ligand at $\delta(\mathrm{P}) 16.6 \mathrm{ppm},{ }^{1} J_{\mathrm{RhP}} 130 \mathrm{~Hz}$. The proposed trans disposition of the complex was supported by the characteristic splitting pattern observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum, as a symmetrical $\mathrm{P}-\mathrm{Rh}-\mathrm{P}$ centre is only possible for such a trans- conformation. The ${ }^{1} J_{\text {RhP }}$ coupling constant is also consistent with other transrhodium complexes. ${ }^{93,206}$ The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1 0}$ was found to contain the anticipated resonances relating to the coordinated ligand. The molecular structure of $\mathbf{3 . 1 0}$ has also been determined and displayed the proposed trans,trans$\{\mathrm{Rh}(\mathrm{CO}) \mathrm{Cl}\}$ disposition, which was not apparent from the NMR data. Following a search of the literature a similar dimeric species with a trans,trans $-\{\mathrm{Rh}(\mathrm{CO}) \mathrm{Cl}\}$
structure has recently been proposed $\left[\left\{\mathrm{RhCl}(\mathrm{CO})\left\{\mathrm{Ph}_{2} \mathrm{P}\left(\mathrm{CH}_{2}\right)_{\mathrm{n}} \mathrm{PPh}_{2}\right\}\right]_{2}(\mathrm{n}=1,3\right.$ or 4$){ }^{206}$ adding further support to the bulk of $\mathbf{3 . 1 0}$ adopting a similar connectivity. Analysis of the bulk material by MALDI mass spectroscopy did not support the dimeric nature of 3.10. The nature of $\mathbf{3 . 1 0}$ is therefore tentatively considered to be dimeric, owing to similarity to known literature examples and also the molecular structure; which must be treated with caution owing to the nature of single crystal X-ray diffraction. The preparation of $\mathbf{3 . 1 0}$ (monomeric or dimeric) is further supported by positive ion FAB mass spectroscopy, which showed the anticipated fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: $\left.\mathrm{m} / \mathrm{z} 983[0.5 \mathrm{M}-\mathrm{Cl}]^{+}\right\}$, and also by elemental analysis (see Experimental Section). The FT-IR spectrum of $\mathbf{3 . 1 0}$ also contained a characteristic $v_{\mathrm{C}=\mathrm{O}}$ absorption band [ $\mathrm{v}_{\mathrm{C}=\mathrm{O}} 1970$ $\left.\mathrm{cm}^{-1}\right]$. ${ }^{194,206}$

### 3.4.2.1 Molecular Structure of $\mathbf{3 . 1 0}$

Yellow crystalline plates suitable for X-ray diffraction were grown by the slow evaporation of a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{Et}_{2} \mathrm{O}$ filtrate of 3.10. The molecular structure of $\mathbf{3 . 1 0}$ was determined using synchrotron radiation due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) (Figure 3.7). Selected lengths and angles are given in Table 3.5. The molecular structure of $\mathbf{3 . 1 0}$ shows $\mathbf{3 . 1}$ to bridge two $\mathrm{RhCl}(\mathrm{CO})$ fragments, via both phosphorus atoms, to form a large 18-membered metallomacrocyclic dimer. The dimer was found to lie on a crystallographic inversion centre located at the centroid of the 18membered ring. As a consequence the asymmetric unit was found to contain half a molecule of 3.10. The geometry about the rhodium centres was distorted square planar, with the $\mathrm{P}(1)-\mathrm{Rh}(1)-\mathrm{P}(2)$ bite angle deviating by some $18^{\circ}$ from the idealised $180^{\circ}$ angle for a trans disposition of groups $[\mathrm{C}(51)-\mathrm{Rh}(1)-\mathrm{Cl}(1) 178.02(12), \mathrm{P}(1)-\mathrm{Rh}(1)-\mathrm{P}(2)$ $\left.161.97(3)^{\circ}\right]$. The phosphorus atoms adopted a distorted tetrahedral arrangement, as indicated by the relevant Rh- $\mathrm{P}-\mathrm{C}$ angles. The nitrogen atoms were found to adopt a distorted pyramidal geometry [sum of component angles $=336$ and $342^{\circ}$ respectively]. The Fe(II) cyclopentadienyl rings were found to be essentially eclipsed and coplanar [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(21)=13.0^{\circ}, \mathrm{C}(28)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(34)=$
$3.4^{\circ}$ ]. This compares well with the value observed in the free ligand (3.1) [torsional twist about $\left.\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(21)=3.4^{\circ}\right]$.


Figure 3.7 Molecular structure of 3.10. All hydrogen atoms and phenyl carbons, except ipso carbons, have been removed for clarity. Symmetry operator for equivalent atoms ' = $-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$.

Following a search of the CSD, $\mathbf{3 . 1 0}$ was found to represent the first crystallographically characterised metallacycle containing an $\mathrm{Rh}_{2} \mathrm{Fe}_{4}$ arrangement of metal centres. In comparison, other large metallocycles have been observed in the literature with the analogous ligand dpph being shown to bridge various metal fragments of different geometry and coordination number; $\left\{\mathrm{Cu}\left(\mathrm{ClO}_{4}\right)\right\},{ }^{226}\left(\right.$ trans $\left.-\mathrm{PdCl}_{2}\right),{ }^{225} \mathrm{CoCl}_{2}{ }^{227}$ and (trans $\left.-\mathrm{Mo}(\mathrm{CO})_{4}\right)^{228}$

Table 3.5 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.10.

| $\mathrm{Rh}(1)-\mathrm{P}(1)$ | 2.3063(9) | $\mathrm{P}(1)-\mathrm{Rh}(1)-\mathrm{P}(2)$ | 161.97(3) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Rh}(1)-\mathrm{P}(2)$ | $2.3130(9)$ | $\mathrm{C}(51)-\mathrm{Rh}(1)-\mathrm{Cl}(1)$ | 178.02(12) |
| $\mathrm{Rh}(1)-\mathrm{Cl}(1)$ | $2.3739(9)$ | $\mathrm{C}(51)-\mathrm{Rh}(1)-\mathrm{P}(1)$ | 90.17(11) |
| $\mathrm{Rh}(1)-\mathrm{C}(51)$ | 1.809(4) | $\mathrm{C}(51)-\mathrm{Rh}(1)-\mathrm{P}(2)$ | 93.82(11) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.834(3)$ | $\mathrm{P}(1)-\mathrm{Rh}(1)-\mathrm{Cl}(1)$ | 90.13(3) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.818(3) | $\mathrm{P}(2)-\mathrm{Rh}(1)-\mathrm{Cl}(1)$ | 85.31(3) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.845(3) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Rh}(1)$ | 100.32(11) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.458(4)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Rh}(1)$ | 120.10(11) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | 1.470(4) | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Rh}(1)$ | 117.71(11) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.476(4)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 115.6(2) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.499 (5) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 112.9(2) |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | 1.516(4) | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 110.0(2) |
| $\mathrm{N}(2)-\mathrm{C}(26)$ | $1.475(4)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 113.1(3) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.470(4) | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}(26)$ | 114.2(3) |
| $\mathrm{N}(2)-\mathrm{C}\left(38{ }^{\prime}\right)$ | 1.451(4) | $\mathrm{N}(2)-\mathrm{C}(26)-\mathrm{C}(25)$ | 108.8(3) |
| $\mathrm{C}(27)-\mathrm{C}(28)$ | 1.506(4) | $\mathrm{C}\left(38^{\prime}\right)-\mathrm{N}(2)-\mathrm{C}(26)$ | 114.7(2) |
| $\mathrm{P}(2)-\mathrm{C}(38)$ | 1.859(3) | $\mathrm{C}(38)-\mathrm{N}(2)-\mathrm{C}(27)$ | 113.9(3) |
| $\mathrm{P}(2)-\mathrm{C}(39)$ | 1.817 (3) | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(27)$ | 113.7(3) |
| $\mathrm{P}(2)-\mathrm{C}(45)$ | 1.816(3) | $\mathrm{N}\left(2^{\prime}\right)-\mathrm{C}(38)-\mathrm{P}(2)$ | 106.4(2) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | $1.6426(17)$ | $\mathrm{C}(38)-\mathrm{P}(2)-\mathrm{Rh}(1)$ | $119.09(11)$ |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | $1.6415(19)$ | $\mathrm{C}(39)-\mathrm{P}(2)-\mathrm{Rh}(1)$ | 103.43(11) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ | 1.6456(16) | $\mathrm{C}(45)-\mathrm{P}(2)-\mathrm{Rh}(1)$ | 120.53(12) |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ | $1.6495(18)$ | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)$ | 13.0 |
|  |  | $\mathrm{C}(28)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(34)$ | 3.4 |

Symmetry operations for equivalent atoms ' $=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$.
$\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24), \mathrm{CpC}_{\text {cent }}=\mathrm{C}(28)$ to $\mathrm{C}(32)$,
$\mathrm{CpD}_{\text {cent }}=\mathrm{C}(33)$ to $\mathrm{C}(37)$.

### 3.4.3 Molybdenum(0) Coordination Chemistry of 3.1

The displacement of nbd from $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd})$ with an equimolar amount of $\mathbf{3 . 1}$ afforded the octahedral complex 3.11, in reasonable yield (58\%), following a 10 d reflux under nitrogen (Equation 3.4).


The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1 1}$ exhibited a new singlet resonance downfield to that of the free ligand at $\delta(\mathrm{P}) 29.0 \mathrm{ppm}[\delta(\mathrm{P})-27.3 \mathrm{ppm}(3.1)]$, indicating a symmetrical coordination complex had been prepared. The conformation of $\mathbf{3 . 1 1}$ was however not apparent from the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, as both cis and trans conformers of $\operatorname{Mo}(\mathrm{CO})_{4}(\mathbf{3 . 1})$ are possible. The preparation of the cis isomer of $\mathbf{3 . 1 1}$ was however confirmed by the complex's molecular structure which shows ligand $\mathbf{3 . 1}$ to coordinate the molybdenum centre via both phosphorus atoms. This cis conformation was further supported by the complexes infrared spectrum which contained four characteristic terminal $\mathrm{v}_{\mathrm{C}=0}$ absorption bands $\left[\mathrm{v}_{\mathrm{C}=0}\right.$ 2018, 1918, 1898, $\left.\left.1870 \mathrm{~cm}^{-1}\right].\right]^{203,208}$ The preparation of the new trimetallic six-coordinate complex was further supported by elemental analysis, which agreed with the formula $\mathbf{3 . 1 1} \cdot 1.75 \mathrm{CH}_{2} \mathrm{Cl}_{2}$. Furthermore the positive ion FAB mass spectrum contained the expected parent ion and fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1061[\mathrm{M}]^{+}, 1005[\mathrm{M}-2 \mathrm{CO}]^{+}\right\}$.

### 3.4.3.1 Molecular Structure of $\mathbf{3 . 1 1}$

Orange crystalline blocks of $\mathbf{3 . 1 1}$ suitable for single crystal X-ray diffraction were grown by the slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CHCl}_{3}$ solution of 3.11. The molecular structure of $\mathbf{3 . 1 1}$ was determined from reflection data collected by the EPSRC National Crystallography Service (Figure 3.8). Selected lengths and angles are given in Table 3.6.


Figure 3.8 Molecular structure of 3.11. All hydrogen atoms and solvent molecules have been omitted for clarity.

The molecular structure of $\mathbf{3 . 1 1}$ showed the asymmetric unit to consist of one unique molecule of $\mathbf{3 . 1 1}$ and half a disordered molecule of $\mathrm{CHCl}_{3}$ of crystallisation. The solvating $\mathrm{CHCl}_{3}$ was modelled as a diffuse region of electron density (Platon squeeze procedure). ${ }^{229}$ The trimetallic complex was found to adopt a distorted octahedral geometry with respect to the molybdenum centre $\left[\mathrm{C}(51)-\mathrm{Mo}(1)-\mathrm{P}(2) 172.82(9)^{\circ}\right.$, $\mathrm{C}(52)-\mathrm{Mo}(1)-\mathrm{P}(1) \quad 169.51(9)^{\circ}$ and $\left.\mathrm{C}(53)-\mathrm{Mo}(1)-\mathrm{C}(54) \quad 178.49(12)^{\circ}\right]$ with $\mathbf{3 . 1}$
coordinating the metal via both phosphorus atoms, to form a nine-membered chelate ring [bite angle, $\mathrm{P}(1)-\mathrm{Mo}(1)-\mathrm{P}(2) 101.83(2)^{\circ}$ ]. The $\mathrm{Mo}-\mathrm{P}$ and $\mathrm{Mo}-\mathrm{C}$ bond lengths are broadly as anticipated, ${ }^{202,203}$ whilst the $\mathrm{P}(1)-\mathrm{Mo}(1)-\mathrm{P}(2)$ bite angle was similar to that found in the analogous four coordinate platinum dichloride complex 3.4 [bite angle, $\left.\mathrm{P}(1)-\operatorname{Pt}(1)-\mathrm{P}(2) 103.05(5)^{\circ}\right]$. The phosphorus atoms were found to adopt a distorted tetrahedral arrangement as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Mo}$ angles, whilst the nitrogen atoms were found to adopt a distorted pyramidal geometry [sum of component angles for $\mathrm{N}(1), \mathrm{N}(2)=331$ and $340^{\circ}$ respectively]. The Fe(II) cyclopentadienyl rings were found to be essentially eclipsed and coplanar [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}$ $\left.\mathrm{C}(21)=11.8^{\circ}, \mathrm{C}(28)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(34)=13.2^{\circ}\right]$, as previously observed in the free ligand [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }} \mathrm{C}(21)=3.4^{\circ}$. The molecular structure of $\mathbf{3 . 1 1}$ was also found to compare well with the analogous polyaromatic derivative $\mathbf{2 . 2 2}$ (Section 2.4.3.1).

Table 3.6 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.11.

| $\mathrm{Mo}(1)-\mathrm{C}(51)$ | 1.980(3) | $\mathrm{P}(1)-\mathrm{Mo}(1)-\mathrm{P}(2)$ | 101.83(2) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Mo}(1)-\mathrm{C}(52)$ | 1.995(3) | $\mathrm{C}(51)-\mathrm{Mo}(1)-\mathrm{C}(52)$ | 84.46(13) |
| $\mathrm{Mo}(1)-\mathrm{C}(53)$ | 2.022(3) | $\mathrm{C}(51)-\mathrm{Mo}(1)-\mathrm{C}(53)$ | 87.94(13) |
| $\mathrm{Mo}(1)-\mathrm{C}(54)$ | 2.063(3) | $\mathrm{C}(52)-\mathrm{Mo}(1)-\mathrm{C}(53)$ | 90.09(13) |
| $\mathrm{Mo}(1)-\mathrm{P}(1)$ | 2.5416(7) | $\mathrm{C}(51)-\mathrm{Mo}(1)-\mathrm{C}(54)$ | 92.23(13) |
| $\mathrm{Mo}(1)-\mathrm{P}(2)$ | 2.5547(8) | $\mathrm{C}(52)-\mathrm{Mo}(1)-\mathrm{C}(54)$ | 91.42(13) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.839(3) | $\mathrm{C}(51)-\mathrm{Mo}(1)-\mathrm{P}(1)$ | 85.07(9) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.844(3) | $\mathrm{C}(52)-\mathrm{Mo}(1)-\mathrm{P}(1)$ | 169.51(9) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.861(3) | $\mathrm{C}(53)-\mathrm{Mo}(1)-\mathrm{P}(1)$ | 88.86(9) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | 1.465(3) | $\mathrm{C}(54)-\mathrm{Mo}(1)-\mathrm{P}(1)$ | 89.66(8) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | 1.478(4) | $\mathrm{C}(52)-\mathrm{Mo}(1)-\mathrm{P}(2)$ | 88.61(9) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | 1.469 (3) | $\mathrm{C}(53)-\mathrm{Mo}(1)-\mathrm{P}(2)$ | 90.21(9) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.500(4) | $\mathrm{C}(54)-\mathrm{Mo}(1)-\mathrm{P}(2)$ | 89.81(8) |
| C(25)-C(26) | 1.519(4) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Mo}(1)$ | 111.66(9) |
| $\mathrm{N}(2)-\mathrm{C}(26)$ | 1.461(3) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Mo}(1)$ | 115.87(9) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ | 1.474(3) | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Mo}(1)$ | 122.96(10) |
| $\mathrm{N}(2)-\mathrm{C}(38)$ | 1.457(4) | $\mathrm{C}(38)-\mathrm{P}(2)-\mathrm{Mo}(1)$ | 113.39(9) |
| $\mathrm{C}(27)-\mathrm{C}(28)$ | 1.509(4) | $\mathrm{C}(39)-\mathrm{P}(2)-\mathrm{Mo}(1)$ | 122.50(10) |
| $\mathrm{P}(2)-\mathrm{C}(38)$ | 1.867(3) | $\mathrm{C}(45)-\mathrm{P}(2)-\mathrm{Mo}(1)$ | 113.21(9) |
| $\mathrm{P}(2)-\mathrm{C}(39)$ | 1.843(3) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 110.3(2) |
| $\mathrm{P}(2)-\mathrm{C}(45)$ | 1.842(3) | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 109.8(2) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | 1.6516(15) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 111.2(2) |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | 1.6537(16) | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(27)$ | 113.5(2) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ | 1.6424(17) | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(38)$ | 114.5(2) |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ | $1.6475(20)$ | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(38)$ | 112.3(2) |
|  |  | $\mathrm{C}\left(15-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)\right.$ | 11.8 |
|  |  | $\mathrm{C}(28)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(34)$ | 13.2 |

$\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24), \mathrm{CpC}_{\text {cent }}=\mathrm{C}(28)$ to $\mathrm{C}(32)$,
$\mathrm{CpD}_{\text {cent }}=\mathrm{C}(33)$ to $\mathrm{C}(37)$.

### 3.4.4 Ruthenium(II) and Gold(I) Coordination Chemistry of 3.1

Treatment of 3.1 with $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ (1 equiv.) and $\mathrm{AuCl}($ (tht) (2 equiv.), in dichloromethane at ambient temperature, gave the tetrametallic complexes $\mathbf{3 . 1 2}$ and $\mathbf{3 . 1 3}$ in good yield (86 and 84\% respectively) (Equation 3.5).


Equation 3.5 (i) $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ for $\mathbf{3 . 1 2}$ or $2 \mathrm{AuCl}(\mathrm{tht})$ for 3.13; solvent $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra [in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ (3.12) or $\mathrm{CDCl}_{3}$ (3.13)] of $\mathbf{3 . 1 2}$ and $\mathbf{3 . 1 3}$ both exhibited a new phosphorus singlet significantly downfield of that of the free ligand at $\delta(\mathrm{P}) 25.2$ (3.12) and 19.4 (3.13) ppm respectively $[\delta(\mathrm{P})-27.3 \mathrm{ppm}(\mathbf{3 . 1})]$. The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of both coordination complexes also contained the anticipated resonances relating to the coordinated diphosphines, in addition to the distinct resonances relating to the $p$-cym auxiliary ligand. Additional support for the preparation of $\mathbf{3 . 1 2}$ and $\mathbf{3 . 1 3}$ comes from the positive ion FAB mass spectra which contained the expected molecular fragments and parent ions $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: m/z $1651[\mathrm{M}]^{+}$(3.12) and $1233\left[\mathrm{M}-\mathrm{AuCl}_{2}\right]$ (3.13)\}. The elemental analysis results for $\mathbf{3 . 1 2}$ and $\mathbf{3 . 1 3}$ were also found to be satisfactory (see Experimental Section). Moreover the preparation of both complexes, and the anticipated P,P-bridging mode of 3.1, was further confirmed by single crystal X-ray diffraction studies (Section 3.4.4.1).

### 3.4.4.1 Molecular Structures of 3.12 and 3.13

Orange crystalline blocks of $\mathbf{3 . 1 2}$ and yellow crystalline tablets of $\mathbf{3 . 1 3}$, suitable for single crystal X-ray diffraction were grown by the slow vapour diffusion of hexane into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of the respective complexes. The molecular structure of $\mathbf{3 . 1 2}$ was determined using reflection data collected in the home laboratory (Figure 3.9), whilst the molecular structure of $\mathbf{3 . 1 3}$ was determined from reflection data collected by the EPSRC National Crystallography Service (Figure 3.10). Selected lengths and angles for $\mathbf{3 . 1 2}$ and 3.13 are given in Table 3.7.


Figure 3.9 Molecular structure of 3.12. All hydrogen atoms and solvent molecules have been removed for clarity. Symmetry operator for equivalent atoms ${ }^{\prime}=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$.

The molecular structures of $\mathbf{3 . 1 2}$ and $\mathbf{3 . 1 3}$ (Figure 3.9 and 3.10 ) both show $\mathbf{3 . 1}$ to coordinate two separate metal centres via both phosphorus atoms. In both instances (3.12 and 3.13), the phosphorus atoms were found to adopt a distorted tetrahedral
geometry as indicated by the respective $\mathrm{C}-\mathrm{P}-\mathrm{M}$ angles. The nitrogen atoms were found to adopt a distorted pyramidal geometry [sum of component angles $338^{\circ}$ (3.12), $338^{\circ}$ and $337^{\circ}$ (3.13)]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings within both tetrametallic complexes were found to be essentially eclipsed and coplanar, as previously observed in the molecular structure of 3.1. In contrast the conformation of the $\mathrm{P}-\mathrm{C}-\mathrm{N}-\mathrm{C}-\mathrm{C}-\mathrm{N}-\mathrm{C}-\mathrm{P}$ backbone of $\mathbf{3 . 1}$ was found to differ between the two complexes, with $\mathbf{3 . 1 2}$ adopting a "more-open" conformation compared to $3.13\left[\mathrm{P}(1) \cdots \mathrm{P}\left(1^{\prime}\right) c a .8 .707 \AA\right.$ (3.12) and $\mathrm{P}(1) \cdots \mathrm{P}(2)$, ca. $6.383(\mathbf{3 . 1 3}) \AA]$. This observation highlights the flexibility of the ligand.

In the case of 3.12, each ruthenium centre was found to adopt a classical "piano-stool" geometry comprising of a $p$-cym ligand, two chlorides and one of the phosphorus donors of 3.1. The geometry of both ruthenium centres was found to be similar to those reported for other ruthenium-phosphine piano-stool complexes. ${ }^{22}$ The auxiliary $p$-cym ligand itself was found to adopt a distorted geometry, with respect to the phenyl ring mean plane, with the $\mathrm{CH}_{3}$ and ${ }^{i} \operatorname{Pr}$ groups tilted slightly towards the ruthenium centre [deviation from phenyl ring mean plane $\mathrm{CH}_{3}=0.0015 \AA$ and ${ }^{i} \mathrm{Pr}=0.0406 \AA$ ]. The geometry of the gold(I) centres within 3.13 were found to be pseudo-linear $[\mathrm{P}(1)-$ $\left.\mathrm{Au}(1)-\mathrm{Cl}(1) 178.53(3)^{\circ}, \mathrm{P}(2)-\mathrm{Au}(2)-\mathrm{Cl}(2) 176.30(4)^{\circ}\right]$, as anticipated. ${ }^{23,144}$ Further inspection of the molecular structure of $\mathbf{3 . 1 3}$ revealed the presence of an intermolecular $\mathrm{Au} \cdots \mathrm{Cl}$ interaction (Figure 3.10). This interaction allowed the formation of discrete dimers between neighbouring inversion-related molecules of $\mathbf{3 . 1 3}$ [ $\mathrm{Au} \cdots \mathrm{Cl} 3.950 \AA$ ] (Figure 3.10). The $\mathrm{Au} \cdots \mathrm{Cl}$ contacts were found to be slightly longer than the sum of the Van der Waals radii $\left(r_{w}\right)\left[r_{w} C l=1.75 \AA, r_{w} A u=1.70 \AA\right.$, sum of $r_{w}=3.45 \AA, A u \cdots \mathrm{Cl}$ $3.950 \AA$ ], suggesting that the interactions are weak. ${ }^{23,230}$


Figure 3.10 The $\mathrm{Au} \cdots \mathrm{Cl}$ contacts observed between adjacent molecules of $\mathbf{3 . 1 3}$.
Symmetry operator for equivalent molecules ' $=-\mathrm{x}+1,-\mathrm{y},-\mathrm{z}+1$.

Table 3.7 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{3 . 1 2}$ and 3.13.

|  | 3.12 | 3.13 |  | 3.12 | 3.13 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{M}(1)-\mathrm{P}(1)$ | 2.3448(4) | 2.2277(9) | $\mathrm{Cl}(1)-\mathrm{M}(1)-\mathrm{P}(1)$ | 83.435(14) | 178.53(4) |
| $\mathrm{M}(1)-\mathrm{Cl}(1)$ | 2.4088(4) | $2.2836(10)$ | $\mathrm{Cl}(1)-\mathrm{M}(1)-\mathrm{Cl}(2)$ | 88.397(14) |  |
| $\mathrm{M}(1)-\mathrm{Cl}(2)$ | 2.4173(4) |  | $\mathrm{P}(1)-\mathrm{M}(1)-\mathrm{Cl}(2)$ | 85.276(14) |  |
| $\mathrm{M}(2)-\mathrm{P}(2)$ |  | $2.2384(10)$ | $\mathrm{P}(2)-\mathrm{M}(2)-\mathrm{Cl}(2)$ |  | 176.30(4) |
| $\mathrm{M}(2)-\mathrm{Cl}(2)$ |  | $2.3004(10)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{M}(1)$ | 112.23(5) | 114.13(13) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.8239(1) | 1.814(4) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{M}(1)$ | 118.23(5) | 110.29(13) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.8182(1) | 1.815(4) | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{M}(1)$ | 111.97(5) | 114.04(13) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.8575(1) | 1.851(4) | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 114.40(10) | 109.5(3) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | 1.4560(1) | $1.469(5)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 111.07(12) | 112.5(3) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | 1.473(2) | $1.486(5)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 115.17(12) | 114.0(3) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.503(2) | 1.507(5) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 112.15(13) | 111.0(3) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.460(2)$ | 1.470(5) | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | 112.65(13) | 115.9(3) |
| $\mathrm{C}(25)-\mathrm{C}\left(25^{\prime}\right)$ | 1.521(3) |  | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}\left(25^{\prime}\right)$ | 111.29(17) |  |
| $\mathrm{C}(25)-\mathrm{C}(26)$ |  | $1.524(5)$ | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}(26)$ |  | 113.6(3) |
| $\mathrm{N}(2)-\mathrm{C}(26)$ |  | $1.475(5)$ | $\mathrm{N}(2)-\mathrm{C}(26)-\mathrm{C}(25)$ |  | 109.8(3) |
| $\mathrm{N}(2)-\mathrm{C}(27)$ |  | $1.477(5)$ | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(27)$ |  | 113.9(3) |
| $\mathrm{C}(27)-\mathrm{C}(28)$ |  | $1.496(5)$ | $\mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(38)$ |  | 109.8(3) |
| $\mathrm{N}(2)-\mathrm{C}(38)$ |  | 1.467(5) | $\mathrm{C}(26)-\mathrm{N}(2)-\mathrm{C}(38)$ |  | 113.7(3) |
| $\mathrm{P}(2)-\mathrm{C}(38)$ |  | 1.848(4) | $\mathrm{N}(2)-\mathrm{C}(27)-\mathrm{C}(28)$ |  | 111.6(3) |
| $\mathrm{P}(2)-\mathrm{C}(39)$ |  | 1.811(4) | $\mathrm{N}(2)-\mathrm{C}(38)-\mathrm{P}(2)$ |  | 109.3(3) |
| $\mathrm{P}(2)-\mathrm{C}(45)$ |  | 1.820(4) | $\mathrm{C}(38)-\mathrm{P}(2)-\mathrm{M}(2)$ |  | 116.10(13) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | 1.6423(8) | $1.6439(19)$ | $\mathrm{C}(39)-\mathrm{P}(2)-\mathrm{M}(2)$ |  | 115.00(13) |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | 1.6417(9) | $1.655(2)$ | $\mathrm{C}(45)-\mathrm{P}(2)-\mathrm{M}(2)$ |  | 110.97(13) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ |  | 1.652(2) | $\begin{gathered} \mathrm{C}(15)-\mathrm{CpA}_{\text {cent }} \\ -\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21) \end{gathered}$ | 1.1 | 21.9 |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ |  | 1.653(2) | $\begin{aligned} & \mathrm{C}(28)-\mathrm{CpC}_{\text {cent }}- \\ & \mathrm{CpD}_{\text {cent }}-\mathrm{C}(34) \end{aligned}$ |  | 4.0 |
| $\mathrm{Ru}-\mathrm{Cym}_{\text {cent }}$ | 1.6929(7) |  |  |  |  |

### 3.5 Electrochemical Properties of $\mathbf{3 . 1}$ and its Coordination Complexes

The electrochemical properties of $\mathbf{3 . 1}$ and its related mononuclear and binuclear complexes have been investigated by cyclic voltammetry, using a standard electrochemical cell (Figure 3.11 left ). All of the compounds studied were found to display a single reversible ferrocene/ferrocenium redox $\left(\mathrm{Fc}_{\mathrm{c}} / \mathrm{Fc}^{+}\right)$couple similar to that of ferrocene and, as a result, all electrochemical potential values are reported relative to the ferrocene/ferrocenium couple (Figure 3.11, right and 3.12 left).

${ }^{a}$ All experiments were performed in a $0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right] / d r y$-degassed $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution using a standard electrochemical cell consisting of a Pt disc working electrode $(\mathrm{d}=1.6 \mathrm{~mm}), \mathrm{Ag} / \mathrm{AgCl}$ reference electrode in a 3 M NaCl solution and a Pt gauze counter electrode at a scan rate of $50 \mathrm{mV} / \mathrm{s}$.
${ }^{\mathrm{b}} \mathrm{E}_{1 / 2}=\left(\mathrm{E}_{\mathrm{pc}}+\mathrm{E}_{\mathrm{pa}}\right) / 2$ reported relative to the ferrocene/ferrocenium couple.

Figure 3.11 Standard electrochemical cell (left), electrochemical data ${ }^{\text {a }}$ for $\mathbf{3 . 1}$ and its mononuclear and binuclear complexes (right).

For 3.1, the half-wave potentials of the Fc groups were found to be $\mathrm{E}_{1 / 2}+0.055 \mathrm{~V}$, whereas for complexes $3.4, \mathbf{3 . 9}, \mathbf{3 . 1 1}, \mathbf{3 . 1 2}$ and 3.13 the half wave potentials were observed in the range $\mathrm{E}_{1 / 2}-0.018$ to +0.135 V . The similarity between the half wave potentials of 3.1 and the coordination complexes suggests that the ferrocene groups
within 3.1 are not severely affected by coordination. The observation of a single $\mathrm{Fc} / \mathrm{Fc}^{+}$ wave for 3.1, 3.9, 3.11 and $\mathbf{3 . 1 3}$ also indicates that no direct or indirect electronic communication between the two ferrocene groups takes place, i.e. no electronic interaction via (saturated) covalent bonds or any significant coulombic interaction through space, as the two ferrocene centres are spaced too far apart from each other. Thus from an electrochemical view point 3.1, 3.9, 3.11 and $\mathbf{3 . 1 3}$ are composed of two, electrochemically equivalent, monoelectronic redox groups. In contrast, the platinum(II) complex (3.4) displays a broad cyclic voltammogram suggesting that the two ferrocene/ferrocenium redox couples are marginally different. The cyclic voltammogram of 3.1 (Figure 3.12, right) is also more complex than may have been anticipated, showing two further irreversible oxidation potentials at $\mathrm{E}_{\mathrm{pa}}-0.015$ and +0.215 V (Figure 3.12).



Figure 3.12 Cyclic voltammogram of Fc (left) and $\mathbf{3 . 1}$ (right) in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}$ [ $\left.\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

These irreversible potentials are tentatively assigned to the irreversible oxidation of both tertiary phosphine groups within 3.1, whilst the appearance of two potentials, one more anodic than the other, suggests sequential electrochemical oxidation of 3.1. This notion, of progressive oxidation is supported by the loss of the irreversible oxidation peaks from
subsequent voltammograms of preformed coordination complexes of 3.1, and also by comparison with analogous ligands discussed herein (vide infra).

In addition to the $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple, the binuclear ruthenium(II) complex $\mathbf{3 . 1 2}$ was found to exhibit a more complex cyclic voltammogram with several oxidation peaks also being observed at more anodic potentials, between $0.7-1.5 \mathrm{~V}$. These peaks may tentatively result from two consecutive irreversible single electron (per ruthenium metal centre) $\mathrm{Ru}^{\text {II }} / \mathrm{Ru}^{\text {III }}$ oxidations. ${ }^{216,231,232}$ Similarly $\mathbf{3 . 1 1}$ showed further irreversible oxidation potentials, between $0.75-1.23 \mathrm{~V}$, which presumably correspond to the $\mathrm{Mo}^{0} / \mathrm{Mo}^{\mathrm{I}}$ and $\mathrm{Mo}^{\mathrm{I}} / \mathrm{Mo}^{\mathrm{II}}$ oxidations respectively of the molybdenum tetracarbonyl fragment. ${ }^{208}$

### 3.6 Preparation and Characterisation of 3.14

The ferrocenyl monophosphine $\mathbf{3 . 1 4}$ was prepared in order to observe how the properties of a comparable monophosphine compared to those of the diphosphine 3.1. To this end, 3.14 was prepared by condensation of the known secondary amine $\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3},{ }^{233}$ with one equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ (Equation 3.6).

3.14

## Equation 3.6

In a similar manner to the analogous aryl substituted monophosphines $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$, 3.14 did not crystallise during the reaction. Complete evaporation of the solvent did however repeatedly yield a viscous oil that was found to be sufficiently pure $\left[b y{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\right.$ NMR, $79 \%$ by integration] to be used directly in coordination studies. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of this viscous oil (in freeze-thawed $\mathrm{CDCl}_{3}$ ) exhibited a new phosphorus singlet resonance at $\delta(\mathrm{P})-27.7 \mathrm{ppm}$, some $c a .18 \mathrm{ppm}$ upfield from that observed for the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. The chemical shift of the characteristic
singlet compared well with analogous polyaromatic monophosphines previously discussed $[\delta(\mathrm{P})-27.6$ (2.23) and -27.7 (2.24) ppm respectively], and also with the comparable diphosphine $3.1[\delta(\mathrm{P})-27.3 \mathrm{ppm}, \Delta \delta(\mathrm{P}) 0.4 \mathrm{ppm}]$. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1 4}$ revealed the anticipated $\delta\left(\mathrm{CH}_{2}\right)$ and $\delta\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ resonances previously observed in the ${ }^{1} \mathrm{H}$ NMR spectrum of the parent amine, ${ }^{233}$ whilst the newly introduced $\mathrm{CH}_{2} \mathrm{P}$ moiety resonated as a characteristic doublet at $\delta(\mathrm{H}) 3.16 \mathrm{ppm}\left[{ }^{2} J_{\mathrm{PH}} 3.2\right.$ $\mathrm{Hz}] .{ }^{22,23}$ Moreover, the successful preparation of $\mathbf{3 . 1 4}$ was supported by positive ion FAB mass spectroscopy which gave a predictable molecular fragment $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}\right.$ $\left.457[\mathrm{M}+\mathrm{O}]^{+}\right\}$. The molecular structure of $\mathbf{3 . 1 4}$ has also been determined by single crystal X-ray diffraction (Section 3.6.1). The electrochemical properties of $\mathbf{3 . 1 4}$ were also briefly investigated by cyclic voltammetry. The cyclic voltammogram of $\mathbf{3 . 1 4}$ contains a ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple at $\mathrm{E}_{1 / 2} 0.139 \mathrm{~V}$, in addition to a further oxidation peak at $\mathrm{E}_{\mathrm{pa}} 0.006 \mathrm{~V}$ (Figure 3.13); values quoted relative to the ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple.


Figure 3.13 Cyclic voltammogram of $\mathbf{3 . 1 4}$ in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

The oxidation peak at $\mathrm{E}_{\mathrm{pa}} 0.006 \mathrm{~V}$ was tentatively assigned to the irreversible oxidation of the phosphorus atom within $\mathbf{3 . 1 4}$ due to the lack of a corresponding reduction potential and similar electrochemical potential to the first phosphine oxidation peaks found in the voltammogram of $\mathbf{3 . 1}\left[\mathrm{E}_{\mathrm{pa}}-0.015 \mathrm{~V}(\mathbf{3 . 1})\right.$, difference in $\mathrm{P}(\mathrm{III}) / \mathrm{P}(\mathrm{V}) \mathrm{E}_{\mathrm{pa}}$ between 3.1 and $\mathbf{3 . 1 4}=0.021 \mathrm{~V}]$. Comparison of the $\mathrm{E}_{1 / 2}$ ferrocene/ferrocenium values of $\mathbf{3 . 1 4}$ with that of $\mathbf{3 . 1}$, revealed an anodic shift of +0.084 V suggesting that the ferrocene group within the monophosphine is harder to oxidise compared to the analogous $\mathrm{Fe}(\mathrm{II}) / \mathrm{Fe}(\mathrm{III})$ couple within the 3.1.

### 3.6.1 Molecular Structure of $\mathbf{3 . 1 4}$

Orange crystalline plates of $\mathbf{3 . 1 4}$ were grown directly from the previously described viscous oil, following storage of the oil at ambient temperature, under a nitrogen atmosphere, for $c a .2$ months. The molecular structure was determined (Figure 3.14), selected lengths and angles are given in Table 3.8.


Figure 3.14 Molecular structure of 3.14. All hydrogen atoms have been removed for clarity.

The molecular structure of $\mathbf{3 . 1 4}$ shows the phosphine to have crystallised in the chiral space group $P 1$ [racemic twin with major enantiomer freely refined to $56.0(6) \%$ ]. The asymmetric unit contained one unique molecule of $\mathbf{3 . 1 4}$. The phosphorus and nitrogen atoms within 3.14 were both found to adopt a distorted pyramidal arrangement, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles and the sum of component angles about $\mathrm{N}(1)$ [sum of component angles for $\mathrm{N}(1)=337^{\circ}$ ]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings within 3.14 were found to be essentially eclipsed and coplanar [torsional twist about $\mathrm{C}(15)-$ $\left.\mathrm{Cp} \mathrm{p}_{\text {cent }}-\mathrm{C} \mathrm{p}_{\text {cent }}-\mathrm{C}(21)=6.7^{\circ}\right]$, similar to those found within the molecular structure of $\mathbf{3 . 1}$. In general, 3.14 was found to have similar structural characteristics to the analogous diphosphine 3.1 [i.e. sum of component angles for $N(1)=336^{\circ}$ (3.1) and $337^{\circ}$ (3.14), geometry of phosphorus atoms for $\mathbf{3 . 1}$ and $\mathbf{3 . 1 4}=$ distorted pyramidal; $\mathrm{C}-\mathrm{P}-\mathrm{C}$ ranged between $97.99(5)-105.06(6) \AA$ ] (Table 3.2 and 3.8).

Table 3.8 Selected lengths $(\AA)$ and angles $\left(^{\circ}\right)$ for 3.14.

| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8349(14)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | $103.24(6)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.8357(14)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $98.43(6)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.8939(14)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13)$ | $103.14(6)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.4611(17)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $116.81(9)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.4733(16)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $111.72(10)$ |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.4660(18)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | $114.03(10)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.5022(18)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | $111.61(11)$ |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | $1.517(2)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $111.95(11)$ |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | $1.6401(6)$ | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}(26)$ | $113.31(13)$ |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | $1.6398(7)$ | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}$ | 6.7 |

[^4]
### 3.7 Gold(I) Coordination Chemistry of 3.14

The coordination chemistry of $\mathbf{3 . 1 4}$ was briefly explored by reaction with an equimolar amount of AuCl (tht), at ambient temperature, to afford the bimetallic gold complex $\mathbf{3 . 1 5}$ in reasonable yield (56\%) (Equation 3.7).


Equation 3.7
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the isolated solid exhibited a new phosphorus singlet resonance at $\delta(\mathrm{P}) 17.4 \mathrm{ppm}$, in addition to several new ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active species between $\delta(\mathrm{P}) 29.8-50.1 \mathrm{ppm}$. The singlet at $\delta(\mathrm{P}) 17.4 \mathrm{ppm}$ accounted for $18 \%$ of the total ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei and was assigned to $\mathbf{3 . 1 5}$, by comparison with the analogous gold complexes 2.28 and $2.29[\delta(P) 18.9$ (2.28) and $18.5 \mathrm{ppm}(\mathbf{2 . 2 9})$ respectively]. The remaining $82 \%$ of the phosphorus containing species were speculatively assigned to the dimeric complex 3.15A (Equation 3.8), by comparison with the coordination chemistry of $\left\{\mathrm{FcCH}_{2}\right)_{2} \mathrm{NCH}_{2} \mathrm{PPh}_{2}$ (3.20); which showed the monophosphine (3.20) to be capable of both mono-P and bidentate- $\mathrm{P}, \mathrm{N}$ coordination modes.


Equation 3.8 Proposed species observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. Dashed line indicates a potential aurophilic interaction.

A search of the CSD revealed no previously reported examples of such a $(\mathrm{Au}\{\mathrm{PCN}\})_{2}$ dimer (3.15A), although examples of $\mathrm{R}_{3} \mathrm{~N}-\mathrm{Au}-\mathrm{PPh}_{3}$ salts $[\mathrm{R}=$ alkyl and aryl] have been previously discussed ${ }^{234,235}$ suggesting that a $\mathrm{P}, \mathrm{N}$ coordination mode may be possible for 3.14. Analysis of the ${ }^{1} \mathrm{H}$ NMR spectrum of the isolated solid also suggested that the $\mathrm{CDCl}_{3}$ solution contained a mixture of coordination complexes, with the $\delta\left(\mathrm{CH}_{2}\right)$, $\delta\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$ and $\delta(\mathrm{Fc})$ regions of the spectrum containing several broad resonances. Further work is clearly required to fully characterise $\mathbf{3 . 1 5}$ by NMR spectroscopy. The preparation of $3.15 / 3.15 \mathrm{~A}$ was further supported by elemental analysis, which showed good agreement with the formula $\mathbf{3 . 1 5} \cdot 0.75 \mathrm{CH}_{2} \mathrm{Cl}_{2}$. The molecular structure of $\mathbf{3 . 1 5}$ has also been determined by single crystal X-ray diffraction (Section 3.7.1).

### 3.7.1 Molecular Structure of 3.15

Yellow crystalline plates suitable for single crystal X-ray diffraction were grown by the slow evaporation of a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{Et}_{2} \mathrm{O}$ filtrate of $\mathbf{3 . 1 5}$. The molecular structure of $\mathbf{3 . 1 5}$ was determined in the home laboratory (Figure 3.15), selected lengths and angles are given in Table 3.9.


Figure 3.15 Molecular structure of 3.15. All hydrogen atoms have been removed for clarity.

The asymmetric unit of $\mathbf{3 . 1 5}$ was found to contain one molecule of the bimetallic complex. The geometry about the metal centre was found to be pseudo-linear, with the $\mathrm{P}-\mathrm{Au}-\mathrm{Cl}$ angle deviating marginally from the idealised angle for a linear disposition $\left[\mathrm{P}(1)-\mathrm{Au}(1)-\mathrm{Cl}(1) 179.79(5)^{\circ}\right]$. The phosphorus atom was found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Au}$ angles, whilst the nitrogen atom adopted a distorted pyramidal geometry [sum of component angles $=339^{\circ}$ ]. In contrast to $\mathbf{3 . 1 4}$, the Fe (II) cyclopentadienyl rings were found to be essentially staggered and coplanar [torsional twist about $\mathrm{C}(15)-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}(21)=28.9^{\circ}$ ], suggesting that the cyclopentadienyl rings of the ferrocenyl group have some conformational freedom. Furthermore there was no evidence of any aurophilic interactions [minimum $\mathrm{Au} \cdots \mathrm{Au}$ separation $c a .8 \AA$ ] or nitrogen coordination of the gold(I) centre $[A u \cdots \mathrm{~N} 3.864 \AA]$.

Table 3.9 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{3 . 1 5}$.

| $\mathrm{Au}(1)-\mathrm{Cl}(1)$ | $2.2910(12)$ | $\mathrm{P}(1)-\mathrm{Au}(1)-\mathrm{Cl}(1)$ | $179.79(5)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Au}(1)-\mathrm{P}(1)$ | $2.2435(11)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Au}(1)$ | $111.89(13)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.812(4)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Au}(1)$ | $114.03(15)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.817(5)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Au}(1)$ | $115.90(13)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.874(4)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $120.5(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.448(5)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $113.6(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.479(5)$ | $\mathrm{C}(25)-\mathrm{N}(1)-\mathrm{C}(14)$ | $110.0(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.473(6)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | $115.2(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.498(6)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $114.0(3)$ |
| $\mathrm{C}(25)-\mathrm{C}(26)$ | $1.501(7)$ | $\mathrm{N}(1)-\mathrm{C}(25)-\mathrm{C}(26)$ | $113.7(4)$ |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | $1.636(2)$ | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)$ | 28.9 |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | $1.655(2)$ |  |  |
| $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24)$. |  |  |  |

### 3.8 Preparation and Characterisation of $\mathbf{3 . 1 6}$ and $\mathbf{3 . 1 7}$

Following the efficient preparation and diverse coordination chemistry of the ferrocenyl phosphines discussed thus far, efforts to vary the diaminyl linker within the general formula, $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2} \mathrm{R}$, were made in an attempt to explore how the coordination and electrochemical properties of the resulting phosphines were effected (Figure 3.16).


Figure 3.16 Variations made to the general formula, $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right) \mathrm{CH}_{2}\right\}_{2} \mathrm{R}$.

To this end the new trimetallophosphine $\mathbf{3 . 1 6}$ was prepared by double condensation of the parent amine, $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$, with two equiv. of the tertiary phosphine synthon $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$. To the best of our knowledge the triferrocenyl imine $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$, and parent amine $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$, have not been previously reported in the literature (see Experimental Section). The trimetallophosphine did not crystallise during the course of the reaction and, as a result, was obtained as a viscous oil following complete removal of the solvent. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated oil exhibited a new phosphorus singlet at $\delta(\mathrm{P})-27.8 \mathrm{ppm}$, which accounted for $87 \%$ of the total ${ }^{31} \mathrm{P}$ NMR active nuclei and was assigned to $\mathbf{3 . 1 6}$ by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $3.1[\delta(\mathrm{P})-27.3 \mathrm{ppm}(\mathbf{3 . 1}), \Delta \delta(\mathrm{P}) 0.5 \mathrm{ppm}]$. The remainder of the ${ }^{31} \mathrm{P}$ NMR active nuclei corresponded to unreacted $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated oil revealed the newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms to resonate as a characteristic doublet at $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 3.02 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 3.6\right.$ $\mathrm{Hz}),{ }^{22,23}$ whilst the remaining two $\mathrm{CH}_{2}$ environments resonated as singlets at $\delta(\mathrm{H}) 3.55$ and 3.51 ppm . Furthermore the preparation of an impure sample of $\mathbf{3 . 1 6}$ was further
supported by a marked reduction of the $v_{\mathrm{NH}}$ absorption band in the infrared spectrum of the isolated oil, compared to that of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$. Moreover the preparation of 3.16 was further supported by the subsequent coordination chemistry of the isolated oil.

In contrast, preliminary reactions of the known parent amine $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}$ ${ }^{236,237}$ with two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, were found to be significantly incomplete by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy following 14 d of stirring at ambient temperature. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the resulting oil, following complete removal of the solvent, revealed three new singlets at $\delta(\mathrm{P})-26.9,-27.6$ and -28.5 ppm , in addition to that of the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. The three new singlets accounted for $79 \%$ of the ${ }^{31} \mathrm{P}$ NMR active nuclei and appeared in a ratio of $c a .1: 5: 1$ by ${ }^{1} \mathrm{H}$ NMR integration. The major resonance at $\delta(\mathrm{P})-27.6 \mathrm{ppm}$ accounted for $55 \%$ of the total ${ }^{31} \mathrm{P}$ NMR active nuclei and was assigned to $\mathbf{3 . 1 7}$ by comparison with $\mathbf{3 . 1}[\delta(\mathrm{P})-27.3 \mathrm{ppm}(\mathbf{3 . 1}), \Delta \delta(\mathrm{P})$ $0.3 \mathrm{ppm}]$. Further work is clearly required to produce $\mathbf{3 . 1 7}$ to a higher purity, however this preliminary work does suggest that preparation of $\mathbf{3 . 1 7}$ is feasible.

### 3.9 Coordination Chemistry of $\mathbf{3 . 1 6}$

The coordination chemistry of the new trimetalloligand, 3.16, was briefly explored by reaction with three readily available transition metal centres $[\mathrm{Au}(\mathrm{I}), \mathrm{Ru}(\mathrm{II})$ and $\operatorname{Pt}(\mathrm{II})]$. Treatment of $\mathbf{3 . 1 6}$ with $\mathrm{AuCl}(\mathrm{tht})\left(2\right.$ equiv.) or $\{\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2}$ ( 1 equiv.) in dichloromethane at ambient temperature, gave the pentametallic complexes $\mathbf{3 . 1 8}$ and 3.19 in reasonable to excellent yield ( 61 and $87 \%$ respectively) (Equation 3.9).


Equation 3.9 (i) $2 \mathrm{AuCl}($ tht $)$ (3.18) or $\{\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ (3.19). Solvent: $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 1 8}$ displayed a new characteristic singlet resonance at $\delta(\mathrm{P}) 17.4 \mathrm{ppm} .{ }^{23}$ In contrast, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of 3.19 contained three distinct singlet resonances at $\delta(\mathrm{P}) 26.1,21.0$ and 16.1 ppm . The singlet at $\delta(\mathrm{P}) 26.1 \mathrm{ppm}$ accounted for $78 \%$ of the ${ }^{31} \mathrm{P}$ NMR active nuclei and was assigned to $\mathbf{3 . 1 9}$, by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the analogous ruthenium $p$-cym complex $\mathbf{3 . 1 2}\left[{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}\right.$ NMR 25.19 ppm (3.12)]. In both instances the ${ }^{1} \mathrm{H}$ NMR (in $\mathrm{CDCl}_{3}$ ) spectrum contained the anticipated resonances relating to the coordination complexes. Further support for the preparation of the new pentametallic complexes $\mathbf{3 . 1 8}$ and $\mathbf{3 . 1 9}$ comes from positive ion FAB mass spectroscopy which revealed predictable molecular fragments $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: m/z $1233[\mathrm{M}-\mathrm{AuCl}-\mathrm{Cl}]^{+}$ (3.18) and $1651[\mathrm{M}]^{+}$(3.19) $\}$. The elemental analysis results for $\mathbf{3 . 1 8}$ and $\mathbf{3 . 1 9}$ were also found to be satisfactory, agreeing with the formulae $\mathbf{3 . 1 8} \cdot 0.75 \mathrm{C}_{6} \mathrm{H}_{14}$ and $\mathbf{3 . 1 9}$. The
molecular structure of $\mathbf{3 . 1 9}$ has also been determined, by single crystal X-ray diffraction, and confirms the bridging nature of the trimetalloligand $\mathbf{3 . 1 6}$ (Section 3.9.1). In contrast, reaction of $\mathbf{3 . 1 6}$ with an equimolar amount of $\mathrm{PtCl}_{2}(\mathrm{cod})$ gave an impure sample of $\operatorname{PtCl}_{2}\{\mathbf{3 . 1 6}\}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ), with the spectrum revealing several phosphorus containing species between $c a . \delta(\mathrm{P}) 26$ to -9 ppm . Comparison of these resonances with other platinum diphosphine complexes suggests that they may relate to a platinum coordination complex of $\mathbf{3 . 1 6}$ (monomeric or polymeric), ${ }^{93,186,196,238}$ however no platinum satellites were apparent. The preparation of some form of $\mathrm{PtCl}_{2}\{\mathbf{3 . 1 6}\}$ complex was supported by the positive ion FAB mass spectroscopy, which gave a predictable fragmentation pattern for a platinum dichloride complex [FAB-MS: m/z 1266 [M-Cl], in addition to elemental analysis, which showed good agreement with the formula $\mathrm{PtCl}_{2}(\mathbf{3 . 1 6}) \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ (see Experimental Section). The FT-IR spectrum of the isolated material also contained two characteristic $\mathrm{V}_{\mathrm{PtCl}}$ absorptions bands at 313 and $288 \mathrm{~cm}^{-1}$, which is in agreement with values previously reported for cis-platinum(II) chloride complexes of diphosphines discussed herein and in the literature. ${ }^{58,93}$ Further work is required to fully understand the coordination chemistry of 3.16, as there are clearly a range of coordination modes (monomeric or polymeric) potentially available to such a novel ligand; as indicated by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy.

### 3.9.1 Molecular Structure of $\mathbf{3 . 1 9}$

Orange crystalline plates suitable for single crystal X-ray diffraction were obtained by the slow diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{3 . 1 9}$ and the molecular structure was determined in the home laboratory (Figure 3.17). Selected lengths and angles are given in Table 3.10.


Figure 3.17 Molecular structure of 3.19. All hydrogen atoms and solvent molecules have been removed for clarity.

The molecular structure of $\mathbf{3 . 1 9}$ was found to contain one molecule of the metal complex and five solvating molecules of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ within the asymmetric unit. Two of the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules of crystallisation were found to be significantly disordered and were modelled as diffuse regions of electron density (Platon squeeze procedure). ${ }^{229}$ The trimetalloligand 3.16 was shown to bridge two $\left[\mathrm{RuCl}_{2}(p-\mathrm{cym})\right]$ fragments by coordination to both phosphorus atoms. The ruthenium centres were both shown to adopt a characteristic piano-stool geometry; $\mathrm{Ru}-\mathrm{Cl}, \mathrm{Ru}-\mathrm{P}$ and $\mathrm{Ru}-\left(p-\mathrm{cym}_{\text {cent }}\right)$ distances were as expected. ${ }^{22}$ The phosphorus atoms were found to adopt a distorted pyramidal geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Ru}$ angles [C-P-Ru ranged between 111.50(19) - 116.7(2) ${ }^{\circ}$ ], whilst
the nitrogen atoms adopted a distorted trigonal pyramidal arrangement [sum of component angles $=328$ and $343^{\circ}$ respectively]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were found to be essentially eclipsed and coplanar, with little variation between the six $C p_{\text {cent }} \cdots \mathrm{Fe}$ lengths (Table 3.10). The cyclopentadiene ring containing $\mathrm{C}(43)$ to $\mathrm{C}(47)$ was found to be disordered over two sets of equivalent positions [major occupancy $54.29(2) \%$ ] and, as a result, the geometry and anisotropic displacement parameters of both the disorder components were restrained.

Table 3.10 Selected lengths $(\AA)$ and angles $\left(^{\circ}\right)$ of 3.19.

| $\mathrm{Ru}(1)-\mathrm{Cl}(1)$ | 2.4107(18) | $\mathrm{P}(1)-\mathrm{Ru}(1)-\mathrm{Cl}(2)$ | 89.28(6) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ru}(1)-\mathrm{Cl}(2)$ | 2.4079(18) | $\mathrm{P}(1)-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ | 83.57(6) |
| $\mathrm{Ru}(2)-\mathrm{Cl}(3)$ | 2.4107(16) | $\mathrm{Cl}(1)-\mathrm{Ru}(1)-\mathrm{Cl}(2)$ | 87.83(6) |
| $\mathrm{Ru}(2)-\mathrm{Cl}(4)$ | $2.4160(17)$ | $\mathrm{P}(2)-\mathrm{Ru}(2)-\mathrm{Cl}(3)$ | 86.96(6) |
| $\mathrm{P}(1)-\mathrm{Ru}(1)$ | $2.3597(16)$ | $\mathrm{P}(2)-\mathrm{Ru}(2)-\mathrm{Cl}(4)$ | 85.34(6) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.818(6) | $\mathrm{Cl}(3)-\mathrm{Ru}(2)-\mathrm{Cl}(4)$ | 87.21(6) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.821(6) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Ru}(1)$ | 111.50(19) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.838(6) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Ru}(1)$ | $115.5(2)$ |
| $\mathrm{P}(2)-\mathrm{Ru}(2)$ | $2.3403(16)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Ru}(1)$ | 112.04(19) |
| $\mathrm{P}(2)-\mathrm{C}(48)$ | 1.854(6) | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 117.6(4) |
| $\mathrm{P}(2)-\mathrm{C}(49)$ | 1.833(6) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 109.8(4) |
| $\mathrm{P}(2)-\mathrm{C}(55)$ | 1.823(6) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 110.1(4) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.467(7)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 108.5(4) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.489(7)$ | $\mathrm{C}(37)-\mathrm{N}(2)-\mathrm{C}(48)$ | 115.8(5) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.500(7)$ | $\mathrm{C}(36)-\mathrm{N}(2)-\mathrm{C}(37)$ | 114.8(5) |
| $\mathrm{N}(2)-\mathrm{C}(36)$ | $1.469(7)$ | $\mathrm{C}(36)-\mathrm{N}(2)-\mathrm{C}(48)$ | 112.5(5) |
| $\mathrm{N}(2)-\mathrm{C}(37)$ | 1.458(8) | $\mathrm{N}(2)-\mathrm{C}(48)-\mathrm{P}(2)$ | 109.9(4) |
| $\mathrm{N}(2)-\mathrm{C}(48)$ | $1.463(7)$ | $\mathrm{C}(48)-\mathrm{P}(2)-\mathrm{Ru}(2)$ | 116.42(19) |
| $\mathrm{Ru}(1) \cdots \mathrm{cym}_{\text {cent }}$ | 1.701(3) | $\mathrm{C}(49)-\mathrm{P}(2)-\mathrm{Ru}(2)$ | 116.7(2) |
| $\mathrm{Ru}(2) \cdots \mathrm{cym}_{\text {cent }}$ | 1.703(3) | $\mathrm{C}(55)-\mathrm{P}(2)-\mathrm{Ru}(2)$ | 112.5(2) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {cent }}$ | 1.621(3) | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)$ | 7.3 |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | 1.643 (3) | $\mathrm{C}(26)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(32)$ | 10.5 |
| $\mathrm{Fe}(2) \cdots \mathrm{CpC}_{\text {cent }}$ | $1.645(3)$ | $\mathrm{C}(38)-\mathrm{CpE}_{\text {cent }}-\mathrm{CpF}_{\text {cent }}-\mathrm{C}(44)$ | 13.8 |
| $\mathrm{Fe}(2) \cdots \mathrm{CpD}_{\text {cent }}$ | 1.649 (3) |  |  |
| $\mathrm{Fe}(3) \cdots \mathrm{CpE}_{\text {cent }}$ | 1.640 (2) |  |  |
| $\mathrm{Fe}(3) \cdots \mathrm{CpF}_{\text {cent }}$ | 1.652(15) |  |  |
| $\begin{aligned} & \mathrm{CpA}_{\text {cent }}=\mathrm{C}(15) \mathrm{t} \\ & \mathrm{CpD}_{\text {cent }}=\mathrm{C}(31) \mathrm{t} \end{aligned}$ | $\begin{aligned} & \text { (19), } \mathrm{CpB}_{\text {cent }}= \\ & \text { (35), } \mathrm{CpE}_{\text {cent }}= \end{aligned}$ | $\begin{aligned} & \text { ) to } \mathrm{C}(24), \mathrm{CpC}_{\mathrm{cent}}=\mathrm{C}(26) \text { to } \mathrm{C}(30) \text {, } \\ & \text { to } \mathrm{C}(42), \mathrm{CpF}_{\mathrm{cent}}=\mathrm{C}(43) \text { to } \mathrm{C}(47) \text {. } \end{aligned}$ |  |

### 3.10 Electrochemical Properties of $\mathbf{3 . 1 6}$ and 3.18

The electrochemical properties of 3.16, 3.18 and their precursor imine and amine compounds have been investigated by cyclic voltammetry, and their oxidation ( $\mathrm{E}_{\mathrm{pa}}$ ) and reduction ( $\mathrm{E}_{\mathrm{pc}}$ ) potentials summarised in Table 3.11. For the imine $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$, the cyclic voltammogram displayed a reversible ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$ couple similar to that of ferrocene, at $\mathrm{E}_{1 / 2}-0.042 \mathrm{~V}$, in addition to a further ferrocene/ferrocenium oxidation peak $\left(\mathrm{E}_{\mathrm{pa}}\right)$ at +0.279 V (Figure 3.18).


Figure 3.18 Cyclic voltammogram of $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$ in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}$ $\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$. Suggested reduction peak ( $\mathrm{E}_{\mathrm{pc}}$ ) of bridging ferrocenyl moiety (*). Electrical potentials quoted relative to the ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple.

The reversible ferrocene/ferrocenium redox $\left(\mathrm{Fc}^{2} / \mathrm{Fc}^{+}\right)$couple at $\mathrm{E}_{1 / 2}-0.042 \mathrm{~V}$ was found to be similar to that of the diferrocenyl phosphines $\mathbf{3 . 1} \mathbf{- 3 . 3}$ ( $\mathrm{E}_{1 / 2}$ ranged between -0.018 -0.075 V , relative to $\mathrm{Fc} / \mathrm{Fc}^{+}$), suggesting that the terminal ferrocenyl groups $\left(\mathrm{Fc}_{\mathrm{t}}\right)$ within $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$ also undergoing simultaneous oxidation and reduction. The second oxidation potential at $\mathrm{E}_{\mathrm{pa}}+0.279 \mathrm{~V}$ was assigned to the bridging ferrocene moiety $\left(\mathrm{Fc}_{\mathrm{b}}\right)$
within the imine. Closer inspection of the voltammogram revealed a slight shoulder at 0.096 V (Figure 3.18, highlighted by *), which was cautiously assigned to the reversible reduction peak ( $\mathrm{E}_{\mathrm{pc}}$ ) of the bridging ferrocene moiety, to give a ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple for $\mathrm{Fc}_{\mathrm{b}}$ at $\mathrm{E}_{1 / 2}+0.188 \mathrm{~V}$. The assignment of these two distinct ferrocenyl environments, within the cyclic voltammogram of $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$, is supported by the characteristic distribution of charge between the two redox waves, $c a$. 2:1 by integration; terminal $\left(\mathrm{Fc}_{\mathrm{t}}\right)$ :bridging $\left(\mathrm{Fc}_{\mathrm{b}}\right)$ ferrocenyl groups.

Table 3.11 Electrochemical data ${ }^{\mathrm{a}}$ for 3.16, $\mathbf{3 . 1 8}$ and the precursor compounds.

| Compound | $\mathrm{E}_{\mathrm{pa}}(\mathrm{V})^{\mathrm{b}}, \mathrm{Fe}^{\mathrm{IIfIII}}$ | $\mathrm{E}_{\mathrm{pc}}(\mathrm{V})^{\mathrm{b}}, \mathrm{Fe}^{\mathrm{II} / I I I}$ |
| :---: | :---: | :---: |
| $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$ | $+0.006,+0.279$ | -0.090 |
| $\left\{\mathrm{FrCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$ | $+0.016,+0.154$ | +0.022 |
| $\mathbf{3 . 1 6}$ | +0.218 | +0.064 |
| $\mathbf{3 . 1 8}$ | +0.105 | -0.034 |

${ }^{\text {a }}$ All experiments were performed in a $0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right] / \mathrm{dry}^{\mathrm{CH}} \mathrm{Cl}_{2}$ solution using a standard electrochemical cell at a scan rate of $50 \mathrm{mV} / \mathrm{s}$.
${ }^{\mathrm{b}} \mathrm{E}_{\mathrm{pc}}$ and $\mathrm{E}_{\mathrm{pa}}$ reported relative to the ferrocene/ferrocenium couple.

In contrast the voltammogram of the trimetalloligand 3.16, and it's parent amine $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$, showed less resolved ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$ couples compared to $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}$, suggesting that as the bonds / atoms between the neighbouring ferrocenyl groups become more saturated, the more electrochemically similar the distinct ferrocenyl environments become. This increasing similarity between the various ferrocene/ferrocenium environments was mirrored in the voltammogram of the pentametallic gold(I) complex 3.18, which contained a single broad ferrocene/ferrocenium redox couple at $\mathrm{E}_{1 / 2} 0.036 \mathrm{~V}$, indicating that the three redox couples are only marginally different. The $\mathrm{E}_{1 / 2}$ of $\mathbf{3 . 1 8}$ was also found to be similar to that of the analogous gold complex $\mathbf{3 . 1 3}\left[\mathrm{E}_{1 / 2}+0.012 \mathrm{~V}(\mathbf{3 . 1 3}), \Delta \mathrm{E}_{1 / 2} 0.024 \mathrm{~V}\right]$, suggesting that the electrochemical properties of the terminal ferrocenyl groups are not significantly affected by variation of the "linker" between the electrochemically active termini.

### 3.11 Preparation and Characterisation of 3.20-3.22

The versatility of the synthetic route used thus far, reductive amination followed by phosphine-based Mannich condensation, was explored further by the preparation of a series of diferrocenyl monophosphines ( $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$ ) (Equation 3.10). In all three cases the new bimetallophosphines precipitated during the course of the reaction, allowing the ligands to be isolated to a high purity (by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ ), and in reasonable yield ( $47-$ $59 \%$ range).


Equation 3.10

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$ all revealed a new phosphorus singlet upfield to that of the $\mathrm{PRCH}_{2} \mathrm{OH}$ starting material $[\delta(\mathrm{P})-27.9$ (3.20), -19.3 (3.21) and -44.5 ppm (3.22) respectively]. The chemical shift of each singlet was found to be similar to those previously reported for the bimetalloligands $\left\{\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PR}\right) \mathrm{CH}_{2}\right\}_{2}$ (3.1-3.3) $[c a . \Delta \delta(\mathrm{P}) 1.0 \mathrm{ppm}]$. Closer inspection of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 2}$ suggested that the slightly broad resonance may be due to coinciding enantiomers of the phosphine $\left[\delta(\mathrm{P})-44.5 \mathrm{ppm} ; \mathrm{W}_{1 / 2} c a .5 \mathrm{~Hz}\right]$. The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of 3.22 supported this with the newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonating as a multiplet at $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 2.49 \mathrm{ppm}$. The multiplet was more complex than the double doublet that may have been expected for such an enantiomer, presumably owing to the $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms also being diastereotopic. ${ }^{58}$ The $\mathrm{FcCH}_{2} \mathrm{~N}$ hydrogen atoms within $\mathbf{3 . 2 2}$ were also found to be diastereotopic, with a classic AB "roof effect" being observed $\left[\delta\left(\mathrm{CH}_{2}\right) 3.56\right.$ and $3.31 \mathrm{ppm} ;{ }^{2} J_{\mathrm{HH}} 13.2$ and 13.6 Hz respectively]. The assignment of these three distinct $\mathrm{CH}_{2}$ environments was supported by their characteristic chemical shifts and also by their characteristic integrals $\left(\mathrm{FcCH}_{2}: \mathrm{CH}_{2} \mathrm{P}\right.$

2:1). In contrast the ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 0}$ and $\mathbf{3 . 2 1}$ contained the anticipated $\mathrm{CH}_{2}$ and ferrocenyl environments previously observed in the parent amine. The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated as characteristic doublets at $\delta\left(\mathrm{PCH}_{2}\right) 3.04$ and 2.41 ppm respectively [ ${ }^{2} J_{\mathrm{PH}} 4.0$ and 1.6 Hz respectively]. ${ }^{22,23}$ The tertiary nature of the nitrogen atom within $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$ was further confirmed by the absence of a $v_{\mathrm{NH}}$ absorption band from the infrared spectra. Moreover the positive ion FAB mass spectra of $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$ revealed the expected fragmentation patterns \{MS $(\mathrm{FAB}+): \mathrm{m} / \mathrm{z} 413\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$(3.20), 623 and $641[\mathrm{M}]^{+}(\mathbf{3 . 2 1}$ and 3.22) $\}$, whilst the elemental analysis results were satisfactory (see Experimental Section).

The electrochemical properties of $\mathbf{3 . 2 0}$ - $\mathbf{3 . 2 2}$ have also been briefly investigated by cyclic voltammetry and their oxidation ( $\mathrm{E}_{\mathrm{pa}}$ ), reduction ( $\mathrm{E}_{\mathrm{pc}}$ ) and $\mathrm{E}_{1 / 2}$ potentials summarised in Table 3.12.

Table 3.12 Electrochemical data ${ }^{a}$ for 3.20 - 3.22.

| Compound | $\mathrm{E}_{1 / 2}(\mathrm{~V}), \mathrm{Fe}^{\text {II/III }}$ | $\mathrm{E}_{\mathrm{pa}}(\mathrm{V}), \mathrm{Fe}^{\text {II/III }}$ | $\mathrm{E}_{\mathrm{pc}}(\mathrm{V}), \mathrm{Fe}^{\text {II/III }}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{3 . 2 0}$ | +0.142 | $-0.009,+0.194$ | +0.092 |
| $\mathbf{3 . 2 1}$ | +0.080 | $-0.070,+0.151$ | +0.009 |
| $\mathbf{3 . 2 2}$ | +0.015 | +0.074 | -0.043 |

${ }^{\text {a }}$ All experiments were performed in a $0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right] / \mathrm{dry}^{\mathrm{CH}_{2} \mathrm{Cl}_{2}}$ solution using a standard electrochemical cell at a scan rate of $50 \mathrm{mV} / \mathrm{s}$. All chemical potentials $\left(\mathrm{E}_{1 / 2}, \mathrm{E}_{\mathrm{pc}}\right.$ and $\mathrm{E}_{\mathrm{pa}}$ ) are reported relative to the ferrocene/ferrocenium couple.

The cyclic voltammograms of all three phosphines revealed a reversible ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple similar to that of ferrocene. The observation of a single $\mathrm{Fc} / \mathrm{Fc}^{+}$wave for $\mathbf{3 . 2 0}$ - $\mathbf{3 . 2 2}$ suggests that each ferrocene moiety behaves as an electrochemically equivalent monoelectronic redox group, undergoing oxidation and reduction simultaneously. In the case of $\mathbf{3 . 2 0}$ and 3.21, the cyclic voltammograms displayed the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple at $\mathrm{E}_{1 / 2} 0.142$ and 0.080 V respectively, in addition to a further oxidation peak at $\mathrm{E}_{\mathrm{pa}} 0.009$ (Figure 3.19, left) and 0.070 V respectively. This additional oxidation peak was tentatively assigned to the irreversible
oxidation of the phosphorus(III) atom. Due to the lack of a corresponding reduction potential and by comparison to other suggested phosphorus oxidation potentials, discussed herein $\left[\mathrm{E}_{\mathrm{pa}} 0.006 \mathrm{~V}\right.$ (3.14)]. In contrast the voltammogram of $\mathbf{3 . 2 2}$ only displayed a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$couple at $\mathrm{E}_{1 / 2} 0.015 \mathrm{~V}$ (Figure 3.19, right), suggesting that the phosphaadamantyl group was not electrochemically oxidised over the potential window studied.


Figure 3.19 Cyclic voltammograms of $\mathbf{3 . 2 0}$ (left) and $\mathbf{3 . 2 2}$ (right) in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}$ [ $\left.\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

### 3.12 Ruthenium(II) Coordination Chemistry of 3.20-3.22

The coordination chemistry of $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$ was briefly investigated by treatment with $\{\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2}(0.5$ equiv. $)$, to afford the trimetallic complexes $\mathbf{3 . 2 3 - 3 . 2 5}$ in good yield ( $83-88 \%$ range) (Equation 3.11).


Equation 3.11 (i) 0.5 equiv. $\{\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2}$, solvent $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum [in $\mathrm{CDCl}_{3}$ ] of $\mathbf{3 . 2 3} \mathbf{- 3 . 2 5}$ exhibited a new phosphorus singlet significantly downfield of that of the free ligands at $\delta(\mathrm{P}) 26.1$ (3.23), 32.3 (3.24) and 20.7 (3.25) ppm respectively. The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 3} \mathbf{- 3 . 2 5}$ contained the anticipated resonances relating to the coordinated monophosphines, in addition to the distinct resonances of the $p$-cym auxiliary ligand. Further support for the preparation of 3.23-3.25 comes from positive ion FAB mass spectroscopy, which gave the expected parent ion and fragmentation patterns $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right)\right.$: m/z 1453 and 894 [M$\mathrm{Cl}]^{+}\left(\mathbf{3 . 2 3}\right.$ and 3.25) and $\left.917[\mathrm{M}]^{+}(\mathbf{3 . 2 4})\right\}$. The elemental analyses for this series of complexes were also found to be satisfactory (see Experimental Section). The electrochemical properties of $\mathbf{3 . 2 3}$ were investigated by cyclic voltammetry. The voltammogram of $\mathbf{3 . 2 3}$ displayed a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple similar to that of 3.12, at $\mathrm{E}_{1 / 2} 0.003 \mathrm{~V}\left(\Delta \mathrm{E}_{1 / 2} 0.02 \mathrm{~V}\right.$ with respect to 3.12), suggesting that the ferrocenyl groups within both complexes are electrochemically similar. In addition to the $\mathrm{Fc} / \mathrm{Fc}^{+}$ couple, the voltammogram of $\mathbf{3 . 2 3}$ also exhibited several oxidation peaks between 0.7 1.5 V . These peaks may tentatively be assigned to two consecutive irreversible single
electron $\mathrm{Ru}^{\mathrm{II}} / \mathrm{Ru}^{\text {III }}$ oxidations (per ruthenium metal centre), and this feature was also observed in the voltammogram of 3.12. ${ }^{231,232}$

### 3.13 Platinum(II) Coordination Chemistry of $\mathbf{3 . 2 0}$

The coordination chemistry of $\mathbf{3 . 2 0}$ was investigated further by treatment with half an equiv. of $\mathrm{PtCl}_{2}$ (cod), to afford the pentametallic complex 3.26, in low yield (41\%), following recrystallisation from hexane (Equation 3.12).


Equation 3.12

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid was found to contain two new ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active species between $\delta(\mathrm{P})-69.5$ and 4.9 ppm . The species centred at $\delta(\mathrm{P}) 4.9 \mathrm{ppm}\left(49 \%\right.$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR integral) resonated as a singlet flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites $\left[{ }^{1} J_{\mathrm{PtP}} 3625 \mathrm{~Hz}\right.$ ], and was assigned to the anticipated pentametallic complex 3.26 by comparison with previously reported cis-platinum dichloride phosphine complexes. ${ }^{58,93,186,196}$ The second, unanticipated species, resonated as two doublets flanked by equidistant platinum satellites at $\delta(\mathrm{P})-2.6$ and -69.5 ppm [ ${ }^{2} J_{\mathrm{pp}} 3.2 \mathrm{~Hz},{ }^{1} J_{\mathrm{PtP}} 3222,3163 \mathrm{~Hz}$ respectively]; suggesting that both in-equivalent phosphorus environments coordinated the same platinum centre in an unsymmetrical cis-P, P manner. One tentative suggestion towards the nature of this unanticipated species is the formation of the unsymmetrical $\mathrm{P}, \mathrm{N}$ chelate complex $\mathbf{3 . 2 6 A}$ in $\mathrm{CDCl}_{3}$ solution (Equation 3.13).


Equation 3.13 "Ring-open" (3.26), "mono ring-closed" (3.26A) and ring-closed dimer (3.26B) conformations.

The assignment of this unknown species as 3.26A is also in agreement with several other features observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy;
i) The large difference in $\delta(\mathrm{P})$ between the two neighbouring phosphorus environments $\left[\mathrm{P}_{\mathrm{A}}=\right.$ coordinated, $\mathrm{P}_{\mathrm{B}}=$ uncoordinated; $\Delta \delta\left(\mathrm{P}_{\mathrm{A}} \mathrm{P}_{\mathrm{B}}\right) 66.9 \mathrm{ppm}$ ].
ii) The similarity between the upfield doublet at $\delta(\mathrm{P})-69.5 \mathrm{ppm}\left[{ }^{1} J_{\mathrm{PtP}} 3222\right]$ and that observed for the well known four-membered chelate $\mathrm{PtCl}_{2}(\mathrm{dppm})(1,1-$ bis(diphenylphosphino)methane) $\left[\delta(\mathrm{P})-64.6 \mathrm{ppm}\left({ }^{1} J_{\mathrm{PtP}} 3074 \mathrm{~Hz}\right), \Delta \delta(\mathrm{P})\right.$ with respect to $\mathbf{3 . 2 6 A}=5.0 \mathrm{ppm}] .{ }^{239}$
iii) The size of the ${ }^{1} J_{\mathrm{PtP}}$ coupling constants ( ${ }^{1} J_{\mathrm{PtP}} 3222$ and 3163 Hz , respectively) with respect to that of $\mathbf{3 . 2 6}\left({ }^{1} J_{\mathrm{PtP}} 3625 \mathrm{~Hz}\right)$, i.e. ${ }^{1} J_{\mathrm{PtP}}$ of Pt-P trans to a chloride $>^{1} J_{\text {PtP }}$ Pt-P trans to an amine.

A search of the literature revealed few examples of previously reported $\mathrm{P}, \mathrm{N}$ four membered platinum complexes, presumably due to the strained nature of the chelate ring. ${ }^{240,241}$ The proposed dissociation of chloride ions from 3.26, thought to afford 3.26A, was then explored further via two in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR experiments. The first in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR experiment was performed to show that chloride dissociation from 3.26 was a plausible mechanism by which 3.26A could be prepared, and involved the addition of $\mathbf{3 . 2 0}$ to a $\mathrm{CDCl}_{3}$ solution of $\mathrm{PtMe}_{2}(\operatorname{cod})$ (2:1 equiv. respectively). The resulting in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum revealed only the characteristic "ring-open" cis-platinum(II) dimethyl complex [ $\delta(\mathrm{P}) 10.2 \mathrm{ppm}(\mathrm{s}),{ }^{1} J_{\mathrm{PPt}} 1840 \mathrm{~Hz}$ ], presumably due
to the strong $\sigma$-donating nature of the $\mathrm{CH}_{3}$ groups preventing $\mathrm{P}, \mathrm{N}$ chelation; thereby supporting the proposed dissociation mechanism. ${ }^{224}$ The second in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR experiment was conducted to verify if dissociation of chloride ions from $\mathbf{3 . 2 6}$ could be enhanced, thereby allowing an in-situ sample of 3.26A to be prepared. Here addition of MeOH ( 5 drops) to a $\mathrm{CDCl}_{3}$ solution of $\mathbf{3 . 2 0}$ and $\mathrm{PtCl}_{2}(\mathrm{cod})$ (1:2 equiv. respectively) was carried out. The resulting ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum in this case, revealed only two characteristic phosphorus environments relating to the $\mathrm{P}, \mathrm{N}$ chelate $\mathbf{3 . 2 6 A}$ at $\delta(\mathrm{P})-2.1$ and $-66.5 \mathrm{ppm}\left[{ }^{1} J_{\mathrm{PPt}}, 3233\right.$ and $3220 \mathrm{~Hz},{ }^{2} J_{\mathrm{PP}} 3.2 \mathrm{~Hz}$ ], presumably due to increased dissociation of chloride ions from $\mathbf{3 . 2 6}$ in the more-polar solvent system $\left(\mathrm{CDCl}_{3}\right.$ / $\mathrm{MeOH})$; thereby suggesting that the coordination mode of $\mathbf{3 . 2 0}$ could be controlled.

As a result of these findings, $\mathbf{3 . 2 0}$ is thought to undergo both P and $\mathrm{P}, \mathrm{N}$ coordination of a platinum(II) dichloride centre in solution, with the proportion of 3.26 and 3.26A being dependant upon the polarity of the solvent system. Furthermore, whilst the dimeric species 3.26B (Equation 3.13) was not observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, its occurrence is still anticipated but unobserved under these conditions.

Further support for the preparation of 3.26, in the solid state, comes from positive ion FAB mass spectroscopy, which revealed the expected molecular fragments \{MS $\left.\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1453[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}\right\}$. Moreover the molecular structure of $\mathbf{3 . 2 6}$ has also been determined by single crystal X-ray diffraction (Section 3.13.1).

### 3.13.1 Molecular Structure of $\mathbf{3 . 2 6}$

Yellow crystalline plates suitable for single crystal X-ray diffraction were grown by the slow vapour diffusion of hexane into a $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{Et}_{2} \mathrm{O}$ solution of 3.26. The molecular structure was determined using synchrotron radiation due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) (Figure 3.20). Selected lengths and angles given in Table 3.13.


Figure 3.20 Molecular structure of 3.26. All hydrogen atoms and solvating $\mathrm{CHCl}_{3}$ molecules of crystallisation have been removed for clarity.

The molecular structure of $\mathbf{3 . 2 6}$ shows the asymmetric unit to contain one molecule of the pentametallic complex and three solvating molecules of $\mathrm{CHCl}_{3}$, two of which were modelled as diffuse regions of electron density due to their disordered nature (Platon squeeze procedure). ${ }^{229}$ The platinum dichloride complex adopts a distorted square planar geometry with respect to the metal centre $\left[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2) 172.13(4)^{\circ}, \mathrm{P}(2)-\mathrm{Pt}(1)-\right.$ $\left.\mathrm{Cl}(1) 169.24(3)^{\circ}\right], 58,93$ with the two ligands $\mathbf{3 . 2 0}$, coordinating the metal in a cis manner, each via one phosphorus atom $\left[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2), 97.67(4)^{\circ}\right]$. The $\mathrm{P}-\mathrm{Pt}(1)-\mathrm{P}$ bite angle between the two coordinated ligands was found to be significantly less than that found within the analogous trimetallic diphosphine complex $\mathbf{3 . 4}[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2) 103.05(5) \AA$ (3.4)], suggesting that the two phosphorus atoms within 3.1 are forced "outwards" upon chelation, in order to accommodate the bulky $\mathrm{P}-\mathrm{C}-\mathrm{N}-\mathrm{C}-\mathrm{C}-\mathrm{N}-\mathrm{C}-\mathrm{P}$ backbone of $\mathbf{3 . 1}$. The phosphorus atoms adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{Pt}-\mathrm{P}-\mathrm{C}$ angles. The nitrogen atoms were adopt a distorted pyramidal geometry [sum of component angles $=339$ and $341^{\circ}$ respectively]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl
rings were found to be essentially coplanar, whilst the torsional twist of the cyclopentadienyl rings was found to vary between the four ferrocenyl groups [torsional twist ranged between $\left.\mathrm{C}-\mathrm{Cp}_{\text {cent }}-\mathrm{Cp}_{\text {cent }}-\mathrm{C}=2.4-23.8^{\circ}\right]$.

Table 3.13 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.26.

| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3603(10)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 97.67(4) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.3676(10)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 86.01(4) |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | 2.2440(10) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 90.81(4) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | 2.2534(10) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 86.37(3) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.814(4) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 169.24(3) |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.820(4) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 172.13(4) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.847(4) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 114.34(13) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.474(5)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 114.23(12) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.462(5)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 110.57(13) |
| $\mathrm{N}(1)-\mathrm{C}(25)$ | $1.482(5)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 115.5(3) |
| $\mathrm{P}(2)-\mathrm{C}(36)$ | 1.823(4) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 111.5(3) |
| $\mathrm{P}(2)-\mathrm{C}(42)$ | 1.807(4) | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(25)$ | 113.9(3) |
| $\mathrm{P}(2)-\mathrm{C}(48)$ | 1.857(4) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(25)$ | 113.9(3) |
| $\mathrm{N}(2)-\mathrm{C}(48)$ | $1.441(5)$ | $\mathrm{C}(36)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 120.70(12) |
| $\mathrm{N}(2)-\mathrm{C}(49)$ | $1.468(5)$ | $\mathrm{C}(42)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 112.91(14) |
| $\mathrm{N}(2)-\mathrm{C}(60)$ | $1.485(5)$ | $\mathrm{C}(48)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | 107.03(13) |
| $\mathrm{Fe}(1)-\mathrm{CpA}_{\text {cent }}$ | 1.643(2) | $\mathrm{N}(2)-\mathrm{C}(48)-\mathrm{P}(2)$ | 113.7(3) |
| $\mathrm{Fe}(1)-\mathrm{CpB}_{\text {cent }}$ | 1.640(2) | $\mathrm{C}(48)-\mathrm{N}(2)-\mathrm{C}(49)$ | 114.6(3) |
| $\mathrm{Fe}(2)-\mathrm{CpC}_{\text {cent }}$ | 1.638(2) | $\mathrm{C}(48)-\mathrm{N}(2)-\mathrm{C}(60)$ | 112.6(3) |
| $\mathrm{Fe}(2)-\mathrm{CpD}_{\text {cent }}$ | 1.650(2) | $\mathrm{C}(49)-\mathrm{N}(2)-\mathrm{C}(60)$ | 113.9(3) |
| $\mathrm{Fe}(3)-\mathrm{CpE}_{\text {cent }}$ | 1.645(2) | $\mathrm{C}(15)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(21)$ | 2.4 |
| $\mathrm{Fe}(3)-\mathrm{CpF}_{\text {cent }}$ | $1.645(3)$ | $\mathrm{C}(26)-\mathrm{CpC}_{\text {cent }}-\mathrm{CpD}_{\text {cent }}-\mathrm{C}(32)$ | 5.9 |
| $\mathrm{Fe}(4)-\mathrm{CpG}_{\text {cent }}$ | 1.647(2) | $\mathrm{C}(50)-\mathrm{CpE}_{\text {cent }}-\mathrm{CpF}_{\text {cent }}-\mathrm{C}(56)$ | 23.8 |
| $\mathrm{Fe}(4)-\mathrm{CpH}_{\text {cent }}$ | 1.654(3) | $\mathrm{C}(61)-\mathrm{CpG}_{\text {cent }}-\mathrm{CpH}_{\text {cent }}-\mathrm{C}(67)$ | 10.6 |

### 3.14 Preparation and Characterisation of 3.27-3.29

In addition to the ferrocenyl phosphines discussed thus far, our group is also interested in the development of new symmetrical ditertiary phosphines of the types $\left(\mathrm{R}_{2} \mathrm{PCH}_{2}\right)_{2} \mathrm{~N}(\mathrm{R})$ and $\left\{\left(\mathrm{R}_{2} \mathrm{PCH}_{2}\right)_{2} \mathrm{~N}\right\}_{2}(\mathrm{R}),{ }^{242-246}$ which have shown interesting coordination, catalytic and self-assembly properties. ${ }^{22,23,59}$ To this end the new ferrocenyl phosphines 3.27 - $\mathbf{3 . 2 9}$ were prepared by the double condensation of the known primary amine $\mathrm{FcCH}_{2} \mathrm{NH}_{2}{ }^{247}$ with two equiv. of the relevant tertiary phosphine synthon, $\mathrm{RPCH}_{2} \mathrm{OH}\left(\mathrm{PR}=\mathrm{PPh}_{2}, \mathrm{PCy}_{2}\right.$ or $\mathrm{PAd}=1,3,5,7$-tetramethyl-2,4,8-trioxa-6phosphaadamantane) (Equation 3.14). In all three cases, solids were deposited during the course of the reaction allowing the ligands to be isolated in high purity (as judged by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR) and in good yield ( $62-73 \%$ ).




$\mathrm{RP}=\mathrm{PPh}_{2} \quad 3.27$ $\mathrm{RP}=\mathrm{PCy}_{2} \quad 3.28$ $\mathrm{RP}=\mathrm{PAd} \quad 3.29$

Equation 3.14

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in freeze-thawed $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 7}$ - $\mathbf{3 . 2 9}$ all exhibited new phosphorus singlets compared to that of the $\mathrm{PRCH}_{2} \mathrm{OH}$ starting material, between $\delta(\mathrm{P})-$ 18.3 to -43.1 ppm . In the case of $\mathbf{3 . 2 7}$ and $\mathbf{3 . 2 8}$ the $-\mathrm{PPh}_{2}$ and $-\mathrm{PCy}_{2}$ groups resonated as singlets at $\delta(\mathrm{P})-28.1$ and -18.3 ppm respectively, whilst the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathbf{3 . 2 9}$ revealed two singlets of similar $\delta(\mathrm{P})$ presumably due to the enantiomic nature of the newly introduced phosphaadamantyl cages $[\delta(\mathrm{P})-42.9$ and -43.1 ppm ; respective ratio by integration $c a .1: 2]$ ( $\alpha$ and $\beta$ enantiomers, Figure 3.2). ${ }^{10,13,219,220}$ The phosphines all showed evidence of oxidation when $\mathrm{CDCl}_{3}$ solutions were left to stand in air.

The ${ }^{1} \mathrm{H}$ NMR spectra (in freeze-thawed $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 2 7}$ - $\mathbf{3 . 2 9}$ all showed characteristic cyclopentadienyl $[\delta(\mathrm{H}) 4.01-4.11 \mathrm{ppm}]$ and $\mathrm{CH}_{2} \mathrm{Fc}[\delta(\mathrm{H}) 3.64-3.86 \mathrm{ppm}]$ resonances,
as anticipated, by comparison with the ${ }^{1} \mathrm{H}$ NMR spectrum of the parent amine. ${ }^{247}$ The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated between $[\delta(\mathrm{H}) 2.57-3.35 \mathrm{ppm}$. In the case of 3.27, the $\mathrm{CH}_{2} \mathrm{P}$ protons appeared as a characteristic doublet $\left[\delta\left(\mathrm{PCH}_{2}\right) 3.35\right.$, ${ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}$, ,,${ }^{22,23}$ whilst in the case of $\mathbf{3 . 2 8}$ the same hydrogen atoms appeared as a singlet $\left[\delta\left(\mathrm{PCH}_{2}\right) 2.57 \mathrm{ppm}\right]$. The enantiomeric nature of the phosphaadamantyl groups within 3.29 was also evident from the ${ }^{1} \mathrm{H}$ NMR spectrum, which showed two broad $\delta\left(\mathrm{PCH}_{2}\right)$ multiplets [ $\delta\left(\mathrm{PCH}_{2}\right) 2.82 \mathrm{ppm},{ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}$ and $2.79 \mathrm{ppm},{ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}$ ]. This assignment was supported by integration of the resonances [2:1, $\left.\mathrm{CH}_{2} \mathrm{P}_{(\alpha+\beta)}: \mathrm{CH}_{2} \mathrm{Fc}\right]$, ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ spectroscopy [broad $\delta\left(\mathrm{CH}_{2}\right)$ multiplets collapsed to singlets] and also by HMQC / DEPT NMR spectroscopy which showed a correlation between the enantiomeric $\delta\left(\mathrm{PCH}_{2}\right)$ hydrogen atoms and two of the three methylene carbon environments. The absence of a $v_{\mathrm{NH}}$ stretch in the infrared spectra of $\mathbf{3 . 2 7 - 3 . 2 9}$ further confirmed the ternary nature of the nitrogen atoms in the newly formed ditertiary phosphines. Additional support for the preparation of $\mathbf{3 . 2 7}$ - $\mathbf{3 . 2 9}$ could be found from elemental analysis, which agreed with the expected empirical formulae (see Experimental Section), and also from the positive ion FAB mass spectroscopy results which gave predictable molecular fragments $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 611\right.$ and $634[\mathrm{M}-\mathrm{H}]^{+}$ (3.27 and 3.28 respectively) and $472\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$(3.29) \}. The molecular structures of 3.28 and 3.29 have also been determined by single crystal X-ray diffraction (Section 3.14.1). The electrochemical properties of $\mathbf{3 . 2 7} \mathbf{- 3 . 2 9}$ have also been briefly investigated by cyclic voltammetry. All three voltammograms for 3.27-3.29 displayed a reversible ferrocene/ferrocenium redox $\left(\mathrm{Fc} / \mathrm{Fc}^{+}\right)$couple, with a half wave potential similar to that of ferrocene under the same experimental conditions (Table 3.14). In the case of $\mathbf{3 . 2 7}$ and $\mathbf{3 . 2 8}$ the voltammograms were observed to be particularly broad at more anodic potentials (Figure 3.21, left), an effect that may be caused by marginal differences between the oxidation potential of the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple and the irreversible oxidation of the tertiary phosphorus(III) centres. In contrast this broadening effect was not observed in the voltammogram for 3.29, suggesting that the phosphaadamantyl groups are not electrochemically oxidised over the potential window studied, as previously observed for the diferrocenyl phosphine $\mathbf{3 . 3}$ and $\mathbf{3 . 2 0}$ (Figure 3.21, right).


Figure 3.21 Cyclic voltammograms of $\mathbf{3 . 2 7}$ (left) and $\mathbf{3 . 2 9}$ (right) in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, $0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

Table 3.14 Electrochemical data ${ }^{a}$ for $3.27-3.29$.

| Compound | $\mathrm{E}_{1 / 2}(\mathrm{~V}), \mathrm{Fe}^{\mathrm{IIfIIII}}$ |
| :---: | :---: |
| $\mathbf{3 . 2 7}$ | 0.005 |
| $\mathbf{3 . 2 8}$ | -0.021 |
| $\mathbf{3 . 2 9}$ | 0.000 |

${ }^{\text {a }}$ All experiments were performed in a $0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right] / \mathrm{dry}^{\mathrm{CH}_{2} \mathrm{Cl}_{2}}$ solution using a standard electrochemical cell at a scan rate of $50 \mathrm{mV} / \mathrm{s}$. ${ }^{\mathrm{b}} \mathrm{E}_{1 / 2}$ are reported relative to the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple.

### 3.14.1 Molecular Structures of $\mathbf{3 . 2 8}$ and $\mathbf{3 . 2 9}$

Orange crystalline blocks (3.28) and colourless crystalline plates (3.29), suitable for single crystal X -ray diffraction, were obtained by layering MeOH onto a $\mathrm{CDCl}_{3}$ solution of $\mathbf{3 . 2 8}$ and by the slow evaporation of a MeOH solution of $\mathbf{3 . 2 9}$. The molecular structures of $\mathbf{3 . 2 8}$ and $\mathbf{3 . 2 9}$ were determined; selected lengths and angles are given in Table 3.15.


Figure 3.22 Molecular structure of 3.29. All hydrogen atoms have been removed for clarity.

Figure 3.22 shows $\mathbf{3 . 2 9}$ as a typical example of this pair of diphosphines, as both $\mathbf{3 . 2 8}$ and 3.29 were found to adopt similar conformations in the solid state. The phosphorus(III) atoms, in both cases, adopted a distorted trigonal pyramidal geometry [C-P-C ranged between $92.17(12)-105.36(8) \AA$ ]. The nitrogen atoms, in both cases, also adopted a distorted trigonal pyramidal geometry [sum of component angles $331^{\circ}$ ( 3.28 and 3.29)]. The cyclopentadienyl rings of the ferrocene groups were both found to be eclipsed and essentially coplanar (torsional twist about the $\mathrm{C}(4)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}{ }^{-}$ $\mathrm{C}(10)$ is 0.6 and $7.8^{\circ}$ respectively). No inter or intramolecular packing features of note were observed in the structures of $\mathbf{3 . 2 8}$ or $\mathbf{3 . 2 9}$.

Table 3.15 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.28 and 3.29. ${ }^{\text {a }}$

|  | 3.28 | 3.29 |  | 3.28 | 3.29 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.8602(18)$ | 1.860(3) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(\mathrm{A})^{\text {a }}$ | 97.74(8) | 102.54(12) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{A})^{\text {a }}$ | $1.8630(19)$ | 1.875(3) | $C(1)-P(1)-C(B)^{\text {a }}$ | 102.96(8) | 102.23(13) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{B})^{\mathrm{a}}$ | 1.8589 (18) | 1.870(3) | $\mathrm{C}(\mathrm{A})-\mathrm{P}(1)-\mathrm{C}(\mathrm{B})^{\mathrm{a}}$ | 103.06(8) | 92.83(13) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.466(2) | $1.472(3)$ | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{P}(1)$ | 115.40(12) | 110.41 (18) |
| $\mathrm{N}(1)-\mathrm{C}(2)$ | 1.468(2) | 1.473(3) | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(2)$ | 109.82(13) | 110.2(2) |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | $1.475(2)$ | 1.481(3) | $\mathrm{C}(2)-\mathrm{N}(1)-\mathrm{C}(3)$ | 110.98(13) | 110.4(2) |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.499(2) | 1.498(4) | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)$ | 110.08(13) | 110.3(2) |
| $\mathrm{P}(2)-\mathrm{C}(2)$ | $1.8615(17)$ | 1.865(3) | $\mathrm{N}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 111.92(14) | 113.2(2) |
| $\mathrm{P}(2)-\mathrm{C}(\mathrm{C})$ | 1.8631(18) | 1.883(3) | $\mathrm{N}(1)-\mathrm{C}(2)-\mathrm{P}(2)$ | 111.52(11) | 114.91(18) |
| $\mathrm{P}(2)-\mathrm{C}(32)$ | 1.8631(17) | 1.887(3) | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(\mathrm{C})$ | 99.26(8) | 98.18(12) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {cent }}$ | 1.6482(9) | $1.6435(13)$ | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{C}(32)$ | 98.23(8) | 103.61(12) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | 1.6489(10) | 1.6383(12) | $\mathrm{C}(\mathrm{C})-\mathrm{P}(2)-\mathrm{C}(32)$ | 105.36(8) | 92.17(12) |
|  |  |  | $\mathrm{C}(4)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(10)$ | 0.6 | 7.8 |

$\mathrm{CpA}_{\text {cent }}=\mathrm{C}(4)$ to $\mathrm{C}(8), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(9)$ to $\mathrm{C}(13)$.
${ }^{\mathrm{a}} \mathrm{A}=14$ (3.28), 17 (3.29); $\mathrm{B}=20$ (3.28), 22 (3.29); $\mathrm{C}=26$ (3.28), 25 (3.29).

### 3.15 Platinum(II) and Palladium(II) Coordination Chemistry of 3.27-3.29

The coordination chemistry of $\mathbf{3 . 2 7} \mathbf{- 3 . 2 9}$ to various transition metal centres was explored in order to understand the ligating modes of this new series of ferrocenyl ditertiary phosphines. Treatment of $\mathbf{3 . 2 7} \mathbf{- 3 . 2 9}$ with an equimolar amount of $\mathrm{MCl}_{2}(\mathrm{cod})$ ( $\mathrm{M}=\mathrm{Pt}$ or Pd ) afforded the four-coordinate complexes $\mathbf{3 . 3 0}-\mathbf{3 . 3 5}$, in good to excellent yield ( $83-99 \%$ range) following ligand displacement of $\operatorname{cod}$ (Equation 3.15).


Equation 3.15
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 0}$ - $\mathbf{3 . 3 2}$ all exhibited new phosphorus singlets between $\delta(\mathrm{P}) 5.5$ to -17.9 ppm (Table 3.16), some $c a . \delta(\mathrm{P}) 26-13 \mathrm{ppm}$ downfield compared to that of the free ligands. In the case of $\mathbf{3 . 3 0}$ and 3.31, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra showed a new singlet at $\delta(\mathrm{P})-9.1$ and 5.5 ppm respectively, whilst in the case of 3.32, the -PAd moieties were found to resonate as two singlets owing to the enantiomic nature of the phosphaadamantyl cages $[\delta(\mathrm{P})-17.9$ and -16.4 ppm ; respective ratio by integration ca. 1:2]. The ratio between the enantiomers of $\mathbf{3 . 3 2}$ was found to be unchanged relative to that of the free ligand (3.29), suggesting that both enantiomers are equally favoured upon coordination and have similar solubility in the precipitating solvent $\left(\mathrm{Et}_{2} \mathrm{O}\right)$. All the new phosphorus resonances for $\mathbf{3 . 3 0}-\mathbf{3 . 3 2}$ were flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites [ ${ }^{1} J_{\mathrm{PtP}} 3377-3473 \mathrm{~Hz}$ (Table 3.16). The characteristically large ${ }^{1} J_{\text {PtP }}$ coupling constants suggests that the platinum(II) complexes adopt a cis conformation in solution similar to that of other platinum(II) dichloride complexes reported herein and in the literature. ${ }^{58,93,186,196}$

The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 0}$ - $\mathbf{3 . 3 2}$ all contained the anticipated resonances relating to the hydrogen atoms within the coordinated ligands (Table 3.16). The $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated between $\delta(\mathrm{H}) 2.60-3.23 \mathrm{ppm}$ and had a characteristic integration (2:1, $\mathrm{CH}_{2} \mathrm{P}: \mathrm{CH}_{2} \mathrm{Fc}$ ). ${ }^{23,58,186}$ In the case of $\mathbf{3 . 3 0}$ and $\mathbf{3 . 3 1}$, the $\mathrm{CH}_{2} \mathrm{P}$ protons resonated as doublets [ ${ }^{2} J_{\mathrm{PH}} 2.8$ and 2.4 Hz respectively] whilst the same hydrogen atoms appeared as a series of broad multiplets in the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 . 3 2}\left[\delta\left(\mathrm{CH}_{2} \mathrm{P}\right) 2.82\right.$ -3.20 ppm ].

Table 3.16 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR [ $\delta$ in ppm, $J$ in Hz ] and FT-IR data $\left(\mathrm{cm}^{-1}\right)$ for 3.30-3.32.

|  | $\delta(\mathrm{P})$ | ${ }^{1} J_{\mathrm{PtP}}$ | $\delta(\mathrm{Fc})$ | $\delta\left(\mathrm{FcCH}_{2}\right)$ | $\delta\left(\mathrm{PCH}_{2}\right)$ | $v_{\mathrm{PtCl}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{3 . 3 0}$ | -9.1 | 3389 | $3.95-4.09$ | 3.45 | 3.23 | 312,292 |
| $\mathbf{3 . 3 1}$ | 5.5 | 3473 | $4.07-4.14$ | 3.36 | 2.60 | 302,279 |
| $\mathbf{3 . 3 2}^{\mathrm{a}}$ | $-17.9,-16.4$ | 3390,3377 | $3.59-3.69$ | $3.20-2.82$ | 320,296 |  |

a $\overline{\delta(\mathrm{Fc}) \text { and } \delta\left(\mathrm{FcCH}_{2}\right) \text { overlapped and could not be assigned with confidence. }}$

Further support for the preparation of $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$ came from the complexes FT-IR spectra which displayed two characteristic $\nu_{\mathrm{PtCl}}$ absorption bands between $279-320$ $\mathrm{cm}^{-1}$ (Table 3.16), ${ }^{58,186,196}$ Furthermore the positive ion FAB mass spectra of $\mathbf{3 . 3 0}-\mathbf{3 . 3 2}$ gave the expected molecular ions $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 877,901\right.$ and $938[\mathrm{M}]^{+}(\mathbf{3 . 3 0}-$ 3.32) , whilst elemental analysis of $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$ was found to be satisfactory (see Experimental Section). The molecular structures of $\mathbf{3 . 3 0}$ - $\mathbf{3 . 3 2}$ have also been determined by single crystal X-ray diffraction (Section 3.15.1).

The electrochemical properties of $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$ have been briefly investigated by cyclic voltammetry. The voltammograms of all three compounds displayed a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$ redox couple similar to that of ferrocene $\left[\mathrm{E}_{1 / 2}+0.040\right.$ (3.30), +0.038 (3.31) and $+0.038 \mathrm{~V}$ (3.32); values relative to the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple]. Comparison of the $\mathrm{E}_{1 / 2}$ values of $\mathbf{3 . 3 0}$ $\mathbf{3 . 3 2}$ with those of the free ligands $\mathbf{3 . 2 7} \mathbf{- 3 . 2 9}$ showed a anodic shift with respect to the
complex ( $\Delta \mathrm{E}_{1 / 2} c a .0 .044 \mathrm{~V}$ ) suggesting that the ferrocenyl groups within $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$ are marginally harder to oxidise.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of the palladium(II) complexes ( $\mathbf{3 . 3 3} \mathbf{- 3 . 3 5}$ ) all showed new phosphorus singlet resonances between $\delta(\mathrm{P}) 29.6-0.0 \mathrm{ppm}$, some 45.0 ppm downfield to that of the free ligands $[\delta(\mathrm{P})-18.3$ to $-43.1 \mathrm{ppm}]$ (Table 3.17). In the case of $\mathbf{3 . 3 5}$, the phosphaadamantyl groups were found to resonate at two distinct values [ $\delta(\mathrm{P}) 1.7$ and $0.0 \mathrm{ppm}, 2: 1$ respectively], owing to the enantiomeric nature of $\mathbf{3 . 2 9}$.

Table 3.17 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR ( $\delta$ in ppm) and FT-IR data $\left(\mathrm{cm}^{-1}\right)$ for $\mathbf{3 . 3 3 -}$ 3.35 .

|  | $\delta(\mathrm{P})$ | $\delta(\mathrm{Fc})$ | $\delta\left(\mathrm{FcCH}_{2}\right)$ | $\delta\left(\mathrm{PCH}_{2}\right)$ | $v_{\mathrm{PdCl}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{3 . 3 3}$ | 7.6 | $3.96-4.09$ | 3.52 | 3.18 | 303,294 |
| $\mathbf{3 . 3 4}$ | 29.6 | $4.08-4.16$ | 3.43 | 2.57 | 301,277 |
| $\mathbf{3 . 3 5}$ | $1.7,0.0$ | $4.26-4.32$ | 3.69 | 2.69 | 314,292 |

The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 3}$ - $\mathbf{3 . 3 5}$ all contained the anticipated resonances relating to the coordinated ligands (Table 3.17), with little change in $\delta(\mathrm{H})$ being observed between the platinum and palladium analogues. The FT-IR spectra of $\mathbf{3 . 3 3 -}$ 3.35 were all found to contain two characteristic $v_{\text {PdCl }}$ absorption bands between 277 $314 \mathrm{~cm}^{-1} .^{1,21,186}$ Further support for the preparation of $\mathbf{3 . 3 3} \mathbf{- 3 . 3 5}$ comes from positive ion FAB mass spectroscopy results which gave the expected fragmentation patterns \{MS


### 3.15.1 Molecular Structures of $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$

Yellow ( $\mathbf{3 . 3 0}$ and 3.31) and orange (3.33) crystalline blocks suitable for X -ray crystallography were grown by either slow evaporation of a $\mathrm{CDCl}_{3}$ solution of $\mathbf{3 . 3 0}$, the vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{3 . 3 1}$, or by the layering of MeOH onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of $\mathbf{3 . 3 2}$. The molecular structures were determined by single crystal X-ray diffraction (Figure 3.23); selected lengths and angles are given in Table 3.18. Each complex adopted a pseudo square planar geometry with respect to the platinum(II) centre, with 3.27-3.29 coordinating the metal via both phosphorus atoms to form a six-membered cis-chelate ring [bite angle ranged between 94.86(3) $\left.95.59(2)^{\circ}\right]$. The phosphorus atoms were found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Pt}$ angles [ $\mathrm{C}-\mathrm{P}-\mathrm{Pt}$ ranged between $\left.109.87(7)-119.27(13)^{\circ}\right]$. The nitrogen atoms, in all cases, adopted a distorted trigonal pyramidal geometry [sum of component angles $=331^{\circ}(\mathbf{3 . 3 0}), 332^{\circ}(\mathbf{3 . 3 1})$ and $329^{\circ}$ (3.32)]. The molecular structures of $\mathbf{3 . 3 1}$ and $\mathbf{3 . 3 2}$ were found to contain one molecule of complex within the asymmetric unit. In contrast, the molecular structure of $\mathbf{3 . 3 0}$ revealed the complex to lie on a crystallographic mirror plane which bisects the $\mathrm{FcCH}_{2} \mathrm{~N}$ moiety and the platinum(II) centre. As a result the asymmetric unit was found to contain only half a molecule of $\mathbf{3 . 3 0}$ [symmetry operator for equivalent atoms: ' $\mathrm{x},-\mathrm{y}+1 / 2, \mathrm{z}$ ]. Further inspection of the $\operatorname{Pt}\{\mathrm{PCNCP}\}$ chelate rings of $\mathbf{3 . 3 0}$ - $\mathbf{3 . 3 2}$ revealed all three complexes to adopt a similarly distorted chair conformation, irrespective of the phosphorus substituents [hinge angle between the plane containing $\mathrm{C}(1), \mathrm{N}(1), \mathrm{C}\left(2\right.$ or $\left.1^{\prime}\right)$ vs $\mathrm{C}(1), \mathrm{P}(1), \mathrm{C}\left(2\right.$ or $\left.1^{\prime}\right), \mathrm{P}\left(2\right.$ or $\left.1^{\prime}\right)$ ranged between; $67.4-71.5^{\circ}$. Hinge angle between the plane containing $\mathrm{C}(1), \mathrm{P}(1), \mathrm{C}\left(2\right.$ or $\left.1^{\prime}\right), \mathrm{P}\left(2\right.$ or $\left.1^{\prime}\right)$ vs $\mathrm{P}(1), \mathrm{Pt}(1), \mathrm{P}\left(2\right.$ or $\left.1^{\prime}\right)$ ranged between $1.4-7.4^{\circ}$. Distance of $\operatorname{Pt}(1)$ and $\mathrm{N}(1)$, below or above the mean plane containing $\mathrm{C}(1), \mathrm{P}(1), \mathrm{C}\left(2\right.$ or $\left.1^{\prime}\right), \mathrm{P}\left(2\right.$ or $\left.1^{\prime}\right)$, ranged between -0.20 to $-0.02 \AA$ and $0.76-$ $0.80 \AA$ respectively]. Moreover comparison across the series of platinum(II) complexes revealed the orientation of the $\mathrm{CH}_{2} \mathrm{Fc}$ group to differ significantly [angle between the plane containing $\mathrm{C}(1), \mathrm{N}(1), \mathrm{C}\left(2\right.$ or $\left.1^{\prime}\right)$ vs $\mathrm{N}(1), \mathrm{C}(2$ or 3$), \mathrm{C}(3$ or 4$) ; 90.0^{\circ}(\mathbf{3 . 3 0}), 110.6^{\circ}$ (3.31) and $61.6^{\circ}(\mathbf{3 . 3 2})$ respectively.], thereby highlighting the conformational freedom of the $\mathrm{CH}_{2} \mathrm{Fc}$ group (Figure 3.23).

Figure 3.23 Molecular structures of $\mathbf{3 . 3 1}$ (left), $\mathbf{3 . 3 0}$ (centre) and $\mathbf{3 . 3 2}$ (right). All hydrogen atoms and solvent molecules of crystallisation have been removed for clarity. In the case of $\mathbf{3 . 3 0}$ all the phenyl ring carbons, except the ipso carbons, have also
been removed for clarity. For $\mathbf{3 . 3 0}$, symmetry operator for equivalent atoms: ' $x,-y+1 / 2, z$

Analysis of the packing plot of $\mathbf{3 . 3 0}$ revealed the crystal lattice to be made up of antiparallel stacked rows of $\mathbf{3 . 3 0}$, running along the $c$-axis (Figure 3.24). The cavities between the stacked-rows contained two $\mathrm{CHCl}_{3}$ molecules of crystallisation. No interor intramolecular packing features of note were observed in the structures of $\mathbf{3 . 3 1}$ or 3.32.


Figure 3.24 Intermolecular packing for 3.30. All hydrogen atoms have removed for clarity.
Table 3.18 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{3 . 3 0}-\mathbf{3 . 3 2}$. ${ }^{\text {a,b }}$

|  | 3.3 | 3.31 | 3.32 |  | 3.3 | 3.31 | 3.32 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3500(7)$ | $2.3679(5)$ | 2.3422(9) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 95.44(3) | 95.593(17) | 94.86(3) |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ |  | $2.3825(5)$ | $2.3364(10)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 87.77(2) | 88.172(17) | 91.25(3) |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | 2.2234(7) | 2.2354(5) | 2.2476 (8) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 87.77(2) | 88.834(18) | 91.33(3) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ |  | 2.2355(5) | 2.2534(9) | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 88.97(3) | 87.880(18) | 82.62(3) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.837(3) | 1.8424(19) | 1.828(3) | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 176.30(3) | 173.591(17) | 173.48(3) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{A})$ | $1.816(3)$ | 1.8340(19) | 1.871(3) | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 176.30(3) | 173.375(18) | 173.69(3) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{B})$ | 1.816 (3) | 1.852(2) | 1.877(3) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 117.96(9) | 116.92(6) | 117.98(12) |
| $\mathrm{C}(1)-\mathrm{N}(1)$ | 1.459(3) | 1.469(2) | 1.460(4) | $\mathrm{C}(\mathrm{A})-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 116.16(9) | 111.63(6) | 117.98(11) |
| N(1)-C(3) |  | 1.484(2) | 1.495(4) | $\mathrm{C}(\mathrm{B})-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 112.90(9) | 114.53(6) | 117.98(10) |
| $\mathrm{N}(1)-\mathrm{C}(2)$ | 1.503(4) | 1.457(2) | 1.459(4) | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{P}(1)$ | 114.3(2) | 112.65(13) | 112.5(2) |
| $\mathrm{P}(2)-\mathrm{C}(2)$ |  | 1.8490(19) | 1.832(3) | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(2)$ | 110.9(3) | 110.32(15) | 109.8(3) |
| $\mathrm{P}(2)-\mathrm{C}(\mathrm{C})$ |  | $1.836(2)$ | 1.877(4) | $\mathrm{C}(2)-\mathrm{N}(1)-\mathrm{C}(3)$ | 109.89(19) | 111.20(15) | 110.2(2) |
| $\mathrm{P}(2)-\mathrm{C}(\mathrm{D})$ |  | 1.846(2) | 1.877(3) | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)$ |  | 110.83(15) | 108.6(2) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {cent }}$ | 1.627(4) | 1.643(1) | 1.646(2) | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{Pt}(1)$ |  | 118.71(6) | 117.65(11) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | 1.639(4) | 1.647 (1) | 1.637(2) | $\mathrm{C}(\mathrm{C})-\mathrm{P}(2)-\mathrm{Pt}(1)$ |  | 109.87(7) | 119.27(13) |
|  |  |  |  | $\mathrm{C}(\mathrm{D})-\mathrm{P}(2)-\mathrm{Pt}(1)$ |  | 115.69(6) | 116.92(11) |
|  |  |  |  | $\begin{aligned} & \mathrm{C}(\mathrm{E})-\mathrm{CpA}_{\text {cent }}- \\ & \mathrm{CpB}_{\mathrm{cent}}-\mathrm{C}(\mathrm{~F}) \end{aligned}$ | 0 | 2.9 | 8 |

[^5]
### 3.16 Chromium(0) Coordination Chemistry of 3.27-3.29

Reaction of 3.27-3.29 with an equimolar amount of $\mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{nbd})$, under nitrogen in THF, gave the six-coordinate octahedral complexes $\mathbf{3 . 3 6}$ - $\mathbf{3 . 3 8}$ as orange crystalline solids following complete removal of the solvent (Equation 3.16).

$\mathrm{PR}=\mathrm{PPh}_{2}$
3.27
$\mathrm{PR}=\mathrm{PCy}_{2} \quad 3.28$
PR $=$ PAd 3.29



THF

3.37
3.38
3.36


Equation 3.16

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 6} \mathbf{- 3 . 3 8}$ all exhibited new phosphorus singlets between $\delta(\mathrm{P}) 29.9-38.9 \mathrm{ppm}$ [free ligand ( $\mathbf{3 . 3 6}-\mathbf{3 . 3 8}$ ); $\delta(\mathrm{P})-18.3--43.1$ ppm]. In the case of $\mathbf{3 . 3 6}$, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum showed a new singlet at $\delta(\mathrm{P})$ 38.9 ppm , whilst two singlets relating to the two enantiomers of $\mathbf{3 . 2 9}$ were observed for $3.38[\delta(P) 31.7$ and 29.9 ppm$]$. In contrast the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{3 . 3 7}$ showed the reaction to be incomplete following the standard 1 h stir at $60^{\circ} \mathrm{C}$, with the new singlet at $\delta(\mathrm{P}) 37.2 \mathrm{ppm}$, assigned to 3.37 , accounting for only $27 \%$ of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ active nuclei. As a consequence the reaction was heated under the same reaction conditions for an additional 4 h . The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the resulting solid showed no significant change to the purity of $\mathbf{3 . 3 7}$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left[\delta(P) 37.2 \mathrm{ppm}, 26 \%\right.$ by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR integral]. As a result, further analysis of $\mathbf{3 . 3 7}$ by ${ }^{1} \mathrm{H}$ NMR and infrared spectroscopy proved inconclusive.

The ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) for $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ contained the anticipated resonances relating to the coordinated ligands (Table 3.19). Furthermore the FT-IR spectra of $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ were found to contain characteristic terminal $v_{\mathrm{C}=\mathrm{O}}$ absorption bands between $1875-2014 \mathrm{~cm}^{-1}$ (Table 3.19) which are in agreement with values previously reported for cis-chromium tetracarbonyl complexes of diphosphines. ${ }^{248,249}$

Table 3.19 Selected ${ }^{31} \mathrm{P}\{1 \mathrm{H}\},{ }^{1} \mathrm{H}$ NMR ( $\delta$ in ppm) and FT-IR data $\left(\mathrm{cm}^{-1}\right)$ for 3.36 3.38 .

|  | $\delta(\mathrm{P})$ | $\delta(\mathrm{Fc})$ | $\delta\left(\mathrm{FcCH}_{2}\right)$ | $\delta\left(\mathrm{PCH}_{2}\right)$ | $v_{\mathrm{C}=\mathrm{O}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{3 . 3 6}$ | 38.9 | $4.10-4.05$ | 3.55 | 3.18 | $2014(\mathrm{~s}), 1921(\mathrm{~s}, \mathrm{~b})$, |
|  |  |  |  | - | $1875(\mathrm{~s}, \mathrm{~b})$ |
| $\mathbf{3 . 3 7}^{\mathrm{a}}$ | 37.2 | - | - | - | - |
| $\mathbf{3 . 3 8}$ | $31.7,29.9$ | $4.13-4.00$ | 3.48 | 3.68 | $2006(\mathrm{~s}), 1883(\mathrm{~s}, \mathrm{~b})$ |

${ }^{\text {a }} 26 \%$ purity by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR.

Further support for the preparation of $\mathbf{3 . 3 6} \mathbf{- 3 . 3 8}$ comes from positive ion FAB mass spectroscopy which gave the expected parent ion and fragmentation patterns \{MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 775,780$ and $835[\mathrm{M}]^{+}(\mathbf{3 . 3 6} \mathbf{- 3 . 3 8}$ respectively) \}. The element analysis for $\mathbf{3 . 3 6}$ also agreed with the proposed chemical formula $\mathrm{C}_{41} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{FeCrO}_{4}$. The molecular structures of $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ have also been determined by single crystal Xray diffraction (Section 3.16.1)

### 3.16.1 Molecular Structures of $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$

Orange crystalline blocks (3.36) and plates (3.38) suitable for X-ray crystallography were grown by layering of MeOH onto a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of the respective complexes. The molecular structure of $\mathbf{3 . 3 8}$ was determined routinely, whilst the crystal structure of $\mathbf{3 . 3 6}$ (Figure 3.25) was determined using multiple diffraction data files (SHELXL 97 .hklf5 format), ${ }^{250}$ after the crystal lattice was found to be pseudomerohedrally twinned [major component $57.33(6) \%$, twin law: $179.9^{\circ}$ rotation about the real axis 101 ]. Selected lengths and angles for $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ are given in Table 3.20 .


Figure 3.25 Molecular structure of 3.36. All hydrogen atoms and phenyl carbons, except ipso carbons, have been removed for clarity.

Figure 3.25 shows $\mathbf{3 . 3 6}$ as a typical example of this pair of chromium tetracarbonyl complexes. Both complexes adopt a distorted octahedral geometry with respect to the chromium centre, with $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ coordinating the metal via both phosphorus atoms to form a six-membered cis-chelate ring [bite angles; 91.15(2) and 89.04(2) ${ }^{\circ}$ respectively]. The phosphorus atoms were found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Cr}$ angles [ $\mathrm{C}-\mathrm{P}-\mathrm{Cr}$ ranged between $\left.92.81(8)-120.62(5)^{\circ}\right]$. The nitrogen atoms adopted a distorted pyramidal geometry [sum of component angles $=339^{\circ}(\mathbf{3 . 3 6})$ and $334^{\circ}(\mathbf{3 . 3 8})$ ]. In contrast the asymmetric units of $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ were found to differ, with two molecules of $\mathbf{3 . 3 6}$ and one molecule of $\mathbf{3 . 3 8}$ being present within the respective asymmetric units. The Fe (II) cyclopentadienyl rings within $\mathbf{3 . 3 8}$ were found to be two-fold disordered over two sets of equivalent positions, with only $\mathrm{C}(4)$ common between the two disorder components [occupancy refined to $60.4(6) \%$ for the major component]. The cyclopentadienyl rings of the ferrocenyl groups within $\mathbf{3 . 3 6}$ and $\mathbf{3 . 3 8}$ were found to be essentially co-planar, whilst the torsional twist between neighbouring rings was found to vary between 5.6 and $21.9^{\circ}$ for the major components.

Table 3.20 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{3 . 3 6}$ and 3.38.

|  | $3.36{ }^{\text {b }}$ | 3.38 |  | $3.36{ }^{\text {b }}$ | 3.38 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cr}(1)-\mathrm{P}(1)$ | 2.3484(8) | $2.3774(5)$ | $\mathrm{P}(1)-\mathrm{Cr}(1)-\mathrm{P}(2)$ | 89.04(2) | 91.153(15) |
| $\mathrm{Cr}(1)-\mathrm{P}(2)$ | $2.3629(8)$ | $2.3927(4)$ | $\mathrm{C}(\mathrm{A})-\mathrm{Cr}(1)-\mathrm{P}(1)$ | 177.05(9) | 176.43(6) |
| $\mathrm{Cr}(1)-\mathrm{C}(\mathrm{A})^{\mathrm{a}}$ | 1.849(3) | 1.8594(18) | $\mathrm{C}(\mathrm{B})-\mathrm{Cr}(1)-\mathrm{P}(1)$ | 92.31(8) | 1.54 (6) |
| $\mathrm{Cr}(1)-\mathrm{C}(\mathrm{B})^{\mathrm{a}}$ | 1.853(3) | $1.8557(17)$ | $\mathrm{C}(\mathrm{C})-\mathrm{Cr}(1)-\mathrm{P}(1)$ | 89.06(9) | 88.23(6) |
| $\mathrm{Cr}(1)-\mathrm{C}(\mathrm{C})^{\mathrm{a}}$ | 1.870(3) | $1.885(2)$ | $\mathrm{C}(\mathrm{D})-\mathrm{Cr}(1)-\mathrm{P}(1)$ | 89.26(8) | 94.36(6) |
| $\mathrm{Cr}(1)-\mathrm{C}(\mathrm{D})^{\mathrm{a}}$ | 1.908(3) | $1.8835(19)$ | $\mathrm{C}(\mathrm{A})-\mathrm{Cr}(1)-\mathrm{P}(2)$ | 88.30 (9) | 90.06(5) |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.848(2) | $1.8432(15)$ | $\mathrm{C}(\mathrm{B})-\mathrm{Cr}(1)-\mathrm{P}(2)$ | 175.12(9) | 6) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{E})^{\text {a }}$ | 1.831(3) | 1.8983(16) | $\mathrm{C}(\mathrm{C})-\mathrm{Cr}(1)-\mathrm{P}(2)$ | 93.76(8) | 90.31(6) |
| $\mathrm{P}(1)-\mathrm{C}(\mathrm{F})^{\text {a }}$ | 1.830(3) | 1.8905(17) | $\mathrm{C}(\mathrm{D})-\mathrm{Cr}(1)-\mathrm{P}(2)$ | 89.65(8) | 93.79(5) |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | 1.461(3) | $1.4705(19)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Cr}(1)$ | 116.82(9) | 114.64(5) |
| $\mathrm{N}(1)-\mathrm{C}(2)$ | $1.455(3)$ | $1.4645(19)$ | $\mathrm{C}(\mathrm{E})-\mathrm{P}(1)-\mathrm{Cr}(1)$ | 119.16(9) | 102.59(7) |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | $1.486(3)$ | $1.4845(19)$ | $\mathrm{C}(\mathrm{F})-\mathrm{P}(1)-\mathrm{Cr}(1)$ | 115.12(8) | 92.81(8) |
| $\mathrm{P}(2)-\mathrm{C}(2)$ | 1.855(2) | $1.8464(15)$ | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{P}(1)$ | 113.83(16) | 111.17(10) |
| $\mathrm{P}(2)-\mathrm{C}(\mathrm{G})^{\text {a }}$ | 1.824(3) | $1.8860(16)$ | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(2)$ | 113.71(19) | 13.10(12) |
| $\mathrm{P}(2)-\mathrm{C}(\mathrm{H})^{\mathrm{a}}$ | 1.833(3) | $1.8955(16)$ | $\mathrm{C}(2)-\mathrm{N}(1)-\mathrm{C}(3)$ | 113.5(2) | 110.71(12) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {ce }}$ | 1.6382(12) | 1.632(3) | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{C}(3)$ | 112.04(19) | 110.56 (11) |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | 1.6461(13) | $1.630(3)$ | $\mathrm{N}(1)-\mathrm{C}(2)-\mathrm{P}(2)$ | 113.46(17) | $113.09(10)$ |
|  |  |  | $\mathrm{C}(2)-\mathrm{P}(2)-\mathrm{Cr}(1)$ | 119.58(9) | $117.65(5)$ |
|  |  |  | $\mathrm{C}(\mathrm{G})-\mathrm{P}(2)-\mathrm{Cr}(1)$ | 110.56(9) | 120.62(5) |
|  |  |  | $\mathrm{C}(\mathrm{H})-\mathrm{P}(2)-\mathrm{Cr}(1)$ | 118.55(8) | 117.19(5) |
|  |  |  | $\mathrm{C}(\mathrm{E})-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(\mathrm{F})$ | 5.6 | 21.9 |

${ }^{\mathrm{a}} \mathrm{A}=38$ (3.36), 34 (3.38); $\mathrm{B}=39$ (3.36), 35 (3.38); $\mathrm{C}=40$ (3.36), 36 (3.38); $\mathrm{D}=41$ (3.36), 37 (3.38); $\mathrm{E}=14$ (3.36), 17 (3.38); $\mathrm{F}=20$ (3.36), 22 (3.38); $\mathrm{G}=26$ (3.36), 25 (3.38); $\mathrm{H}=32$ (3.36), 30 (3.38).
${ }^{\mathrm{b}}$ Bond lengths and angles given for only one of the molecules of $\mathbf{3 . 3 6}$ within the asymmetric unit. The remaining molecule of $\mathbf{3 . 3 6}$ adopts a very similar conformation and geometry. $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(4)$ to $\mathrm{C}(8), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(9)$ to $\mathrm{C}(13)$ ( $\mathbf{3 . 3 6}$ and 3.38).

### 3.17 Gold(I) Coordination Chemistry of 3.27

The metalloligand 3.27 was also reacted with two equiv. of $\mathrm{AuCl}(\mathrm{tht})$, in dichloromethane at ambient temperature, to afford the trimetallic complex $\mathbf{3 . 3 9}$ in good yield (68\%) (Equation 3.17).


Equation 3.17

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 9}$ exhibited a new phosphorus singlet at $\delta(\mathrm{P}) 16.7 \mathrm{ppm}$, some $c a . \delta(\mathrm{P}) 45 \mathrm{ppm}$ downfield from that of 3.27. The characteristic $\delta(\mathrm{P})$, and occurrence of a singlet resonance, within the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum implies that $\mathbf{3 . 2 7}$ bridges two distinct gold chloride centres via both phosphorus atoms. ${ }^{23}$ The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 3 9}$ revealed mostly broad resonances that appeared in the anticipated regions of the NMR spectrum, by comparison to 3.27 and previously discussed coordination complexes. A variable temperature (VT) ${ }^{1} \mathrm{H}$ NMR experiment (in $\mathrm{CDCl}_{3}$ ) was conducted over the temperature range +50 to $-50^{\circ} \mathrm{C}$ (range limited by solvent boiling and melting points), in an attempt to resolve these broad resonances. Unfortunately the temperature range was not sufficient enough to display the various ${ }^{1} \mathrm{H}$ environments within 3.39 as either an assembled average or as distinct signals (Figure 3.26). However, a simple comparison between the ${ }^{1} \mathrm{H}$ NMR data of 3.29 at $+50^{\circ} \mathrm{C}$ and that of the analogous coordination compounds (3.30, 3.33 and 3.36) was made, and allowed the cautious assignment of the spectrum as follows; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, at $\left.+50^{\circ} \mathrm{C}\right): \delta 4.22\left(\mathrm{bs}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right), 4.18\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$ and $3.78\left(\mathrm{~s}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right)$.


Figure 3.26 Variable temperature ${ }^{1} \mathrm{H}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) for $\mathbf{3 . 3 9}$, recorded in the range +50 to $-50^{\circ} \mathrm{C}$ (range limited by solvent boiling and melting points) and displayed in the region of $\delta(\mathrm{H}) 3.2-4.9 \mathrm{ppm}$.

Further support for the preparation of $\mathbf{3 . 3 9}$ was provided by positive ion FAB mass spectroscopy which revealed the expected parent ion and fragmentation pattern \{MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1076[\mathrm{M}]^{+}, 1075[\mathrm{M}-\mathrm{H}]^{+}, 1040\left[\mathrm{M}-\mathrm{Cl}^{+}\right\}$. Moreover the elemental analysis results for $\mathbf{3 . 3 9}$ agreed with the chemical formula $\mathbf{3 . 3 9} \cdot 0.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

### 3.18 Unsymmetrical Ditertiary Phosphines

Nonsymmetric ditertiary phosphines have seldom been investigated in comparison to their symmetric counterparts, possibly reflecting the need to perform multistep syntheses. ${ }^{9,58,251-254}$ Our group has recently reported the preparation of two unsymmetrical ditertiary phosphines of the type $\mathrm{RPCH}_{2} \mathrm{~N}(\mathrm{X}) \mathrm{CH}_{2} \mathrm{PR}^{\prime}$ [where $\mathrm{PR}=$ $\mathrm{PPh}_{2}, \mathrm{PR}^{\prime}=\mathrm{PAd}$ and $\mathrm{X}=\mathrm{C}_{6} \mathrm{H}_{5}(\mathbf{3 A})$ or $\left.\mathrm{C}_{6} \mathrm{H}_{5}\left(4-\mathrm{CH}_{3}\right)(\mathbf{3 B})\right]$ (Scheme 3.2). These unsymmetric ligands allow for the preparation of novel heterobimetallic coordination compounds of $\mathrm{Ru} / \mathrm{Au}$ and $\mathrm{Ir} / \mathrm{Au} .{ }^{58}$ These unsymmetrical phosphines were prepared via a simple two-step condensation methodology which exploited the preferential
precipitation of the monophosphine during pathway B (Scheme 3.2). The same elegant procedure was therefore utilised during the attempted preparation of $\mathrm{Ph}_{2} \mathrm{PCH}_{2}\left(\mathrm{CH}_{2} \mathrm{Fc}\right) \mathrm{CH}_{2} \mathrm{PAd}$, as part of our ongoing studies into the preparation of unsymmetrical ditertiary phosphines.


Scheme 3.2 Two-step condensation procedure utilised to prepare the unsymmetrical ditertiary phosphines 3A, 3B.

The slow addition (via cannula) of an equimolar methanolic solution of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, to a methanolic solution of $\mathrm{FcCH}_{2} \mathrm{NH}_{2}$ was monitored via in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. Following 1 h of stirring at ambient temperature, the in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum revealed two new phosphorus singlets, compared with that of the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material $[\delta(\mathrm{P})-20.9 \mathrm{ppm}, 21 \%$ and $-27.6 \mathrm{ppm}, 16 \%$ by NMR integration]. The singlet at $\delta(\mathrm{P})-27.6 \mathrm{ppm}$ was assigned to the previously discussed diphosphine $3.27[\delta(\mathrm{P})-28.1 \mathrm{ppm}(3.27), \Delta \delta(\mathrm{P}) 0.5 \mathrm{ppm}]$, whilst the other resonance was assigned to the desired monophosphine by comparison with analogous monophosphine examples. ${ }^{22,61,255}$ Further monitoring of the reaction solution via insitu ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, following a further 4 h of stirring at RT, revealed the ditertiary phosphine resonance to significantly increase relative to that of the monophosphine and starting material signals $[\delta(\mathrm{P})-20.9 \mathrm{ppm}, 17 \%$ and -27.6 ppm , $78 \%$ by NMR integration], suggesting that pathway A is significantly favoured (Scheme 3.2, Equation 3.18).

3.27

Equation 3.18
Indeed, additional stirring of the reaction solution at ambient temperature afforded an orange precipitate after 24 h , which was isolated and confirmed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy to be 3.27. Further analysis of the resulting filtrate via ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy revealed a mixture of mono and bis phosphines [ca. 1:1 by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR]. As a consequence the preparation of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{Fc}\right) \mathrm{CH}_{2} \mathrm{PAd}$ via the synthetic route described in Scheme 3.2 was not pursued further, as the monophosphine intermediate could not be cleanly isolated.

A new synthetic strategy for the preparation of unsymmetrical ditertiary phosphines of the form $\mathrm{RPCH}_{2} \mathrm{XCH}_{2} \mathrm{PR}^{\prime}$ was therefore required for primary amines, whose "intermediate" monophosphine analogues could not be readily isolated. One synthetic strategy to achieve this goal would be to chemically prevent further condensation of the desired monophosphine following the initial condensation reaction. This could potentially be achieved by using a protecting group, such as tert-butyloxycarbonyl (BOC). Once the initial condensation had taken place, the protecting group could be removed to give the desired monophosphine, which in turn could by reacted with a phosphine synthon of choice (Scheme 3.3).

The new protected ferrocenyl amine, 3.40, was therefore prepared, in excellent yield ( $93 \%$ ), by reaction of $\mathrm{FcCH}_{2} \mathrm{NH}_{2}$ with di-tert-butyldicarbonate (diBOC). The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4 0}$ displayed the anticipated tert-butyl $[\delta(\mathrm{H}) 1.39$ $\mathrm{ppm}]$ and cyclopentadienyl $[\delta(\mathrm{H}) 4.07-4.11 \mathrm{ppm}]$ hydrogen atoms by comparison with the ${ }^{1} \mathrm{H}$ NMR spectrum of the parent amine. ${ }^{247}$ The $\mathrm{CH}_{2}$ protons resonated as a doublet at $\delta(\mathrm{H}) 3.93 \mathrm{ppm}$, presumably due to a three bond coupling to the neighbouring secondary amine proton [ ${ }^{3} J_{\mathrm{HH}} 4.8 \mathrm{~Hz}$ ]. The secondary nature of the nitrogen atom was further suggested by the characteristic integral of the broad amine singlet at $\delta(\mathrm{NH}) 4.62 \mathrm{ppm}\left[\mathrm{NH}: \mathrm{CH}_{2}: \mathrm{C}_{5} \mathrm{H}_{4} ; 1: 2: 4\right]$.




3.41


Scheme 3.3 Potential new route to an unsymmetrical phosphine.

Further supporting evidence for the preparation of $\mathbf{3 . 4 0}$ comes from positive ion FAB mass spectroscopy, which gave the expected parent ion and fragmentation pattern $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 241[\mathrm{M}]^{+}, 240[\mathrm{M}-\mathrm{H}]^{+}, 242[\mathrm{M}+\mathrm{H}]^{+}\right\}$, in addition to elemental analysis which agreed with the proposed empirical formula $\left(\mathrm{C}_{16} \mathrm{H}_{21} \mathrm{O}_{2} \mathrm{NFe}\right)$. The FTIR spectrum of 3.40 contained characteristic $v_{\mathrm{C} \equiv \mathrm{O}}$ and $v_{\mathrm{NH}}$ absorption bands at $v_{\mathrm{C} \equiv 0}$ 1686, $v_{\mathrm{NH}} 3325$ and $1528 \mathrm{~cm}^{-1} .{ }^{194}$ The molecular structure of $\mathbf{3 . 4 0}$ has also been determined by single crystal X-ray diffraction (Section 3.18.1).

The electrochemical properties of $\mathbf{3 . 4 0}$ have also been briefly investigated by cyclic voltammetry. The voltammogram of $\mathbf{3 . 4 0}$ displayed a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple, similar to that of ferrocene, at $\mathrm{E}_{1 / 2}+0.010 \mathrm{~V}$ (value relative to the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple). This suggests that the ferrocenyl group within $\mathbf{3 . 4 0}$ is relatively unaffected by the increased functionality, as previously observed in the voltammograms of the symmetrical ditertiary phosphines $3.27-3.29$.

The reaction of 3.40 with an equimolar amount of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ in MeOH was monitored via in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy. The in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR
spectrum, of the reaction solution following a 3 d RT stir, showed no change compared to that of the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. Further monitoring of the reaction solution via in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy after a further 3 d reflux, revealed very little change, with a new singlet that accounted for just $1 \%$ of the total ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei being observed at $\delta(\mathrm{P})-21.4 \mathrm{ppm}$. The singlet was tentatively assigned to $\mathbf{3 . 4 1}$, by comparison with similar monophosphines. ${ }^{22,61,255}$ The minor nature of this resonance, after the 3 d reflux, suggests that the desired Mannich-based condensation reaction is unfavoured presumably due to steric and/or electronic effects relating to the protecting group. As a result the preparation of an unsymmetrical ditertiary phosphine via Scheme 3.3 was also not possible.

### 3.18.1 Molecular Structure of $\mathbf{3 . 4 0}$

Orange crystalline plates suitable for X-ray crystallography were grown by slow evaporation of a MeOH solution of $\mathbf{3 . 4 0}$. The molecular structure of $\mathbf{3 . 4 0}$ was determined (Figure 3.27); selected lengths and angles are given in Table 3.21.


Figure 3.27 Molecular structure of 3.40. All hydrogen atoms, except $\mathrm{H}(1)$, have been omitted for clarity.

The molecular structure of $\mathbf{3 . 4 0}$ shows the protected amine to have crystallised with one molecule of $\mathbf{3 . 4 0}$ within the asymmetric unit. The carbonyl carbon, $\mathrm{C}(12)$ was found to adopt a trigonal planar geometry, as anticipated [sum of component angles $359^{\circ}$. The double bond character of the tert-butyl ester was evident by comparison of the $\mathrm{C}-\mathrm{O}$ bond lengths $[\mathrm{C}-\mathrm{O}>\mathrm{C}=\mathrm{O} ; \mathrm{C}(12)-\mathrm{O}(2) 1.3544(18), \mathrm{C}(12)-\mathrm{O}(1)$ 1.2196(17)]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were essentially eclipsed and coplanar [torsional twist about the $\mathrm{C}(2)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }} \mathrm{C}(8)$ is $7.2^{\circ}$ ].

Analysis of the intermolecular packing revealed a single intermolecular hydrogen bond between neighbouring molecules of $\mathbf{3 . 4 0}\left[\mathrm{N}\left(1 \mathrm{~A}^{\prime}\right)-\mathrm{H}\left(1 \mathrm{~A}^{\prime}\right) \cdots \mathrm{O}(1), \mathrm{N}\left(1 \mathrm{~A}^{\prime}\right) \cdots \mathrm{O}(1)\right.$ $2.8486(17) ~ \AA, ~ H\left(1 \mathrm{~A}^{\prime}\right) \cdots \mathrm{O}(1) \quad 2.090(19) ~ \AA, \quad \mathrm{~N}\left(1 \mathrm{~A}^{\prime}\right)-\mathrm{H}\left(1 \mathrm{~A}^{\prime}\right) \cdots \mathrm{O}(1) \quad 158.3(18)^{\circ}$, symmetry operation ' $=x,-y+3 / 2, z-1 / 2]$, which allowed the formation of 1 D molecular chains along the $c$-axis (Figure 3.28).


Figure 3.28 Intermolecular hydrogen bonding between neighbouring molecules of 3.40. All hydrogen atoms, except those involved in the hydrogen bonding, have been removed for clarity. Symmetry operator for equivalent atoms ' $=x,-y+3 / 2, z-1 / 2$.

Table 3.21 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.40.

| $\mathrm{C}(1)-\mathrm{C}(11)$ | $1.496(2)$ | $\mathrm{N}(1)-\mathrm{C}(11)-\mathrm{C}(1)$ | $112.33(13)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{N}(1)-\mathrm{C}(11)$ | $1.4546(19)$ | $\mathrm{C}(11)-\mathrm{N}(1)-\mathrm{C}(12)$ | $121.45(13)$ |
| $\mathrm{N}(1)-\mathrm{C}(12)$ | $1.3350(19)$ | $\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{N}(1)$ | $125.20(14)$ |
| $\mathrm{O}(1)-\mathrm{C}(12)$ | $1.2196(17)$ | $\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{O}(2)$ | $124.27(14)$ |
| $\mathrm{O}(2)-\mathrm{C}(12)$ | $1.3544(18)$ | $\mathrm{O}(2)-\mathrm{C}(12)-\mathrm{N}(1)$ | $110.52(12)$ |
| $\mathrm{O}(2)-\mathrm{C}(13)$ | $1.4681(19)$ | $\mathrm{C}(12)-\mathrm{O}(2)-\mathrm{C}(13)$ | $119.41(11)$ |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {cent }}$ | $1.6445(7)$ | $\mathrm{C}(1)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(1)$ | 3.5 |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | $1.6481(8)$ |  |  |
| $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(1)$ to $\mathrm{C}(5), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(6)$ to $\mathrm{C}(10)$. |  |  |  |

### 3.19 Preparation and Characterisation of 3.42

The development of new phosphinoamines of the form $\left(\mathrm{R}_{2} \mathrm{P}\right)_{2} \mathrm{~N}(\mathrm{R})$ continues to attract much attention, as such phosphines have shown diverse catalytic and coordination properties. ${ }^{15,238,256,257}$ As part of ongoing studies into the diversity of $\mathrm{P}-$ $\mathrm{N}(\mathrm{R})-\mathrm{P}$ derivatives, the new ferrocenyl phosphine $\mathbf{3 . 4 2}$ has been prepared by the aminolysis of $\mathrm{FcCH}_{2} \mathrm{NH}_{2}$ with the commercially available chlorophosphine $\mathrm{ClPPh}_{2}$ (Equation 3.19).

i) $\mathrm{NEt}_{3}$
ii) $2 \mathrm{ClPPh}_{2}$
THF

3.42

Equation 3.19

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4 2}$ exhibited a new phosphorus singlet at $\delta(\mathrm{P}) 59.4 \mathrm{ppm}, c a .23 \mathrm{ppm}$ upfield to that of the $\mathrm{ClPPh}_{2}$ starting material $[\delta(\mathrm{P})$ 81.9 ppm, in $\mathrm{CDCl}_{3}$ ]. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4 2}$ showed the characteristic cyclopentadienyl and $\mathrm{CH}_{2}$ protons to resonate between $\delta(\mathrm{H}) 3.33-$ 4.18 ppm , as anticipated by comparison with $\mathrm{FcCH}_{2} \mathrm{NH}_{2} .{ }^{247}$ The cyclopentadienyl hydrogen atoms $[\delta(\mathrm{H}) 3.33-3.85 \mathrm{ppm}]$ resonated some $c a . \delta(\mathrm{H}) 0.5 \mathrm{ppm}$ upfield to those within the parent amine, whilst the $\mathrm{CH}_{2}$ protons resonated as a broad triplet $\left[\delta\left(\mathrm{CH}_{2}\right) 4.18 \mathrm{ppm},{ }^{3} J_{\mathrm{PH}} 20.4 \mathrm{~Hz}\right] c a . \delta(\mathrm{H}) 0.7 \mathrm{ppm}$ downfield of their parent amine counterparts. The ternary nature of the nitrogen atom was further confirmed by the absence of a $v_{\mathrm{NH}}$ absorption band in the infrared spectrum, in addition to the lack of a $\delta(\mathrm{NH})$ signal in the ${ }^{1} \mathrm{H}$ NMR spectrum of $3.42\left[\delta(\mathrm{NH}) 1.42, \mathrm{FcCH}_{2} \mathrm{NH} \mathrm{H}_{2}\right]$. Moreover the positive ion FAB mass spectrum of $\mathbf{3 . 4 2}$ was found to contain the expected parent ion and fragmentation patterns $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 584[\mathrm{M}]^{+}, 384\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right]^{+}\right\}$, whilst elemental analysis results agreed with the formula $\mathbf{3 . 4 2} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$. The molecular structure of $\mathbf{3 . 4 2}$ has also been determined (Section 3.19.1).

The electrochemical properties of the new phosphinoamine have also been briefly investigated by cyclic voltammetry. The voltammogram of $\mathbf{3 . 4 2}$ contained a
reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple similar to that of ferrocene, at $\mathrm{E}_{1 / 2}+0.099 \mathrm{~V}$, in addition to a further oxidation peak at $\mathrm{E}_{\mathrm{pa}}-0.054 \mathrm{~V}$ (values relative to the $\mathrm{Fc} / \mathrm{Fc}^{+}$ couple) (Figure 3.29). This additional oxidation potential was tentatively assigned to the irreversible oxidation of both phosphorus atoms within 3.42, due to the lack of a corresponding reduction potential and similar $\mathrm{E}_{\mathrm{pa}}$ to other suggested $-\mathrm{PPh}_{2}$ oxidations discussed herein $\left[\mathrm{E}_{\mathrm{pa}} 0.006 \mathrm{~V}\right.$ (3.14)]. The observed anodic shift (ca. 100 mV ) of the ferrocene/ferrocenium redox couple, relative to that of ferrocene, shows that the electrochemical properties of the $\mathrm{Fe}(\mathrm{II}) / \mathrm{Fe}(\mathrm{III})$ centre are significantly affected by the close proximately of the PNP coordination site, with the couple requiring higher potentials to become redox active.


Figure 3.29 Cyclic voltammogram of $\mathbf{3 . 4 2}$ in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

### 3.19.1 Molecular Structure of $\mathbf{3 . 4 2}$

Yellow crystalline laths suitable for X-ray crystallography were grown by the slow evaporation of a MeOH filtrate of $\mathbf{3 . 4 2}$. The molecular structure was determined using synchrotron radiation, due to the size of the crystals (at least one dimension $<$ 0.05 mm ) and their poorly diffracting nature (Figure 3.30). Selected lengths and angles are given in Table 3.22.


Figure 3.30 Molecular structure of 3.42. All hydrogen atoms have been removed for clarity.

The molecular structure of $\mathbf{3 . 4 2}$ shows the asymmetric unit to contain one molecule of 3.42. The phosphorus atoms were found to adopt a distorted pyramidal geometry, as indicated by the relevant N-P-C angles [N-P-C ranged between 101.2(2) $\left.105.2(2)^{\circ}\right]$. The nitrogen atom, $\mathrm{N}(1)$, was found to adopt a near regular trigonal planar geometry [sum of component angles $359^{\circ}$ ]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were essentially eclipsed and coplanar (torsional twist about the $\mathrm{C}(2)-\mathrm{CpA}_{\text {cent }}{ }^{-}$ $\mathrm{CpB}_{\text {cent }}-\mathrm{C}(8)$ is $\left.7.2^{\circ}\right)$.

Table 3.22 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.42.

| $\mathrm{P}(1)-\mathrm{N}(1)$ | $1.698(4)$ | $\mathrm{P}(1)-\mathrm{N}(1)-\mathrm{P}(2)$ | $122.4(2)$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(12)$ | $1.839(5)$ | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{P}(1)$ | $122.2(3)$ |  |  |
| $\mathrm{P}(1)-\mathrm{C}(18)$ | $1.817(5)$ | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{P}(2)$ | $114.6(3)$ |  |  |
| $\mathrm{P}(2)-\mathrm{N}(1)$ | $1.707(4)$ | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{N}(1)$ | $114.8(4)$ |  |  |
| $\mathrm{P}(2)-\mathrm{C}(24)$ | $1.836(5)$ | $\mathrm{N}(1)-\mathrm{P}(1)-\mathrm{C}(12)$ | $103.1(2)$ |  |  |
| $\mathrm{P}(2)-\mathrm{C}(30)$ | $1.833(5)$ | $\mathrm{N}(1)-\mathrm{P}(1)-\mathrm{C}(18)$ | $105.2(2)$ |  |  |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.490(6)$ | $\mathrm{C}(12)-\mathrm{P}(1)-\mathrm{C}(18)$ | $101.2(2)$ |  |  |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA}_{\text {cent }}$ | $1.648(2)$ | $\mathrm{N}(1)-\mathrm{P}(2)-\mathrm{C}(24)$ | $104.4(2)$ |  |  |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}_{\text {cent }}$ | $1.654(2)$ | $\mathrm{N}(1)-\mathrm{P}(2)-\mathrm{C}(30)$ | $103.4(2)$ |  |  |
|  | $\mathrm{C}(24)-\mathrm{P}(2)-\mathrm{C}(30)$ |  |  |  | $104.9(2)$ |
|  | $(2)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}$ |  |  |  |  |
| cent | $\mathrm{C}(8)$ | 7.2 |  |  |  |
| $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(2)$ to $\mathrm{C}(6), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(7)$ to $\mathrm{C}(11)$. |  |  |  |  |  |

### 3.20 Platinum(II) Coordination Chemistry of 3.42

The coordination chemistry of $\mathbf{3 . 4 2}$ was briefly investigated by reaction with an equimolar amount of $\mathrm{PtCl}_{2}(\mathrm{cod})$, to afford the four-coordinate platinum(II) dichloride complex 3.43 in good yield (75\%) (Equation 3.20).


Equation 3.20

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) of $\mathbf{3 . 4 3}$ showed a new phosphorus singlet at $\delta(\mathrm{P}) 17.8 \mathrm{ppm}$, some $c a . \delta(\mathrm{P}) 42 \mathrm{ppm}$ downfield from that of $\mathbf{3 . 4 2}[\delta(\mathrm{P}) 59.4 \mathrm{ppm}$, in $\mathrm{CDCl}_{3}$ ]. The new phosphorus resonance was flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites [ ${ }^{1} J_{\mathrm{PtP}} 3290 \mathrm{~Hz}$ ]. The characteristically large ${ }^{1} J_{\mathrm{PtP}}$ coupling constant suggests that $\mathbf{3 . 4 3}$ adopts a cis conformation in solution, similar to that of the analogous $\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PR}\right)_{2}$ platinum(II) dichloride complexes 3.30-3.32 $\left({ }^{1} J_{\mathrm{PtP}} 3377-3473\right.$ Hz ). ${ }^{58,93}$ Further comparison of the ${ }^{1} J_{\mathrm{PtP}}$ coupling constant to those reported for similar platinum(II) dichloride complexes also supported a cis conformation (ca. ${ }^{1} J_{\text {PtP }}$

3300 Hz ). ${ }^{15,238}$ The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) of $\mathbf{3 . 4 3}$ showed the anticipated ferrocenyl resonances of the coordinated ligand $[\delta(\mathrm{H}) 3.33-3.84 \mathrm{ppm}]$ whilst the $\mathrm{CH}_{2}$ hydrogen atoms, which resonated as a triplet in $3.42\left[\delta\left(\mathrm{CH}_{2}\right) 4.18 \mathrm{ppm},{ }^{3} J_{\mathrm{PH}}\right.$ 20.4 Hz , appear as a broad singlet some $\Delta \delta(\mathrm{H}) 0.4 \mathrm{ppm}$ upfield upon coordination [ $\left.\delta\left(\mathrm{CH}_{2}\right) 3.80 \mathrm{ppm}\right]$. Furthermore the positive ion FAB mass spectrum of $\mathbf{3 . 4 3}$ gave
 $\left.814[\mathrm{M}-\mathrm{Cl}]^{+}\right\}$, whilst elemental analysis for $\mathbf{3 . 4 3}$ agreed with the formula 3.43 $\cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$. The FT-IR spectrum of $\mathbf{3 . 4 3}$ also contained two characteristic $\nu_{\mathrm{PtCl}}$ absorptions bands, at $v_{\text {PtCl }} 310$ and $290 \mathrm{~cm}^{-1}$, similar to those observed for other phosphinoamine platinum dichloride complexes. ${ }^{238}$ The molecular structure of $\mathbf{3 . 4 3}$ has also been determined via single crystal X-ray diffraction (Section 3.20.1).

The electrochemical properties of $\mathbf{3 . 4 3}$ have also been briefly investigated by cyclic voltammetry. The voltammogram of $\mathbf{3 . 4 3}$ contained a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple similar to that of $\mathbf{3 . 4 2}$, at $\mathrm{E}_{1 / 2}+0.107 \mathrm{~V}\left(\Delta \mathrm{E}_{1 / 2} 0.009 \mathrm{~V}\right.$, relative to the $\mathrm{Fc} / \mathrm{Fc}^{+}$couple) (Figure 3.31).


Figure 3.31 Cyclic voltammogram of $\mathbf{3 . 4 3}$ in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 0.1 \mathrm{M}\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right]$ at a scan rate of $50 \mathrm{mVs}^{-1}$.

The similarity between the $\mathrm{Fc} / \mathrm{Fc}^{+}$redox waves of $\mathbf{3 . 4 2}$ and $\mathbf{3 . 4 3}$ suggests that whilst the electrochemical properties of the ferrocene moiety are affected by the close
proximately of the PNP coordination site, by comparison with ferrocene, the redox couple is relatively unaffected by platinum(II) coordination at the same site. Furthermore the absence of the oxidation potential ( $\mathrm{E}_{\mathrm{pa}}-0.054 \mathrm{~V}$ ), previously observed in the voltammogram of $\mathbf{3 . 4 2}$, adds further support to the correct assignment of the potentials as the irreversible oxidation of the phosphorus(III) centres.

### 3.20.1 Molecular Structure of $\mathbf{3 . 4 3}$

Orange crystalline plates, suitable for X-ray crystallography, were grown by the slow evaporation of a $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO} / \mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution of 3.43. The molecular structure of 3.43 was determined using multiple diffraction data files (SHELXL 97 .hklf5 format) ${ }^{250}$ collected by the EPSRC National Crystallography Service, after the crystal lattice was found to be merohedrally twinned [major component $86.054(30) \%$, twin law; $180^{\circ}$ about the reciprocal axis $10.001-0.83$ ] (Figure 3.32). Selected lengths and angles are given in Table 3.23.


Figure 3.32 Molecular structure of 3.43. All hydrogen atoms have been removed for clarity.

The molecular structure of $\mathbf{3 . 4 3}$ showed the complex to adopt a distorted square planar geometry with respect to the platinum(II) centre (Table 3.23), with $\mathbf{3 . 4 2}$ coordinating the metal via both phosphorus atoms to form a strained four-membered cis-chelate ring [bite angle; 72.15(4) ${ }^{\circ}$ ]. The strained nature of the PNPPt ring is evident by comparison with the bite angle of the analogous six-membered cischelate complexes $\mathbf{3 . 3 0} \mathbf{- 3 . 3 2}$ [ca. $23^{\circ}$ difference in bite angle $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ 95.44(3) (3.30), 95.593(17) (3.31) and 94.86(3) (3.32)]. The phosphorus atoms were found to adopt a distorted pyramidal geometry, as indicated by the relevant $\mathrm{Pt}-\mathrm{P}-$ $\mathrm{C} / \mathrm{N}$ angles $[\mathrm{Pt}-\mathrm{P}-\mathrm{C} / \mathrm{N}$ angles ranged between 93.84(12) - 112.96(17)], whilst the nitrogen atom $\mathrm{N}(1)$ was found to adopt a near perfect trigonal planar geometry [sum of component angles $359^{\circ}$ ]. The $\mathrm{Fe}(\mathrm{II})$ cyclopentadienyl rings were eclipsed and essentially coplanar [torsional twist about the $\mathrm{C}(2)-\mathrm{CpA}_{\text {cent }}-\mathrm{CpB}_{\text {cent }}-\mathrm{C}(8)$ is $0.2^{\circ}$ ], as was previously observed in $\mathbf{3 . 4 2}$.

Table 3.23 Selected lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.43.

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.2042(9)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $72.15(4)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.2088(10)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $91.66(4)$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.3503(10)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $98.45(4)$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.3599(10)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $97.73(4)$ |
| $\mathrm{P}(1)-\mathrm{N}(1)$ | $1.696(3)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $169.68(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(12)$ | $1.806(4)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $170.60(4)$ |
| $\mathrm{P}(1)-\mathrm{C}(18)$ | $1.807(4)$ | $\mathrm{N}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $94.10(11)$ |
| $\mathrm{P}(2)-\mathrm{N}(1)$ | $1.699(3)$ | $\mathrm{N}(1)-\mathrm{P}(1)-\mathrm{C}(12)$ | $109.44(17)$ |
| $\mathrm{P}(2)-\mathrm{C}(24)$ | $1.803(4)$ | $\mathrm{N}(1)-\mathrm{P}(1)-\mathrm{C}(18)$ | $110.45(17)$ |
| $\mathrm{P}(2)-\mathrm{C}(30)$ | $1.796(4)$ | $\mathrm{C}(12)-\mathrm{P}(1)-\mathrm{C}(18)$ | $103.92(17)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.498(6)$ | $\mathrm{N}(1)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | $93.84(12)$ |
| $\mathrm{Fe}(1) \cdots \mathrm{CpA} \mathrm{Cent}_{\text {cent }}$ | $1.644(2)$ | $\mathrm{N}(1)-\mathrm{P}(2)-\mathrm{C}(24)$ | $112.96(17)$ |
| $\mathrm{Fe}(1) \cdots \mathrm{CpB}$ cent | $1.642(2)$ | $\mathrm{N}(1)-\mathrm{P}(2)-\mathrm{C}(30)$ | $108.22(17)$ |
|  |  | $\mathrm{C}(24)-\mathrm{P}(2)-\mathrm{C}(30)$ | $106.61(19)$ |
|  |  | $\mathrm{P}(1)-\mathrm{N}(1)-\mathrm{P}(2)$ | $99.88(17)$ |
|  |  | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{P}(1)$ | $127.1(3)$ |
|  |  | $\mathrm{C}(1)-\mathrm{N}(1)-\mathrm{P}(2)$ | $132.0(3)$ |
|  |  | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $112.5(3)$ |
| $\mathrm{CpA} \mathrm{c}_{\text {cent }}=\mathrm{C}(2)$ to $\mathrm{C}(6), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(7)$ to $\mathrm{C}(11)$. | 0.2 |  |  |

### 3.21 Preparation and Characterisation of 3.44.

Bidentate ligands that combine both hard and soft donor atoms have also seen considerable interest over the last few decades. Iminophosphines are a typical example of such compounds, where the phosphorus(III) atom acts as a soft donor whilst the nitrogen atom acts as a hard donor site. Ligands of this type are of interest as their known hemilability, where the coordination mode alternates between mono and bidentate, allows the formation of coordinate unsaturated metal centres which have potential catalytic application. ${ }^{258-262}$ As part of ongoing studies into the preparation of iminophosphines, ${ }^{186,263}$ the new ferrocenyl iminophosphine, 3.44, was prepared in good yield by the condensation of an equimolar amount of aminomethyl ferrocene with the known substituted tertiary phosphine $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO}$ (Equation 3.21). ${ }^{264}$


Equation 3.21
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid, recorded following a 4 h reflux of the above reagents in MeOH , revealed the presence of several phosphorus containing species between $\delta(\mathrm{P}) 1.1$ to -1.3 ppm . The major singlet at $\delta(\mathrm{P}) 1.1 \mathrm{ppm}$ was assigned to 3.44 and accounted for $76 \%$ of the total ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei, whilst the next most prominent singlet was assigned to the $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO}$ starting material $[\delta(\mathrm{P}) 0.0 \mathrm{ppm}, 13 \%$ by NMR integration] suggesting that the reaction was incomplete. ${ }^{264}$ Careful monitoring of subsequent repeat reactions, by in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, revealed that prolonged reflux ( $>4 \mathrm{~h}$ ) only served to reduced the purity of $\mathbf{3 . 4 4}$ further [after 24 h reflux, $\delta(\mathrm{P}) 0.7 \mathrm{ppm}$ (in $\mathrm{C}_{6} \mathrm{D}_{6}$ ), $67 \%$ by integration]. Nevertheless the purity of $\mathbf{3 . 4 4}$, by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, was deemed sufficient enough for the isolated material to be used directly in coordination studies. The iminophosphine also showed evidence of oxidation, by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, when $\mathrm{CDCl}_{3}$ solutions containing 3.44 were left to stand in air $[\delta(\mathrm{P}) c a .33 \mathrm{ppm}$, for the corresponding phosphine oxide].

The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated material revealed a new imine triplet at $\delta(H \mathrm{C}=\mathrm{N}) 7.36 \mathrm{ppm}\left[{ }^{3} J_{\mathrm{HH}} 4.4 \mathrm{~Hz}, 1 \mathrm{H}\right]$. This, coupled with a minor aldehyde resonance at $\delta(\mathrm{CHO}) 9.48 \mathrm{ppm}$ further supported the preparation of $\mathbf{3 . 4 4}$ and the assignment of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum. ${ }^{264}$ The cyclopentadienyl and $\mathrm{CH}_{2} \mathrm{Fc}$ hydrogron atoms within $\mathbf{3 . 4 4}$ appeared as broad resonances between $\delta(\mathrm{H}) 3.84-4.01$ ppm, whilst the remaining nonaromatic hydrogen atoms resonated as broad multiplets similar to those observed in the ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the parent aldehyde $\left[\delta(\mathrm{H}) 3.74(\mathrm{~m}, 1 \mathrm{H}, \mathrm{PCH}), \delta \mathrm{CH}_{2} 2.73\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{A} \mathrm{H}_{\mathrm{B}}\right), 2.57(\mathrm{~m}, 1 \mathrm{H}\right.$, $\left.\mathrm{CH}_{\mathrm{A}} H_{B}\right)$; mean $\Delta \delta(\mathrm{H}) c a .0 .2 \mathrm{ppm}$ relative to $\left.\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO}\right] .{ }^{264}$ Furthermore, the presence of a strong $v_{\mathrm{C}=\mathrm{N}}$ absorption band at $1667 \mathrm{~cm}^{-1}$, confirmed the unsaturated nature of the nitrogen atom within 3.44. The preparation of $\mathbf{3 . 4 4}$, and its susceptibility to aerobic oxidation, were further supported by positive ion FAB mass spectroscopy which revealed the predictable molecular fragments $\left\{\mathrm{MS}_{( }\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}\right.$ $531[\mathrm{M}+\mathrm{O}], 516[\mathrm{M}+\mathrm{H}]^{+}$and $\left.199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}\right\}$. The electrochemical properties of $\mathbf{3 . 4 4}$ were not investigated by cyclic voltammetry due to the low purity and the phosphines tendancy towards aerobic oxidation.

### 3.22 Platinum(II) Coordination Chemistry of 3.44

Treatment of $\mathbf{3 . 4 4}$ with an equimolar amount of $\mathrm{PtCl}_{2}(\mathrm{cod})$, at ambient temperature, gave 3.45 in excellent yield (95\%) (Equation 3.22).


Equation 3.22
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4 5}$ revealed a new phosphorus singlet flanked by equidistant platinum satellites at $\delta(\mathrm{P}) 12.3 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3745 \mathrm{~Hz}$, some $c a$. $\delta(\mathrm{P}) 11 \mathrm{ppm}$ downfield from that of $\mathbf{3 . 4 4}[\delta(\mathrm{P}) 1.1 \mathrm{ppm}(\mathbf{3 . 4 4})]$. The characteristically large ${ }^{1} J_{\mathrm{PtP}}$ coupling constant suggests that $\mathbf{3 . 4 5}$ adopted a cis conformation in $\mathrm{CDCl}_{3}$ solution, with the phosphorus and nitrogen atoms coordinating the metal centre. ${ }^{186}$

The occurrence of only one new phosphorus species also suggests that $\mathbf{3 . 4 5}$ forms a stable six membered $\mathrm{P}, \mathrm{N}$-chelate complex.

The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of $\mathbf{3 . 4 5}$ contained a broad $\delta(H \mathrm{C}=\mathrm{N}$ ) resonance at $\delta(\mathrm{H}) 8.37 \mathrm{ppm}, c a .1 \mathrm{ppm}$ downfield compared to the same hydrogen atom in 3.44, an effect presumably indicative of coordination. The PCH and diastereotopic $\mathrm{PhC}(\mathrm{H}) \mathrm{CH}_{A} H_{B}$ hydrogen atoms, previously observed in $\mathbf{3 . 4 4}$ and $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO},{ }^{264}$ were also marginally shifted upon coordination. In contrast to 3.44 , the $\mathrm{FcCH}_{2}$ hydrogen atoms within 3.45 were observed to be diastereotopic [ $\delta\left(\mathrm{CH}_{\mathrm{A}} H_{\mathrm{B}} \mathrm{Fc}\right) 5.77,4.94 \mathrm{ppm}$ and $\left.{ }^{2} J_{\mathrm{HH}} 13.2 \mathrm{~Hz}\right]$. Analysis by $2 \mathrm{D}{ }^{1} \mathrm{H}$ NMR (COSY) spectroscopy confirmed the diastereotopic nature of the $\mathrm{CH}_{\mathrm{A}} \mathrm{H}_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}$ hydrogen atoms (Figure 3.33, highlighted in red). Analysis by HMQC further supported this assignment, with both hydrogen environments $\left[\delta\left(\mathrm{CH}_{\mathrm{A}} H_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}\right)\right]$ coupling to the same methylene carbon atom [ $\delta\left(\mathrm{CH}_{2}\right) 65.3 \mathrm{ppm}$ ]. One tentative suggestion for this change to diastereotopic protons $\left(\mathrm{CH}_{2}\right)$ upon coordination, is that the conformation of $\mathbf{3 . 4 5}$ forces one of the methylene hydrogen environments $\left(\mathrm{H}_{\mathrm{A}}\right)$ to point directly towards the platinum centre $\left[\delta\left(\mathrm{CH}_{\mathrm{A}} \mathrm{H}_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}\right) 5.77 \mathrm{ppm}\right]$, whilst the other $\left(\mathrm{H}_{\mathrm{B}}\right)$ points away [ $\delta\left(\mathrm{CH}_{\mathrm{A}} H_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}\right) 4.94 \mathrm{ppm}$ ]; thereby allowing $\mathrm{H}_{\mathrm{A}}$ to be shielded from the applied field to a greater extent than $\mathrm{H}_{\mathrm{B}}$. Such an effect is in agreement with the observed difference in $\delta(\mathrm{H})$ between the two hydrogen environments [ $\left.\Delta \delta\left(\mathrm{CH}_{A} H_{B}\right) 0.83 \mathrm{ppm}\right]$. The 2D ${ }^{1} \mathrm{H}$ NMR (COSY) spectrum of $\mathbf{3 . 4 5}$ also revealed the hydrogen atoms of the imine and $\mathrm{PhC}(\mathrm{H}) \mathrm{CH}_{A} H_{B}$ to be weakly coupled, an effect which is not resolved by the broad signals in the $1 \mathrm{D}{ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 . 4 5}$ (Figure 3.33, highlighted in green).


Figure 3.33 2D ${ }^{1} \mathrm{H}$ NMR (COSY) spectrum of 3.45. Coupling between diastereotopic $\mathrm{CH}_{\mathrm{A}} H_{B} \mathrm{C}_{5} \mathrm{H}_{4}$ hydrogen atoms (highlighted in red) and coupling between $\mathrm{PhC}(\mathrm{H}) \mathrm{CH}_{A} H_{B}$ and $H \mathrm{C}=\mathrm{N}$ hydrogen atoms (highlighted in green).

Furthermore, the FT-IR spectrum of $\mathbf{3 . 4 5}$ was found to contain a characteristic $v_{\mathrm{C}=\mathrm{N}}$ absorption band at $1640 \mathrm{~cm}^{-1}$. The observation of characteristic $v_{\mathrm{PtCl}}$ absorptions bands within 3.45 was however not possible due to a lack of spectrometer with an appropriate scan range. The preparation of $\mathbf{3 . 4 5}$ was further confirmed by positive ion FAB mass spectroscopy, which gave the anticipated fragmentation pattern \{MS $\left.\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 746[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}\right\}$, and also by elemental analysis, which showed good agreement with the empirical formula $\mathrm{C}_{32} \mathrm{H}_{30} \mathrm{NPFePtCl}_{2}$. The electrochemical properties of $\mathbf{3 . 4 5}$ have also been briefly investigated by cyclic voltammetry. The voltammogram of $\mathbf{3 . 4 5}$ contained a reversible $\mathrm{Fc} / \mathrm{Fc}^{+}$redox couple at $\mathrm{E}_{1 / 2}+0.043 \mathrm{~V}$.

### 3.23 Ruthenium(II) and Gold(I) Coordination Chemistry of 3.44

Treatment of 3.44 with $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ ( 0.5 equiv.) and $\mathrm{AuCl}($ tht $)$ ( 1 equiv.) at ambient temperature, gave the bimetallic complexes 3.46 and 3.47 , in poor yield following recrystallisation from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with hexane (34 and $39 \%$ respectively) (Equation 3.23).


Equation 3.23 (i) $\mathrm{AuCl}($ tht $)$ (3.46) or $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ (3.47). Solvent: $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of the isolated solids, in both cases, revealed several ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR active nuclei. In the case of $\mathbf{3 . 4 6}$, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) revealed the presence of several phosphorus containing species between $\delta(\mathrm{P}) 29.2-46.4 \mathrm{ppm}$, two of which accounted for $71 \%$ of the total ${ }^{31} \mathrm{P}$ active nuclei [ $\delta(\mathrm{P}) 45.2$ and 44.8 ppm respectively, [ratio by NMR integral 4.5:1]. The singlet at $\delta(\mathrm{P}) 44.8 \mathrm{ppm}$ was assigned to $\mathbf{3 . 4 6}$, by comparison with other gold(I) chloride phosphine complexes, ${ }^{23}$ whilst the broader singlet at $\delta(\mathrm{P}) 45.2 \mathrm{ppm}$ was tentatively assigned to a combination of the two diastereomer isomers of three-coordinate $\mathrm{P}-\mathrm{N}$ chelate complex 3.46A (Figure 3.34).



Figure 3.34 Suggested two-coordinate (3.46) and three-coordinate (3.46A) gold complexes.

Treatment of 3.44 with $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$ ( 0.5 equiv.) also revealed several phosphorus containing species downfield of that of $\mathbf{3 . 4 4}$, between $\delta(\mathrm{P}) 21.0-34.0$ ppm by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ), three of which accounted for $91 \%$ of the total ${ }^{31} \mathrm{P}$ active nuclei [respective ratio by NMR integral $c a$. 4:3:1]. The singlets at $\delta(\mathrm{P}) 23.6$ and 23.1 ppm , were tentatively assigned to the two diastereomer isomers of the six-membered $\mathrm{P}-\mathrm{N}$ chelate complex 3.47A (Figure 3.35), by virtue of their similar chemical shift $[\Delta \delta(\mathrm{P}) 0.5 \mathrm{ppm}]$, whilst the remaining singlet at $\delta(\mathrm{P}) 21.0$ ppm, was assigned to the neutral complex $\mathbf{3 . 4 7}$ by comparison with other phosphorus containing ruthenium piano stool complexes. ${ }^{22,58}$ Careful monitoring of a $\mathrm{CDCl}_{3}$ solution of 3.47 and $\mathbf{3 . 4 7 A}$, over a period of four days, revealed the gradual decrease of the singlets between $\delta(\mathrm{P}) 21.0-34.0 \mathrm{ppm}$ and the emergence of further singlets significantly downfield [ $\delta(\mathrm{P}) c a .105$ and 59 ppm$]$, suggesting that one or all of the piano stool complexes are unstable in $\mathrm{CDCl}_{3}$ solution.


Figure 3.35 Suggested monodentate (3.47) and bidentate (3.47A) ruthenium(II) complexes of $\mathbf{3 . 4 4}$ observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR.

The hemilabile behaviour of 3.44, following treatment with $\mathrm{AuCl}($ tht $)$ and $[\mathrm{RuCl}(\mu-$ $\mathrm{Cl})(p$-cym $)]_{2}$, was also observed via ${ }^{1} \mathrm{H}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ), with a mixture of broad resonances observed, relating to the anticipated hydrogen atoms (see Experimental Section). Further support for the preparation of 3.46 and 3.47, comes from the FT-IR spectra which contained characteristic $\nu_{\mathrm{C}=\mathrm{N}}$ absorption bands at 1643 and $1636 \mathrm{~cm}^{-1}$ respectively. ${ }^{194}$ Moreover, the positive ion FAB mass spectra gave the anticipated parent ions and fragmentation patterns \{MS (FAB ${ }^{+}$): m/z 747 and $822[\mathrm{M}]^{+}, 712$ and $786[\mathrm{M}-\mathrm{Cl}]^{+}$( $\mathbf{3 . 4 6}$ and $\mathbf{3 . 4 7}$ respectively) $\}$. The elemental analysis results for $\mathbf{3 . 4 6}$ and $\mathbf{3 . 4 7}$ also showed good agreement with the chemical formulae $\mathbf{3 . 4 6 A u} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ and $\mathbf{3 . 4 7} \cdot 1.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$.

### 3.24 Preparation and Characterisation of 3.48

In addition to the novel ferrocenyl phosphine chemistry discussed previously, initial attempts have been made to prepare more "constrained" ferrocenyl phosphines in order to investigate their coordination chemistry and electrochemical properties. To this end the recently reported macrocyclic amine $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Fe}$, ${ }^{265}$ was reacted with two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ to afford 3.48 as an orange solid, in reasonable yield (73\%) (Equation 3.24).




Equation 3.24
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of the isolated solid exhibited a new phosphorus singlet at $\delta(\mathrm{P})-27.0 \mathrm{ppm}$, some $c a . \delta(\mathrm{P}) 17 \mathrm{ppm}$ upfield compared with that of the $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ starting material. The singlet accounted for $91 \%$ of the total active ${ }^{31} \mathrm{P}$ nuclei and was assigned to $\mathbf{3 . 4 8}$ by virtue of similar $\delta(\mathrm{P})$ to those observed for previous ferrocenyl diphosphines discussed herein. The ${ }^{1} \mathrm{H}$ NMR spectrum (in $\mathrm{CDCl}_{3}$ ) of 3.48 contained two characteristic cyclopentadienyl singlets at $\delta(\mathrm{H}) 3.93$ and 3.86 ppm , in addition to three broad singlets related to the three distinct $\mathrm{CH}_{2}$ environments within the macrocyclic ring $\left[\delta(\mathrm{H}) 3.49\left(\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.92\left(\mathrm{NCH}_{2} \mathrm{CH}_{2}\right)\right.$, $\left.1.42\left(\mathrm{NCH}_{2} \mathrm{CH}_{2}\right)\right] .{ }^{265}$ The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ hydrogen atoms resonated as a characteristic doublet at $\delta(\mathrm{H}) 3.30 \mathrm{ppm},{ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz} .^{22,23}$ The ternary nature of the nitrogen atoms within $\mathbf{3 . 4 8}$ was also supported by the absence of a $v_{\mathrm{NH}}$ absorption band from the infrared spectrum of $\mathbf{3 . 4 8}$, in addition to the lack of a $\delta(\mathrm{NH})$ resonance in the ${ }^{1} \mathrm{H}$ NMR spectrum.

Additional support for the preparation of $\mathbf{3 . 4 8}$ comes from the positive ion FAB mass spectroscopy which gave the anticipated parent ion and fragmentation pattern \{MS $\left.\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 280[\mathrm{M}]^{+}, 281[\mathrm{M}+\mathrm{H}]^{+}\right\}$. Unfortunately time did not allow for sufficient study of the coordination chemistry of $\mathbf{3 . 4 8}$. However initial in-situ and preparative scale reactions with $\mathrm{PtCl}_{2}(\mathrm{cod})$ afforded a range of phosphorus containing species by
${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy (in $\mathrm{CDCl}_{3}$ ) [ca. $\left.\delta(\mathrm{P})-19-32 \mathrm{ppm}\right]$, none of which displayed equidistant ${ }^{195} \mathrm{Pt}$ satellites, whilst further analysis proved inconclusive. Further work is clearly required in this area.

### 3.25 Conclusion

In summary, a range of new tertiary phosphines with ferrocenyl appendages have been prepared, characterised and coordinated to a range of soft transition metal centres. The coordination chemistry of $\mathbf{3 . 1}$ was extensively studied and revealed the phosphine to be capable of bridging two transition metal centres either dimerically or monomerically, as well as forming new examples of cis and trans chelate complexes. Variations of the chemistry used to prepare $\mathbf{3 . 1} \mathbf{- 3 . 3}$, allowed the synthesis of a new trimetallo-diphosphine $\mathbf{3 . 1 6}$ in addition to the new monophosphines $\mathbf{3 . 1 4}$ and $\mathbf{3 . 2 0}$ 3.22. The coordination chemistry of $\mathbf{3 . 1 6}$ and $\mathbf{3 . 2 0}$ afforded two rare examples of pentametallic diphosphine coordination complexes (3.18, 3.19 and 3.26).

A further series of new ditertiary phosphines of the form $\left(\mathrm{RPCH}_{2}\right)_{2} \mathrm{NCH}_{2} \mathrm{Fc}(3.27-$ 3.29) have also been discussed and their coordination chemistry to readily available transition metals reported. A new synthetic strategy towards the synthesis of unsymmetrical diphosphines of the form $\mathrm{RPCH}_{2} \mathrm{~N}(\mathrm{X}) \mathrm{CH}_{2} \mathrm{PR}^{\prime}$ was also attempted, in addition to the preparation and coordination chemistry of a new phosphinoamine (3.42). Furthermore, new examples of a macrocyclic ferrocenyl diphosphine (3.48) and the iminophosphine (3.44) have also been prepared and characterised.

The electrochemical properties of the majority of compounds discussed in this chapter have been investigated by cyclic voltammetry, (when purity, yield and stability would allow), and whilst the characteristic $\mathrm{Fe}(\mathrm{II}) / \mathrm{Fe}(\mathrm{III})$ redox couples reported were found to vary over the range of phosphines and complexes studied [ $\mathrm{E}_{1 / 2}-0.042$ to +0.142 V ], no considerable, unusual or selective changes were observed that would demand any further electrochemical investigation.

## Chapter 4

The Synthesis and Coordination Chemistry of Novel Tertiary Phosphines Bearing a Single Polyaromatic or Ferrocenyl Group

### 4.1 Introduction

Compounds bearing organometallic or planar aromatic groups, in addition to a hard donor site, have found extensive use within transition metal coordination chemistry owing to their luminescent, electrochemical and binding properties. ${ }^{128,130,187,210}$ The coordination complexes of such compounds have also shown important biological properties, such as DNA binding ( $\mathbf{4 a})^{266}$ and cytotoxicity ( $\mathbf{4 b}$ and $\left.\mathbf{4 c}\right)^{267,268}$ (Figure 4.1).


Figure 4.1 Recent examples of complexes that display DNA binding and cytoxicity.

Interestingly, phosphines bearing planar aromatic or organometallic moieties have seldom been investigated for such biological roles. Given our group's interest in the functionalisation of primary amines via an efficient Mannich-based condensation reaction, ${ }^{21,23,58,60}$ this chapter reports the syntheses of $(\mathrm{R}) \mathrm{N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}$ and (R) $\mathrm{NHCOCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}(\mathrm{R}=$ functionalised planar aromatic or organometallic group) and their subsequent coordination to some biologically relevant transition metals.

### 4.2 Synthesis and Characterisation of 4.1 and 4.2

The new diphosphines 4.1 and 4.2 were prepared via consecutive Mannich-based condensation of two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ with one equiv. of the respective planar aromatic amine (Equation 4.1). In both instances the progress of the reaction was monitored by in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy.


Equation 4.1
The in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra showed that neither reaction proceed to completion following prolonged stirring at ambient temperature or reflux ( 6 d ), with signals from a mixture of products, $\mathrm{Ph}_{2} \mathrm{CH}_{2} \mathrm{OH}$ and reaction intermediates $\left[\mathrm{Ph}_{2} \mathrm{PH}\right.$ and $\mathrm{RN}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{P}$ (4.1a and 4.2a)] being observed. The formation of 4.1 and 4.2 was however alluded to by the appearance of a characteristic $\mathrm{PCN}(\mathrm{R}) \mathrm{CP}$ singlet within the respective in-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra $[\delta(\mathrm{P})-28.5(4.1)$ and $-26.3(4.2) \mathrm{ppm}$, respectively]. ${ }^{21,23,186}$ Unfortunately, the phosphorus purity of this characteristic singlet was never found to be greater than $c a .25 \%$ in either case. Prolonged stirring at reflux (4.1), and RT (4.2), did however afford a small amount of yellow precipitate, which was isolated in poor yield (ca. $23 \%$ ) following concentration of the solvent.

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\mathrm{CDCl}_{3}$ ) of this isolated material varied depending upon the primary amine used in the reaction. Following reaction of 9-aminomethyl anthracene with $\mathrm{Ph}_{2} \mathrm{CH}_{2} \mathrm{OH}$, the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the isolated solid displayed a characteristic diphosphine singlet at $\delta(\mathrm{P})-28.1 \mathrm{ppm},{ }^{21,23,186}$ which accounted for $72 \%$ of the total ${ }^{31} \mathrm{P}$ NMR active nuclei (remaining $28 \%, \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ by ${ }^{31} \mathrm{P}$ integration), indicating that the diphosphine (4.1) had been successfully
isolated. In contrast the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the solid obtained from the reaction of 4-methyl-7-amino-coumarin with $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, displayed a characteristic mono-phosphine singlet at $\delta(\mathrm{P})-19.6 \mathrm{ppm}(\mathbf{4 . 2 a})$, by comparison with the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of similar mono-phosphines. ${ }^{61,255}$

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4 . 1}$ and 4.2a support the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR assignment, with the respective spectra containing characteristic $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ resonances at $\delta(\mathrm{H}) 3.59$ and 3.81 ppm respectively. ${ }^{22,23}$ The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ moieties resonated as a characteristic doublet [ ${ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz}$ ], ${ }^{22,23}$ in the case of $\mathbf{4 . 1}$, and as a broad singlet within the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{4 . 2 a}$. The tertiary nature of the nitrogen atom within 4.1 was confirmed by the characteristic $2: 1$ integral ratio observed between the $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ and $\delta\left(\mathrm{CH}_{2} \mathrm{~N}\left(\mathrm{C}_{14} \mathrm{H}_{9}\right)\right)$ resonances. The secondary nature of the amine in 4.2a was supported by the appearance of a broad $\delta(\mathrm{NH})$ singlet, [ $\delta \mathrm{H} 4.20(\mathrm{bs}, 1 \mathrm{H}, \mathrm{NH})]$ and by the $\delta(\mathrm{NH})$ resonances characteristic integral ratio (1:2, NH: $\mathrm{CH}_{2} \mathrm{P}$ ). The assignment of the $\delta(\mathrm{NH})$ resonance was confirmed by the signals collapse upon shaking with $\mathrm{D}_{2} \mathrm{O}$.

The infrared spectra of 4.1 and 4.2a also supported the secondary and tertiary nature of their respective nitrogen atoms, with no $v_{\mathrm{NH}}$ band being observed for 4.1, whilst an indicative $v_{\mathrm{NH}}$ absorption band was observed at $3311 \mathrm{~cm}^{-1}$ for 4.2a. The preparation of 4.2a was further confirmed by determination of the molecular structure by X-ray crystallography (Section 4.2.1).

### 4.2.1 Molecular Structure of 4.2a

Colourless crystalline plates suitable for X-ray crystallography were obtained by slow evaporation of a MeOH solution of 4.2a. The molecular structure was determined using synchrotron radiation due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature (Figure 4.2). Selected bond lengths and angles are given in Table 4.1.


Figure 4.2 Molecular structure of 4.2a. All hydrogen atoms, except $\mathrm{H}(1)$, have been removed for clarity.

The crystal structure of 4.2 a showed the asymmetric unit to contain one molecule of the monophosphine. The phosphorus atom was found to adopt a distorted pyramidal geometry, as indicated to the relevant $\mathrm{C}-\mathrm{P}-\mathrm{C}$ angles (Table 4.1). The geometry of the carbonyl carbon, $\mathrm{C}(17)$, was found to be trigonal planar as anticipated $[\mathrm{O}(2)-$ $\mathrm{C}(17)-\mathrm{O}(1) 115.7(3)^{\circ}, \mathrm{O}(2)-\mathrm{C}(17)-\mathrm{C}(18) 126.6(3)^{\circ}, \mathrm{O}(1)-\mathrm{C}(17)-\mathrm{C}(18) 117.7(3)^{\circ}$; sum of component angles $\left.=360^{\circ}\right]$. The double bond character of the $\alpha, \beta$-unsaturated carbonyl group was also evident by comparison of the $\mathrm{O}(1)-\mathrm{C}(17), \mathrm{O}(2)-\mathrm{C}(17)$, $\mathrm{C}(18)-\mathrm{C}(19)$ and $\mathrm{C}(19)-\mathrm{C}(20)$ bond lengths $[\mathrm{O}(1)-\mathrm{C}(17)>\mathrm{C}(17)-\mathrm{O}(2), \mathrm{C}(19)-$ $\mathrm{C}(20)>\mathrm{C}(18)-\mathrm{C}(19) ; 1.378(4), 1.221(4), 1.343(4)$ and $1.444(4) \AA$ respectively]. The solid state structure was also found to contain a single intermolecular hydrogen bond between neighbouring asymmetric units, $\mathrm{N}(1)-\mathrm{H}(1) \cdots \mathrm{O}\left(2^{\prime}\right)\left[\mathrm{N}(1) \cdots \mathrm{O}\left(2^{\prime}\right) 3.006(4) \AA\right.$, $\mathrm{H}(1) \cdots \mathrm{O}\left(2^{\prime}\right) 2.14(4) \AA, \mathrm{N}(1)-\mathrm{H}(1) \cdots \mathrm{O}\left(2^{\prime}\right) 174(3)^{\circ}$, symmetry operation ${ }^{\prime}=-\mathrm{x}+1$,
$y+1 / 2,-z+1 / 2]$, which gave rise to the formation of intermolecular zig-zag chains of 4.2a which run along the $b$-axis (Figure 4.3).


Figure 4.3 The intermolecular zig-zag chain observed within the molecular structure of 4.2a. All hydrogen atoms, except those involved in hydrogen bonding, and phosphorus phenyl carbons have been removed for clarity. Symmetry operator ' $=$ $-\mathrm{x}+1, \mathrm{y}+1 / 2,-\mathrm{z}+1 / 2$.

Further analysis of the packing plot revealed neighbouring intermolecular chains to be interdigitated, in an anti-parallel manner, with two sets of intermolecular $\pi \cdots \pi$ stacks observed between neighbouring coumarin units (Figure 4.4). The first $\pi \cdots \pi$ intermolecular interaction was situated at the centre of the unit cell and involved two "eclipsed" anti-parallel coumarin units (Figure 4.4, highlighted in blue) [average mean separation $=3.500 \AA$, c.f. graphite $3.45 \AA^{92}$; face-to-face tilt $\left.=0^{\circ}\right]$. The second $\pi \cdots \pi$ interaction was significantly slipped by comparison and involved coumarin units at the edges of the unit cell, [C‥C $3.515 \AA$, c.f. graphite $3.45 \AA$; face-to-face tilt $\left.=0^{\circ}\right]$ (Figure 4.4, highlighted in red).


Figure 4.4 The packing of 4.2a (left) and selected detail (right). All hydrogen atoms not involved in intermolecular bonding have been removed for clarity.

Table 4.1 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4.2a.

| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.823(3)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | $101.22(14)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.833(3)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | $102.27(14)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.847(3)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13)$ | $100.21(15)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.440(4)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $108.2(2)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.371(4)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $123.1(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(16)$ | $1.382(3)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $119.3(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(17)$ | $1.378(4)$ | $\mathrm{C}(16)-\mathrm{O}(1)-\mathrm{C}(17)$ | $121.4(2)$ |
| $\mathrm{O}(2)-\mathrm{C}(17)$ | $1.221(4)$ | $\mathrm{O}(1)-\mathrm{C}(17)-\mathrm{O}(2)$ | $115.7(3)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.425(4)$ | $\mathrm{O}(2)-\mathrm{C}(17)-\mathrm{C}(18)$ | $126.6(3)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | $1.343(4)$ | $\mathrm{O}(1)-\mathrm{C}(17)-\mathrm{C}(18)$ | $117.7(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | $1.507(4)$ | $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | $121.7(3)$ |
|  |  | $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(21)$ | $119.8(3)$ |
|  |  | $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(21)$ | $118.5(3)$ |

### 4.3 Coordination chemistry of 4.1 and 4.2a.

Ligand displacement of cod from $\mathrm{PtCl}_{2}(\operatorname{cod})$ with one (4.1) or two (4.2a) equiv. of the respective phosphine, in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at ambient temperature, gave the platinum(II) complexes 4.3 and 4.4 in good to excellent yield (99 and 68\% respectively) (Scheme 4.1).


Scheme 4.1
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of $\mathbf{4 . 3}$ and $\mathbf{4 . 4}$ both contained new singlet resonances at $\delta(\mathrm{P})-7.0$ and 6.3 ppm respectively, some 20 ppm downfield compared with those of the parent ligands. In both cases each singlet was flanked by two equidistant ${ }^{195} \mathrm{Pt}$ satellites ( ${ }^{1} J_{\text {PtP }} 3416$ and 3709 Hz , respectively). The characteristically large ${ }^{1} J_{\text {PtP }}$ coupling constant infers that both platinum(II) complexes adopt a cis conformation in solution. ${ }^{58,186,196}$ The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4 . 3}$ and $\mathbf{4 . 4}$ both showed a more complex splitting pattern than observed in the ${ }^{1} \mathrm{H}$ NMR spectra of the free ligands, with respect to the $\mathrm{CH}_{2} \mathrm{P}$ protons. The ${ }^{1} \mathrm{H}$ NMR spectrum of 4.3 showed the $\mathrm{CH}_{2} \mathrm{P}$ protons as a multiplet at $\delta(\mathrm{H}) 3.53 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 3.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{PH}} 36.0 \mathrm{~Hz}\right)$, whilst the corresponding protons appeared as a doublet in the case of $4.4\left[\delta(H) 4.24 \mathrm{ppm}\left({ }^{2} J_{\mathrm{PH}} 6.4 \mathrm{~Hz}\right)\right]$. Further support for the cis conformation of 4.4, in the solid state, came from the complexes infrared spectroscopy which showed two $v_{\text {PtCl }}$ absorption bands at 318 and $282 \mathrm{~cm}^{-1}$. Furthermore elemental analysis was satisfactory for both complexes and the positive ion FAB mass spectra for each compound gave the expected fragmentation patterns [MS (FAB ${ }^{+}$): m/z $834\left[\mathrm{M}-\mathrm{Cl}^{+}(4.3)\right.$ and $[\mathrm{M}]^{+}, 977[\mathrm{M}-\mathrm{Cl}]^{+}$
(4.4)]. The preparation of the cis isomer of 4.3 was further confirmed by X-ray crystallography (Section 4.3.1).

### 4.3.1 Molecular structure of 4.3.

Colourless crystalline plates suitable for X-ray crystallography were grown by slow diffusion of MeOH into a $\mathrm{CHCl}_{3}$ solution of 4.3. The molecular structure was then determined using synchrotron radiation due to the small crystal size (at least one dimension $<0.05 \mathrm{~mm}$ ) and also using two diffraction data files, after the crystal lattice was found to be merohedrally twinned [major component $76.19(18) \%$, twin law; $180^{\circ}$ rotation about reciprocal axis 001 1] (Figure 4.5). Selected bond lengths and angles are given in Table 4.2.


Figure 4.5 Molecular structure of 4.3. All hydrogen atoms and solvent molecules of crystallisation have been removed for clarity.

The molecular structure of $\mathbf{4 . 3}$ showed the asymmetric unit to consist of one unique molecule of 4.3 and two solvating chloroform molecules. The complex was found to adopt a distorted square planar geometry with respect to the metal centre $[\mathrm{P}(1)-$ $\mathrm{Pt}(1)-\mathrm{Cl}(2) 177.34(17)^{\circ}$ and $\left.\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1) 172.59(18)^{\circ}\right]$ with 4.1 coordinating the platinum(II) centre via both phosphorus atoms, to form a six membered cis-chelate ring [bite angle, $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{P}(1) 94.38(15)^{\circ}$ ]. The phosphorus atoms within 4.3 were
found to adopt a distorted tetrahedral geometry, as indicated by the relevant $\mathrm{C}-\mathrm{P}-\mathrm{Pt}$ angles (Table 4.2). The nitrogen atom, $\mathrm{N}(1)$, adopted a distorted trigonal pyramidal geometry [sum of component angles $=332^{\circ}$ ]. No unusual packing or inter / intramolecular bonding was observed.

Table 4.2 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4.3

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.258(4)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $177.34(17)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | $2.211(4)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $172.59(18)$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $2.354(5)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | $87.99(15)$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.354(4)$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $87.78(16)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.794(17)$ | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $89.68(16)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.835(19)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | $94.38(15)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.810(16)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $114.4(5)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.47(2)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $111.1(6)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.471(18)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | $117.4(6)$ |
| $\mathrm{N}(1)-\mathrm{C}(29)$ | $1.47(2)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $112.9(12)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.50(2)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $110.8(13)$ |
| $\mathrm{P}(2)-\mathrm{C}(29)$ | $1.797(17)$ | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(29)$ | $112.7(12)$ |
| $\mathrm{P}(2)-\mathrm{C}(30)$ | $1.829(17)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(29)$ | $108.8(13)$ |
| $\mathrm{P}(2)-\mathrm{C}(36)$ | $1.817(17)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $113.2(14)$ |
|  |  | $\mathrm{N}(1)-\mathrm{C}(29)-\mathrm{P}(2)$ | $116.4(12)$ |
|  |  | $\mathrm{C}(29)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | $118.5(6)$ |
|  |  | $\mathrm{C}(30)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | $109.4(5)$ |
|  |  | $\mathrm{C}(36)-\mathrm{P}(2)-\mathrm{Pt}(1)$ | $116.9(6)$ |

### 4.4 Functionalised Ditertiary Phosphines Bearing Peptide-Coupled Polyaromatic and Ferrocenyl Groups

Following the successful preparation of the biologically relevant platinum(II) dichloride complexes 4.3 and 4.4, the sequential use of three well known reactions allowed the synthesis of a series of novel diphosphines of the form ( R ) $\mathrm{NHCOCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2}(4.22-4.29)$, $(\mathrm{R}=$ planar aromatic or ferrocenyl group) from readily available aromatic amines. In contrast to 4.1 and 4.2a, this new series of diphosphines will incorporate a peptide "linker" into the generic ligand design in an attempt to promote hydrogen bonding and enhance flexibility within the novel phosphine and subsequent coordination complexes. Both of which are desirable properties for compounds capable of performing applications such as DNA binding. ${ }^{269,270}$

The synthetic route used to prepare $\mathbf{4 . 2 2}$ - 4.29 involved the initial peptide coupling of aromatic amines with carbobenzyl-oxyglycine via a conventional carbodiimide coupling, ${ }^{271}$ to afford the substituted benzyl methylcarbamates $4.5-4.13$. The removal of the benzyl-formate group from 4.5 - $\mathbf{4 . 1 3}$ was efficiently achieved by sacrificial hydrogenation using cyclohexene and palladium on charcoal as a catalyst, ${ }^{271}$ to afford the functionalised aliphatic amines $4.14-\mathbf{4 . 2 1}$. The synthesis was completed via Mannich-based condensation of $\mathbf{4 . 1 4 - 4 . 2 1}$ with two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$, to afford the new phosphines 4.21 - $\mathbf{4 . 2 9}$ (Equation 4.4). ${ }^{21,23,58,60}$

### 4.4.1 Synthesis and Characterisation of benzyl methylcarbamates (4.5-4.13) and the aminoacetamides (4.14-4.21)

The benzyl methylcarbamates $\mathbf{4 . 5} \mathbf{- 4 . 1 3}$ were prepared in yields ranging between 22 and $92 \%$ using a known method of peptide coupling (Equation 4.2). ${ }^{271}$ Literature searches suggest that $4.7-4.10,4.12$ and 4.13 have not previously been reported, and as a result they are discussed, as part of the series, herein. The yield of carbamate, in all cases, appeared to be largely dependent upon the solubility of the aromatic amine in THF at ambient temperature. This was particularly evident in the
case of 2-aminoanthracene which required harsher reaction conditions to prepare 4.7 ( 23 h reflux in THF).


4.5
4.6
4.7
4.8

4.12

4.13

Equation 4.2

The ${ }^{1} \mathrm{H}$ NMR spectra [in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ or $\mathrm{CDCl}_{3}(4.12)$ ] of 4.5 - $\mathbf{4 . 1 3}$ displayed two characteristic resonances of equal intensity between $\delta(\mathrm{H}) 5.1-3.7 \mathrm{ppm}$, which were assigned to the methylene groups within the carbamates, by comparison with literature examples. ${ }^{271}$ The benzyl protons resonated as a singlet between $\delta(\mathrm{H}) 5.1-$ 5.0 ppm , whilst the remaining methylene protons ( $\alpha$ to the peptide moiety) resonated as a doublet between $\delta(\mathrm{H}) 4.0-3.7 \mathrm{ppm}\left[J_{\mathrm{HH}} 5.2-6.0 \mathrm{~Hz}\right]$. In the case of $4.5,2 \mathrm{D}$ COSY ${ }^{1} \mathrm{H}$ NMR analysis showed the $\mathrm{CH}_{2}$ 's $J_{\mathrm{HH}}$ splitting pattern to be associated with a coupling between the methylene protons and another ${ }^{1} \mathrm{H}$ NMR active environment which resonated as a triplet at $\delta(\mathrm{H}) 7.5 \mathrm{ppm}\left(J_{\mathrm{HH}} 6.0 \mathrm{~Hz}\right)$. The triplet was tentatively assigned to one of the NH protons within 4.5 by integration, splitting pattern and following HMQC NMR analysis, which showed the triplet to lack a corresponding NMR active ${ }^{13} \mathrm{C}$ resonance. A third characteristic singlet was also present in the majority of carbamates $[\delta(\mathrm{H}) 11.2-9.1 \mathrm{ppm}]$ and was assigned to the remaining NH proton by integration $\left[\mathrm{NH}: \mathrm{CH}_{2}=1: 2\right]$ and also by virtue of the resonances collapse upon shaking with $\mathrm{D}_{2} \mathrm{O}$.

Furthermore the preparation of $\mathbf{4 . 5} \mathbf{- 4 . 1 3}$ was supported by the compound's infrared spectra which contained strong amide and carbamate absorption bands, as anticipated [range $v_{\mathrm{NH}} 3426-3252 \mathrm{~cm}^{-1}$, amide band I $v_{\mathrm{C}=\mathrm{O}} 1695-1656$ and amide band II $v_{\mathrm{NH}}$ $1583-1518 \mathrm{~cm}^{-1}$ respectively]. ${ }^{194}$ Elemental analysis and mass spectroscopy (EI and FAB) results also supported the proposed formulae (see Experimental Section).

Using a well established method of benzyl-formate reduction, ${ }^{271}$ a series of 2aminoacetamides ( $\mathbf{4 . 1 4 - 4 . 2 1 )}$ were synthesised by sacrificial hydrogenation of $\mathbf{4 . 5}$ 4.13 with an excess of activated palladium on charcoal and cyclohexene (Equation 4.3). Following a search of the literature the aminoacetamides $\mathbf{4 . 1 5} \mathbf{- 4 . 2 1}$ have not previously been reported and are therefore discussed, as part of the series, here. The 2 -aminoacetamides ( $4.14 \mathbf{- 4 . 2 1}$ ) were all prepared in good yield (yields ranged between $80-100 \%$ ) by the $1-6 \mathrm{~h}$ reflux of a suspension containing the above reagents.


Efforts to cleave the $\mathrm{C}-\mathrm{N}$ carbamate bond within 4.13 however proved fruitless under the same reaction conditions. Attempts to react $\mathbf{4 . 1 3}$ using harsher reaction conditions also failed, with the extreme attempt being a 120 h reflux at $130^{\circ} \mathrm{C}$.

The ${ }^{1} \mathrm{H}$ NMR spectra $\left[\right.$ in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ or $\left.\mathrm{CDCl}_{3}(\mathbf{4 . 2 1})\right]$ of $\mathbf{4 . 1 4 - 4 . 2 1}$ all exhibited one characteristic singlet in the region of $\delta(\mathrm{H}) 3.6-3.1 \mathrm{ppm}$. The singlet was assigned to the methylene protons $\alpha$ to the peptide moiety, by direct comparison with the same protons in the carbamate precursors $(\mathbf{4 . 5} \mathbf{- 4 . 1 2}) ; \Delta \delta(\mathrm{H}) 0.6-0.4 \mathrm{ppm}$. The absence of the benzyl resonance $[\delta(\mathrm{H}) 5.1-5.0 \mathrm{ppm}, 4.5$ - 4.12] and the simplification of the aromatic region of the ${ }^{1} \mathrm{H}$ NMR spectra also suggested the successful hydrogenation of 4.5 - 4.12.

The infrared spectra of 4.14 - $\mathbf{4 . 2 1}$ also contained characteristically strong peptide absorption bands, as anticipated [values ranged between $v_{\mathrm{NH}} 3395-3226, v_{\mathrm{C}=\mathrm{O}} 1696$ -1624 and $\left.v_{\mathrm{NH}} 1590-1521 \mathrm{~cm}^{-1}\right] .{ }^{194}$ Further characterisation data can be found in the Experimental Section in addition to structural data gained from single crsystals grown from solutions of $\mathbf{4 . 1 4}$ and $\mathbf{4 . 1 5}$ (Sections 4.4.2 and 4.4.3).

### 4.4.2 Molecular structure of $\left[\left(\mathrm{C}_{6} \mathrm{H}_{5}\right) \mathrm{NHCOCH}_{2} \mathrm{NH}_{3}\right]\left[\left(\mathrm{C}_{6} \mathrm{H}_{5}\right) \mathrm{NHCOCH}_{2} \mathrm{NHCO}_{2}\right](4.14 \mathrm{a})$

Colourless crystalline rods suitable for single crystal X-ray diffraction were obtained by slow evaporation of an ethanolic solution of 4.14 and the molecular structure determined. Selected bond lengths and angles are given in Tables 4.3 and 4.4.


Figure 4.6 Molecular packing of 4.14a. The minor disorder component and all hydrogen atoms not involved in intermolecular hydrogen bonding have been removed for clarity.

Compound 4.14 did not crystallise as the expected neutral species, rather it was found as a salt, with the asymmetric unit consisting of an ammonium cation of 4.14, a carbamic derivative of $\mathbf{4 . 1 4}$ and a solvating water molecule. The preparation of both ions is thought to be a consequence of incomplete hydrogenation of 4.5, an effect observed in the ${ }^{1} \mathrm{H}$ NMR spectrum of 4.5 upon closer inspection. The molecular structure depicted in Figure 4.6 is therefore not considered to be representative of the bulk material obtained after hydrogenation of 4.5. All three components were found to be hydrogen bonded to each other within the asymmetric unit $\left[\mathrm{N}(2) \cdots \mathrm{O}(4) 2.798(5) \AA, \mathrm{H}(2) \cdots \mathrm{O}(4) 1.91(5) \AA, \mathrm{N}(2)-\mathrm{H}(2) \cdots \mathrm{O}(4) 172(4)^{\circ}\right.$; $\mathrm{N}(4) \cdots \mathrm{O}(5) 2.995(5) \AA, \mathrm{H}(4) \cdots \mathrm{O}(5) 2.15(5) \AA, \mathrm{N}(4)-\mathrm{H}(4) \cdots \mathrm{O}(5) 171(4)^{\circ}$. The phenyl ring within the ammonium cation was found to be two-fold disordered over two sets
of positions with $\mathrm{C}(12)$ and $\mathrm{C}(15)$ common between the two disorder components (occupancy refined to $51.0(6) \%$ for the major component). The geometry about the carbonyl carbons was found to be trigonal planar as expected [sum of component angles about $C(2), C(9)$ and $C(11)=360^{\circ}$, see Table 4.3]. Further analysis of the intermolecular packing revealed an extensive intermolecular hydrogen bonding network, further to that observed within the asymmetric unit, with all hydrogen donors and acceptors within the salt being involved in the formation of a further seven intermolecular hydrogen bonds (Figure 4.7, Table 4.4). The cations and anions within the crystal lattice were found to be connected both directly and indirectly (via the solvating water molecules) to form a stacked thick-sheet structure (highlighted in red, Figure 4.7). Each molecular sheet is made up of a hydrophilic centre containing the polar $\mathrm{NH} / \mathrm{CO} / \mathrm{OH}$ groups, whilst the edges of the sheets comprise of the hydrophobic phenyl groups (Figure 4.7).


Figure 4.7 Packing plot of 4.14a, stacked thick-sheet structure (highlighted in red). The minor disorder component and all hydrogen atoms not involved in intermolecular hydrogen bonding have been removed for clarity.

Table 4.3 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{4 . 1 4 a}$.

| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1.469(5)$ | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $110.3(3)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.518(5)$ | $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{C}(1)$ | $120.5(4)$ |
| $\mathrm{C}(2)-\mathrm{O}(1)$ | $1.220(5)$ | $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{N}(2)$ | $125.5(4)$ |
| $\mathrm{C}(2)-\mathrm{N}(2)$ | $1.338(5)$ | $\mathrm{N}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | $114.0(4)$ |
| $\mathrm{N}(2)-\mathrm{C}(3)$ | $1.424(5)$ | $\mathrm{C}(2)-\mathrm{N}(2)-\mathrm{C}(3)$ | $128.3(4)$ |
| $\mathrm{C}(9)-\mathrm{O}(2)$ | $1.267(5)$ | $\mathrm{O}(2)-\mathrm{C}(9)-\mathrm{O}(3)$ | $123.9(4)$ |
| $\mathrm{C}(9)-\mathrm{O}(3)$ | $1.275(5)$ | $\mathrm{O}(2)-\mathrm{C}(9)-\mathrm{N}(3)$ | $117.7(4)$ |
| $\mathrm{C}(9)-\mathrm{N}(3)$ | $1.358(5)$ | $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{N}(3)$ | $118.4(4)$ |
| $\mathrm{N}(3)-\mathrm{C}(10)$ | $1.446(5)$ | $\mathrm{C}(9)-\mathrm{N}(3)-\mathrm{C}(10)$ | $120.5(3)$ |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | $1.514(6)$ | $\mathrm{N}(3)-\mathrm{C}(10)-\mathrm{C}(11)$ | $116.2(3)$ |
| $\mathrm{C}(11)-\mathrm{O}(4)$ | $1.243(5)$ | $\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{N}(4)$ | $123.8(4)$ |
| $\mathrm{C}(11)-\mathrm{N}(4)$ | $1.337(5)$ | $\mathrm{O}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | $118.9(4)$ |
| $\mathrm{N}(4)-\mathrm{C}(12)$ | $1.424(5)$ | $\mathrm{N}(4)-\mathrm{C}(11)-\mathrm{C}(10)$ | $117.3(4)$ |
|  |  | $\mathrm{C}(11)-\mathrm{N}(4)-\mathrm{C}(12)$ | $126.2(4)$ |

Table 4.4 Hydrogen bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4.14a. ${ }^{\text {a }}$

| $\mathrm{D}-\mathrm{H} \cdots \mathrm{A}$ | $(\mathrm{D}-\mathrm{H})$ | $(\mathrm{H} \ldots \mathrm{A})$ | $(\mathrm{D} \ldots \mathrm{A})$ | $<(\mathrm{DHA})$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{N}(1)-\mathrm{H}(1 \mathrm{~A}) \cdots \mathrm{O}\left(5^{\prime}\right)$ | $0.95(5)$ | $2.02(5)$ | $2.895(5)$ | $153(4)$ |
| $\mathrm{N}(1)-\mathrm{H}(1 \mathrm{~B}) \cdots \mathrm{O}\left(3^{\prime \prime}\right)$ | $0.93(5)$ | $1.93(5)$ | $2.826(5)$ | $160(4)$ |
| $\mathrm{N}(1)-\mathrm{H}(1 \mathrm{~B}) \cdots \mathrm{O}\left(2^{\prime \prime}\right)$ | $0.93(5)$ | $2.47(5)$ | $2.957(5)$ | $113(3)$ |
| $\mathrm{N}(1)-\mathrm{H}(1 \mathrm{C}) \cdots \mathrm{O}\left(3^{*}\right)$ | $0.89(5)$ | $1.90(5)$ | $2.745(5)$ | $158(4)$ |
| $\mathrm{N}(2)-\mathrm{H}(2) \cdots \mathrm{O}(4)$ | $0.89(5)$ | $1.91(5)$ | $2.798(5)$ | $172(4)$ |
| $\mathrm{N}(3)-\mathrm{H}(3) \cdots \mathrm{O}(2+)$ | $0.86(5)$ | $1.96(5)$ | $2.805(4)$ | $172(4)$ |
| $\mathrm{N}(4)-\mathrm{H}(4) \cdots \mathrm{O}(5)$ | $0.86(5)$ | $2.15(5)$ | $2.995(5)$ | $171(4)$ |
| $\mathrm{O}(5)-\mathrm{H}(5 \mathrm{~B}) \cdots \mathrm{O}(2+)$ | $0.90(5)$ | $1.85(5)$ | $2.744(4)$ | $176(5)$ |
| $\mathrm{O}(5)-\mathrm{H}(5 \mathrm{~A}) \cdots \mathrm{O}(1 \#)$ | $0.80(6)$ | $2.08(6)$ | $2.805(4)$ | $152(5)$ |

[^6]
### 4.4.3 Molecular structure of $\left[\left(\mathrm{C}_{10} \mathrm{H}_{7}\right) \mathrm{NHCOCH}_{2} \mathrm{NH}_{3}\right][\mathrm{EtO}](4.15 a)$

Colourless crystalline plates suitable for single crystal X-ray diffraction were obtained by slow vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into an EtOH solution of $\mathbf{4 . 1 5}$ (Figure 4.8) and the molecular structure determined. Selected bond lengths and angles are given in Tables 4.5.


Figure 4.8 Molecular structure of $\left[\left(\mathrm{C}_{10} \mathrm{H}_{7}\right) \mathrm{NHCOCH}_{2} \mathrm{NH}_{3}\right][\mathrm{EtO}]$ (4.15a). All hydrogen atoms, except $\mathrm{H}(2)$ and the minor disorder components have been omitted for clarity.

Analysis of the crystal structure suggests that $\mathbf{4 . 1 5}$ did not crystallise as the expected neutral species, rather it was found to have crystallised as a salt (4.15a), with the asymmetric units containing one unique ammonium cation of 4.15 and an ethanoate counterion. The preparation of this unexpected salt is supported by least squares difference maps obtained during refinement which showed the ammonium hydrogen atoms, while the alcohol hydrogen atom of the solvate of crystallisation remained absent. The molecular structure of 4.15 a was also shown to be significantly disordered, with the ethanoate anion and the naphthyl group / nitrogen atom $\mathrm{N}(2)$ being disordered over two sets of positions [anion: $\mathrm{C}(13)$ common between both disorder components, occupancy refined to $55.7(12) \%$ for the major component, cation: $\mathrm{C}(2)$ common between both disorder components; occupancy refined to $93.2(3) \%$ for the major component]. This disorder within 4.15a made it difficult to model the ammonium hydrogen atoms with confidence. The peptide hydrogen atom, $\mathrm{H}(2)$, was however modelled using the geometry of the neighbouring carrier atom
$\mathrm{N}(2)$. A search of the CSD yielded no similar examples of an ammonium alkoxide, so, given the disorder, the amine / ethanol interpretation cannot be entirely ruled out.

Analysis of the intermolecular packing for 4.15a revealed the presence of intermolecular chains, which ran along the c-axis. The chains were formed by intermolecular hydrogen bonds between the disordered amide $\mathrm{N} H$ 's of the ammonium cation (from the respective disorder components) and the carbonyl oxygen of a neighbouring cation $\left[\mathrm{N}(2) \cdots \mathrm{O}\left(1^{\prime}\right) 2.838(4) \AA, \mathrm{H}(2) \cdots \mathrm{O}\left(1^{\prime}\right) 1.97 \AA, \mathrm{~N}(1)-\right.$ $\mathrm{H}(2) \cdots \mathrm{O}\left(1^{\prime}\right) \quad 167^{\circ} ; \quad \mathrm{N}(2 \mathrm{X}) \cdots \mathrm{O}\left(1^{\prime}\right) \quad 2.88(5) ~ \AA, \quad \mathrm{H}(2 \mathrm{X}) \cdots \mathrm{O}\left(1^{\prime}\right) 2.12 \AA, \mathrm{~N}(2 \mathrm{X})-$ $\mathrm{H}(2 \mathrm{X}) \cdots \mathrm{O}\left(1^{\prime}\right) 144^{\circ}$, symmetry operator for equivalent atoms ${ }^{\prime}=\mathrm{x},-\mathrm{y}+1 / 2, \mathrm{z}-1 / 2, \mathrm{X}=$ minor disorder component]. (Figure 4.9).


Figure 4.9 Packing plot of 4.15a. The minor disorder components and all hydrogen atoms, except those involved in hydrogen bonding, have been removed for clarity.

Table 4.5 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4.15a.

| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1.472(4)$ | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $110.9(3)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.498(5)$ | $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{C}(1)$ | $120.5(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(2)$ | $1.249(4)$ | $\mathrm{N}(2)-\mathrm{C}(2)-\mathrm{C}(1)$ | $115.5(3)$ |
| $\mathrm{N}(2)-\mathrm{C}(2)$ | $1.329(5)$ | $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{N}(2)$ | $124.0(3)$ |
| $\mathrm{N}(2)-\mathrm{C}(3)$ | $1.421(5)$ | $\mathrm{N}(2 \mathrm{X})-\mathrm{C}(2)-\mathrm{C}(1)^{\mathrm{a}}$ | $111(2)$ |
| $\mathrm{N}(2 \mathrm{X})-\mathrm{C}(2)^{\mathrm{a}}$ | $1.29(5)$ | $\mathrm{O}(1)-\mathrm{C}(2)-\mathrm{N}(2 \mathrm{X})^{\mathrm{a}}$ | $122(2)$ |
| $\mathrm{N}(2 \mathrm{X})-\mathrm{C}(3 \mathrm{X})^{\mathrm{a}}$ | $1.54(8)$ | $\mathrm{C}(2)-\mathrm{N}(2)-\mathrm{C}(3)$ | $125.6(3)$ |

[^7]
### 4.4.4 Synthesis and Characterisation of the Functionalised Ditertiary

 Phosphines 4.22-4.29Reaction of two equiv. of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ with 4.14 - 4.21, under nitrogen, gave the new functionalised ditertary phosphines $\mathbf{4 . 2 2}$ - $\mathbf{4 . 2 9}$ (Equation 4.4).



The diphosphines $4.22,4.23,4.25,4.27$ and 4.28 were all readily isolated in good to excellent yield ( $64-100 \%$ ) as solids following a $3-23 \mathrm{~h}$ stir at ambient temperature. The diphosphine $\mathbf{4 . 2 6}$ did not crystallise during the course of the reaction, however the viscous oil that was obtained after complete removal of the solvent was sufficiently pure (by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR, $80 \%$ ) to be used directly in coordination studies. In the case of $\mathbf{4 . 2 4}$ and $\mathbf{4 . 2 9}$ prolonged stirring at ambient temperature also did not yield the desired diphosphines as a solids. In-situ ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy showed the resulting solutions to contain a mixture of the respective bisphosphine ( 4.24 and 4.29), monophosphine intermediates and unreacted $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$. Attempts to force the reactions to completion by reflux unfortunately proved ineffective, with the most extreme condition being a 10 d reflux in the case of 4.24. Attempts to isolate the two ligands by concentration of the solvent under reduced pressure, also proved unsuccessful. As a result full
characterisation of the diphosphines 4.24 and 4.29 was not possible. However, in the case of the anthracene derivative (4.24), successful attempts were made to prepare the monophosphine 4.24a, by dropwise addition of an equimolar methanolic solution of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ to a stirred methanolic solution of 4.16.

All of the isolated phosphines exhibited one characteristic singlet within their ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra $\left[\right.$ in $\mathrm{CDCl}_{3}$ or $\left.\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)\right]$ in the $c a$. region $\delta(\mathrm{P})-21$ to -29 ppm (Table 4.6). In the case of diphosphines 4.22, 4.23, 4.25-4.28 this resonance appeared at $c a . \delta(\mathrm{P})-26 \mathrm{ppm}$ whilst in the mono phosphine (4.24a) the resonance appeared at $\delta(\mathrm{P})-21.6 \mathrm{ppm}$.

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4 . 2 2}$ - $\mathbf{4 . 2 9}$ [in $\mathrm{CDCl}_{3}$ or $\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right]$ all contained two characteristic resonances ranging between $\delta(\mathrm{H}) 3.8-3.3 \mathrm{ppm}$ which relate to the methylene linkers within 4.22 - 4.29 (Table 4.6). The newly introduced $\mathrm{CH}_{2} \mathrm{P}$ moieties were found to resonate as a doublet, or a broad singlet, between $\delta(\mathrm{H}) 3.7$ 3.3 ppm due to a two bond coupling between the $\mathrm{CH}_{2}$ protons and the neighbouring $100 \%$ NMR active ${ }^{31} \mathrm{P}$ nucli (when present ${ }^{2} J_{\mathrm{PH}}$ ranged between $5.2-2.4 \mathrm{~Hz}$ ). The methylene protons $\alpha$ to the peptide group resonated as a singlet between $\delta(\mathrm{H}) 3.8$ 3.5 ppm , as anticipated by comparison with the parent amines. The characteristic ratio between the integrals of the methylene resonances within the diphosphines and mono phosphine added further support to the secondary and tertiary nature of their respective nitrogen atoms (diphosphine, $\mathrm{CH}_{2} \mathrm{P}: \mathrm{COCH}_{2} 2: 1$ and mono phosphine $\mathrm{CH}_{2} \mathrm{P}: \mathrm{COCH}_{2}$ 1:1). The secondary nature of the amine in 4.24a was further confirmed by a broad NH singlet at $\delta(\mathrm{NH}) 10.06 \mathrm{ppm}$. The assignment of the NH hydrogen was further supported by comparison with the chemical shift of similar protons within the parent carbamate $\left[(4.7) \delta\left(\mathrm{CH}_{2} \mathrm{NHCO}\right) 10.25 \mathrm{ppm}, \Delta \delta(\mathrm{H}) 0.19\right.$ $\mathrm{ppm})$ and by integration $\left[\mathrm{CH}_{2} \mathrm{P}: \mathrm{NH} 2: 1\right]$.

Table 4.6 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR data (ppm, Hz) and IR data $\left(\mathrm{cm}^{-1}\right)$ for 4.22 4.28.

|  | $\delta(\mathrm{P})$ | $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ | $\delta\left(\mathrm{COCH}_{2} \mathrm{~N}\right)$ | $v_{\mathrm{NH}}$ | $v_{\mathrm{C}=\mathrm{O}}{ }^{\mathrm{c}}$ | $v_{\mathrm{NH}}{ }^{\mathrm{d}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{4 . 2 2}$ | -26.4 | 3.7 | 3.7 | 3300 | 1519 | 1677 |
| $\mathbf{4 . 2 3}$ | -26.3 | 3.7 | 3.8 | 3319 | 1522 | 1684 |
| $\mathbf{4 . 2 4 a ^ { a }}$ | -21.6 | 3.6 | 3.6 | 3317,3222 | 1513 | 1664 |
| $\mathbf{4 . 2 5}$ | -26.3 | 3.6 | 3.7 | 3314 | 1500 | 1687 |
| $\mathbf{4 . 2 6}$ | -28.6 | 3.3 | 3.5 | 3312 | 1519 | 1651 |
| $\mathbf{4 . 2 7}$ | -26.3 | 3.7 | 3.7 | 3282 | 1532 | 1677 |
| $\mathbf{4 . 2 8}$ | -26.2 | 3.7 | 3.7 | 3314 | 1577 | 1717,1685 |

${ }^{\text {a }}$ Spectra recorded in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$. All other spectra recorded in $\mathrm{CDCl}_{3}$.
b $80 \%$ pure by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy.
${ }^{\text {c }}$ amide band I. ${ }^{\text {d }}$ amide band II.

The secondary nature of the amine in 4.24a was further supported by the phosphine's infrared spectrum which contained an additional $v_{\mathrm{NH}}$ absorption at $3222 \mathrm{~cm}^{-1}$ (Table 4.6). As anticipated the infrared spectra of $\mathbf{4 . 2 2} \mathbf{- 4 . 2 8}$ also contained strong peptide absorption bands [range between: $v_{\mathrm{NH}} 3319-3282$, $v_{\mathrm{C}=\mathrm{O}} 1717-1651$ and $v_{\mathrm{NH}} 1577-$ $1500 \mathrm{~cm}^{-1}$ respectively]. ${ }^{194}$ Further characterisation data can be found in the Experimental Section.

### 4.5 Coordination Chemistry of 4.22, 4.23, 4.25-4.28.

Platinum(II) complexes have been shown to have biological relevance with regard to DNA binding and cytotoxicity towards several cancer cell lines. ${ }^{272,273}$ As a consequence ligands $4.22,4.23,4.25-4.28$ were coordinated to platinum(II) via ligand displacement of cod from $\mathrm{PtCl}_{2}$ (cod) to yield the platinum(II) dichloride complexes 4.30-4.35, in good to excellent yield (72-100\%) (Equation 4.5).

4.22, 4.23, 4.25-4.28

4.22 and 4.30

4.23 and 4.31

Equation 4.5

4.25 and 4.32

4.28 and 4.35

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra $\left[\right.$ in $\mathrm{CDCl}_{3}$ or $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ ] of $\mathbf{4 . 3 0} \mathbf{- 4 . 3 5}$ all showed a new singlet resonance between $\delta(\mathrm{P})-5.0$ to -11.1 ppm which was flanked by equidistant ${ }^{195} \mathrm{Pt}$ satellites (Table 4.7). The characteristically large ${ }^{1} J_{\mathrm{PtP}}$ coupling constants [range between 3419 and 3393 Hz ] suggests that all the complexes adopted a cis conformation in solution. ${ }^{58}$

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4 . 3 0} \mathbf{- 4 . 3 4}$ displayed two resonances between $\delta(\mathrm{H}) 3.9-3.2$ ppm (Table 4.7), which were assigned to the methylene links within the coordinated ligand, by direct comparison with the ${ }^{1} \mathrm{H}$ NMR spectra of the free ligands $\left[\delta\left(\mathrm{CH}_{2}\right)\right.$ $\left.3.8-3.3 \mathrm{ppm}, \mathrm{CH}_{2} \mathrm{P}: \mathrm{COCH}_{2} \mathrm{~N} 2: 1\right]$. In contrast the ${ }^{1} \mathrm{H}$ NMR spectrum of 4.35 contained three poorly resolved singlets $\left[\delta\left(\mathrm{CH}_{2}\right) 3.73-3.71 \mathrm{ppm}\right]$, with similar integrals, within the characteristic methylene region suggesting that the methylene links within 4.35 are slightly different by ${ }^{1} \mathrm{H}$ NMR; an effect not observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ spectroscopy. The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4 . 3 0} \mathbf{- 4 . 3 3}$ showed the $\mathrm{CH}_{2} \mathrm{P}$ protons to resonate as broad shouldered doublets, as may have been anticipated, due to a combination of ${ }^{2} J_{\mathrm{PH}}$ and ${ }^{3} J_{\mathrm{PtH}}$ coupling constants [values ranged between; ${ }^{2} J_{\mathrm{PH}}$ $2.8-1.2$ and ${ }^{3} J_{\mathrm{PtH}} 18.0-15.2 \mathrm{~Hz}$ ] whilst the $\mathrm{CH}_{2} \mathrm{P}$ protons within the spectra of 4.34 and 4.35 appeared as broad resonances.

Table 4.7 Selected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR (in $\mathrm{CDCl}_{3}$ or $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ ) [ $\delta$ in ppm, ${ }^{1} J$ in Hz ] and IR data (in $\mathrm{cm}^{-1}$ ) for 4.30-4.35.

|  | $\delta(\mathrm{P})$ | ${ }^{1} J_{\text {PtP }}$ | $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ | $\delta\left(\mathrm{COCH}_{2} \mathrm{~N}\right)$ | $\mathrm{V}_{\mathrm{PtCl}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4.30 | -6.4 | 3411 | 3.8 | 3.4 | 314, 290 |
| 4.31 | -5.0 | 3416 | 3.8 | 3.6 | 314, 291 |
| $4.32^{\mathrm{a}}$ | -8.0 | 3406 | 3.9 | 3.8 or 3.5 | 313, 291 |
| 4.33 | -11.1 | 3393 | 3.6 | 3.2 | 310, 283 |
| 4.34 | -9.3 | 3405 | 3.7 | 3.7 | 316, 296 |
| $4.35^{\mathrm{b}}$ | -9.7 | 3419 | 4.3 | 3.6 | 314, 293 |

Additional evidence in support of the cis conformation of $\mathbf{4 . 3 0} \mathbf{- 4 . 3 5}$ can be seen in the complexes infrared spectra which contain two characteristic $\mathrm{v}_{\mathrm{PtCl}}$ absorption bands, ${ }^{58,186,196}$ in addition to the anticipated peptide absorptions (values range between $v_{\mathrm{NH}} 3345-3280 \mathrm{~cm}^{-1}$, amide band I $v_{\mathrm{CO}} 1684-1618 \mathrm{~cm}^{-1}$ and amide band II $\left.v_{\mathrm{NH}} 1577-1512 \mathrm{~cm}^{-1}\right) .{ }^{194}$ The positive ion FAB mass spectroscopy results for each complex gave the expected fragmentation patterns $\left\{\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}=[\mathrm{M}-\mathrm{Cl}]^{+}\right.$ (4.30-4.35)\}, whilst the elemental analysis results were satisfactory. Additional evidence for the preparation of $\mathbf{4 . 3 0} \mathbf{- 4 . 3 2}$ and $\mathbf{4 . 3 4}$ comes from single crystal X-ray studies (Section 4.5.1.).

### 4.5.1 Molecular structures of 4.30 - $\mathbf{4 . 3 2}$ and 4.34

Colourless crystalline plates ( $\mathbf{4 . 3 0}$ and 4.34), rods (4.31) and laths (4.32), suitable for X-ray crystallography were obtained by slow vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CHCl}_{3}$ or $\mathrm{CHCl}_{3} /\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SO}(\mathbf{4 . 3 0})$ solution of the respective complex. The molecular structures of $\mathbf{4 . 3 1}$ and $\mathbf{4 . 3 2}$ were determined using synchrotron radiation, due to the small crystal size (at least one dimension $<0.05 \mathrm{~mm}$ ) and/or poorly diffracting nature, whilst the molecular structures of $\mathbf{4 . 3 0}$ and 4.34 were determined using $\operatorname{MoK} \alpha$ radiation within the home laboratory. Selected bond lengths and angles are given in Table 4.8.


Figure 4.10 Molecular structure of 4.31. All hydrogen atoms, solvent molecules of crystallisation and phosphorus phenyl carbon atoms, except the ipso carbons, have been omitted for clarity.

Figure 4.10 shows the molecular structure of $\mathbf{4 . 3 1}$ as a typical example of this family of platinum(II) complexes ( $\mathbf{4 . 3 0} \mathbf{- 4 . 3 2}$ and 4.34). The complexes were all found to adopt a distorted square planar geometry with respect to the platinum(II) centre $[\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ and $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ ranged between $176.93(15)-170.95(3) \AA]$. The ligands 4.22, 4.23, 4.25 and 4.27 coordinate to the metal centre via both phosphorus atoms, to form a six-membered cis-chelate ring [bite angle ranged between $95.80(8)-92.96(3) \AA$. In all cases, the phosphorus atoms were found to adopt a distorted tetrahedral arrangement, as indicated by the relevant $\mathrm{Pt}-\mathrm{P}-\mathrm{C}$ angles [Pt-P-C ranged between 119.2(5) - 107.4(1) $\AA$, Table 4.8]. In all cases, the nitrogen
atom $\mathrm{N}(1)$ adopted a distorted trigonal pyramidal geometry [sum of component angles ranged between $344-335^{\circ}$ respectively], whereas the nitrogen atom $\mathrm{N}(2)$ was assumed to adopt a distorted trigonal planar geometry [ $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(16)$ ranged between $128.2(2)-123.2(8)^{\circ}$, sum of component angles not possible due to $\mathrm{H}(2)$ being refined geometrically]. The carbonyl carbon, $\mathrm{C}(15)$ was found to adopted a perfect trigonal planar geometry in three out of the four complexes with $\mathrm{C}(15)$ of 4.32 adopting a near trigonal planar geometry [sum of component angles $=360^{\circ}$ (4.30, 4.31 and 4.34$)$ and $359^{\circ}(4.32)$ ].

One clear difference between the solid state structures of the four complexes is evident when considering the orientation of the planar aromatic group with respect to the platinum(II) centre. Complexes 4.32 and 4.34 were both found to contain one intramolecular hydrogen bond, $\mathrm{N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1)[\mathrm{N}(2)-\mathrm{H}(2 \mathrm{~A}) \ldots \mathrm{N}(1) ; \mathrm{N}(2) \cdots \mathrm{N}(1)$ $2.722(17)$ and $2.694(11) \AA, \mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1) 2.20$ and $2.26 \AA, \mathrm{~N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1) 110.1$ and $117.3^{\circ}$ respectively], which is thought to cause the large planar aromatic groups to be angled forwards over the platinum(II) centre, to form a "scorpion-like" conformation (Figure 4.11). Whereas, in the case of $\mathbf{4 . 3 0}$ and 4.31, no intramolecular bonding was observed, allowing the phenyl and naphthyl groups to angle away from the metal centre, thereby minimising intramolecular repulsion between the planar aromatic groups and the $\mathrm{PPh}_{2}$ groups of the complex (Figure 4.10). The conformation of the planar aromatic group also appeared to have an effect upon the carbonyl angle $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(14)$ within the peptide linker of the complexes, with the "scorpion-like" conformation displaying a significantly shorter angle than that observed in the "open" complexes [ $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(14)$ : 121.3(15) (4.30), 122.8(3) (4.31), $115.5(13)(4.32)$ and $116.7(10)(4.34)]$.



Figure 4.11 The molecular structure of 4.32 (left) and the "scorpion-like" conformation observed for $\mathbf{4 . 3 2}$ (right). All hydrogen atoms, except $\mathrm{H}(2)$, and phosphorus phenyl carbons except ipso carbons (right), have been omitted for clarity.

Inspection of the packing plots of $\mathbf{4 . 3 0}$ and $\mathbf{4 . 3 1}$ showed both complexes to contain at least one intermolecular hydrogen bond. In the crystal structure of $\mathbf{4 . 3 0}$ all three molecules of complex within the asymmetric unit were found to be involved in hydrogen bonding. Two intermolecular hydrogen bonds were found between neighbouring molecules of $\mathbf{4 . 3 0}\left[\mathrm{N}(4)-\mathrm{H}(4 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) ; \mathrm{N}(4) \cdots \mathrm{Cl}\left(1^{\prime}\right) 3.299(12) \AA\right.$, $\mathrm{H}(4 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) 2.42 \AA, \mathrm{~N}(4)-\mathrm{H}(4 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) 172^{\circ}$, symmetry operator ${ }^{\prime}=-\mathrm{x}+3 / 2$, $\mathrm{y}-1 / 2,-\mathrm{z}+1 / 2$ and $\mathrm{N}(6)-\mathrm{H}(6 \mathrm{~A}) \cdots \mathrm{Cl}(4 \mathrm{C}) ; \mathrm{N}(6) \cdots \mathrm{Cl}\left(4{ }^{\prime \prime}\right) 3.174(11) \AA \AA, \mathrm{H}(6 \mathrm{~A}) \cdots \mathrm{Cl}\left(4^{\prime \prime}\right)$ $2.33 \AA$ Å, $\mathrm{N}(6)-\mathrm{H}(6 \mathrm{~A}) \cdots \mathrm{Cl}\left(4^{\prime \prime}\right) 160^{\circ}$, symmetry operator " $\left.=\mathrm{x}+1 / 2,-\mathrm{y}+1 / 2, \mathrm{z}+1 / 2\right]$, whilst a third intermolecular hydrogen bond was found within the same asymmetric unit between a molecule of 4.30 and a $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SO}$ of crystallisation $[\mathrm{N}(2)-\mathrm{H}(2) \cdots \mathrm{O}(4)$; $\left.\mathrm{N}(2) \cdots \mathrm{O}(4) 2.90(2) \AA, \mathrm{H}(2) \cdots \mathrm{O}(4) 2.04 \AA, \mathrm{~N}(2)-\mathrm{H}(2) \cdots \mathrm{O}(4) 169^{\circ}\right]$ (Figure 4.12).


Figure 4.12 The intermolecular hydrogen bonding of 4.30. Hydrogen atoms except those involved in hydrogen bonding have been removed for clarity. Symmetry operations for equivalent atoms; ' $=-\mathrm{x}+3 / 2, \mathrm{y}-1 / 2,-\mathrm{z}+1 / 2 ;{ }^{\prime}=\mathrm{x}+1 / 2,-\mathrm{y}+1 / 2, \mathrm{z}+1 / 2$.

The crystal structure of 4.31 was found to contain one weak intermolecular hydrogen bond between neighbouring molecules of $4.31\left[\mathrm{~N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) ; \mathrm{N}(2) \cdots \mathrm{Cl}\left(1^{\prime}\right)\right.$ $3.627(3) \AA, \mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) 3.26 \AA, \mathrm{~N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right) 108^{\circ}$, symmetry operator ${ }^{\prime}=$ $x+1, y, z]$. Further analysis of this intermolecular packing showed the hydrogen bond, $\mathrm{N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{Cl}\left(1^{\prime}\right)$, gives rise to continuous chains of 4.31 , which run along the $a$-axis within the crystal lattice (Figure 4.13). No notable intermolecular packing was observed for $\mathbf{4 . 3 2}$ or $\mathbf{4 . 3 4}$.


Figure 4.13 Intermolecular chains in 4.31. Hydrogen atoms not involved in hydrogen bonding and solvent molecules of crystallisation have been removed for clarity. Symmetry operator ' $=x+1, y, z$.
Table 4.8 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $\mathbf{4 . 3 0} \mathbf{- 4 . 3 2}$ and $\mathbf{4 . 3 4}$.

|  | 4.30 | 4.31 | 4.32 | 4.34 |  | 4.30 | 4.31 | 4.32 | 4.34 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | $2.230(4)$ | 2.2306(7) | 2.238(3) | $2.2143(13)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 176.93(15) | 170.95(3) | 174.10(14) | 175.91(5) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | 2.230(4) | 2.2346 (8) | 2.228(3) | $2.2143(13)^{\text {a }}$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 175.33(14) | 176.90(3) | 173.24(13) | $175.91(5)^{\text {a }}$ |
| $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 2.357(4) | 2.3611(7) | $2.356(3)$ | $2.3406(12)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(1)$ | 88.49(14) | 90.13(3) | 89.56(13) | 87.57(5) |
| $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $2.355(4)$ | $2.3586(8)$ | 2.359(3) | $2.3406(12)^{\text {a }}$ | $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | $88.98(14)$ | 89.23(3) | 86.40(13) | $87.57(5)^{\text {a }}$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | 1.811(16) | 1.807(3) | 1.837(15) | 1.807(6) | $\mathrm{Cl}(1)-\mathrm{Pt}(1)-\mathrm{Cl}(2)$ | 89.02(13) | 87.68(3) | 88.04(13) | $88.97(6)^{\mathrm{a}}$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | 1.822(17) | 1.814(3) | 1.821(14) | $1.814(5)$ | $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 93.37(14) | 92.96(3) | 95.61(13) | $95.80(8)^{\text {a }}$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.826(14) | 1.844(3) | 1.837(13) | 1.806(6) | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 113.6(5) | 115.30(10) | 119.2(5) | 114.3(2) |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | 1.467(18) | 1.448(4) | 1.475(18) | 1.488(8) | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 113.6(5) | 107.36(11) | 108.7(5) | 112.78(19) |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | 1.448(18) | 1.457(3) | 1.465(18) | 1.477(11) | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pt}(1)$ | 115.3(5) | 116.76(10) | 116.9(5) | 117.1(2) |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | 1.51(2) | $1.535(4)$ | 1.53(2) | 1.464(14) | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | 110.0(9) | 110.6(2) | 114.5(9) | 111.0(4) |
| $\mathrm{C}(15)-\mathrm{O}(1)$ | 1.22(2) | $1.219(4)$ | 1.185(18) | 1.180(12) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | 114.8(12) | 116.2(2) | 112.0(11) | 112.0(4) |
| $\mathrm{C}(15)-\mathrm{N}(2)$ | 1.35(2) | 1.347(4) | 1.306(19) | 1.360(12) | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(\mathrm{X})^{\mathrm{b}}$ | 112.8(12) | 113.6(2) | 109.7(11) | 110.7(7) |
| $\mathrm{N}(2)-\mathrm{C}(16)$ | 1.43(2) | $1.423(4)$ | 1.427(18) | 1.367(13) | $\mathrm{C}(14)-\mathrm{N}(1)-\mathrm{C}(\mathrm{X})^{\mathrm{b}}$ | 114.7(12) | 113.8(2) | 113.6(11) | 112.0(4) |
| $\mathrm{N}(1)-\mathrm{C}(\mathrm{X})^{\mathrm{b}}$ | 1.471(19) | $1.459(4)$ | 1.438(18) | 1.488(8) | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | 115.0(14) | 114.8(2) | 115.6(11) | 115.2(8) |
|  |  |  |  |  | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(14)$ | $121.3(15)$ | 122.8(3) | $115.5(13)$ | $116.7(10)$ |
|  |  |  |  |  | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{N}(2)$ | 124.6(16) | 125.1(3) | 133.2(15) | 127.2(9) |
|  |  |  |  |  | $\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{C}(14)$ | 114.1(15) | 112.1(3) | 110.5(12) | 116.1(8) |
|  |  |  |  |  | $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(16)$ | 128.2(17) | 126.3(3) | 125.2(12) | 123.2(8) |

[^8]
### 4.5.2 Palladium(II) Coordination Chemistry of 4.28

The coordination chemistry of $\mathbf{4 . 2 8}$ was explored further. To this end, displacement of cod from $\mathrm{PdCl}_{2}(\mathrm{cod})$ or $\mathrm{Pd}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod})$ with one equiv. of 4.28 , yielded complexes 4.36 and 4.37 in good yield. (Equation 4.6).


Equation 4.6
The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra (in $\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)$ of 4.36 and 4.37 fully supported the $\mathrm{P}, \mathrm{P}-$ chelation of the respective palladium(II) centres by 4.28, due to the downfield shift in ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR signal compared with that of the free ligand $[\delta(\mathrm{P})-26.7 \mathrm{ppm}(4.28)$, in $\mathrm{CDCl}_{3} ; \delta(\mathrm{P})$ ranged between 22.6 to $-11.0 \mathrm{ppm}(4.36$ and 4.37$)$, in $\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right]$. As anticipated the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of $\mathbf{4 . 3 6}$ contained a singlet resonance at $\delta(\mathrm{P})$ 6.0 ppm , indicative of a symmetrical coordination centre. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of 4.37 however was found to be more complex than expected, with three resonances being observed at $\delta(\mathrm{P}) 22.6,6.0$ and -11.0 ppm . The signals at $\delta(\mathrm{P}) 22.6$ and -11.0 ppm both appeared as doublets, with equal integrals and coupling constant ( ${ }^{2} J_{\mathrm{PP}} 48.6 \mathrm{~Hz}$ ) and were assigned to 4.37 , by virtue of the unsymmetrical nature of the expected coordination centre. The third minor resonance appeared as a singlet at $\delta(\mathrm{P}) 6.0 \mathrm{ppm}$ and was assigned to the cis-palladium dichloride complex 4.36 by direct comparison with the previously discussed ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data $[\Delta \delta(\mathrm{H}) 0.04$ $\mathrm{ppm}]$. The inadvertent preparation of $\mathbf{4 . 3 6}$ during the synthesis of 4.37 is thought to be due to the evolution of methane from the palladium(II) centre, an effect that can be tentatively attributed to trace amounts of HCl in the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solvent. The ${ }^{1} \mathrm{H}$ NMR spectra of 4.36 and 4.37 both show distinct resonances relating to the methylene protons within the two complexes $[\delta(\mathrm{H}) 4.2-3.2 \mathrm{ppm}]$, in addition to the $\mathrm{Pd}-\mathrm{CH}_{3}$
protons in the case of $\mathbf{4 . 3 7}[\delta(\mathrm{H}) 0.1 \mathrm{ppm}$, bs]. The unsymmetrical nature of 4.37 was inferred further from the ${ }^{1} \mathrm{H}$ NMR spectrum which showed two independent $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ singlets, compared with the single resonance observed in the ${ }^{1} \mathrm{H}$ NMR spectrum of $4.36\left[\delta(\mathrm{H}) 4.16\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)(4.36), 3.94\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)\right.$ and $3.80 \mathrm{ppm}(\mathrm{bs}, 2 \mathrm{H}$, $\left.\left.\mathrm{CH}_{2} \mathrm{P}\right)(4.37)\right]$. Furthermore the positive ion FAB mass spectroscopy data for each complex gave the expected fragmentation patterns $\left[\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 771[\mathrm{M}-\mathrm{Cl}]^{+}\right.$ (4.36) and $771\left[\mathrm{M}-\mathrm{CH}_{3}\right]^{+}$(4.37)], whilst the elemental analysis results were satisfactory. The molecular structure of 4.37 has also been determined (Section 4.5.2.1).

### 4.5.2.1 Molecular structure of 4.37

Colourless crystalline plates, suitable for X-ray crystallography, were obtained by slow vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 4.37 (Figure 4.14, selected bond lengths and angles are given in Table 4.9).


Figure 4.14 Molecular structure of 4.37 (left); and the "scorpion-like" conformation observed for 4.37 (right). Symmetry operator for equivalent atoms ' $=x,-y+1 / 2, z$. $\mathrm{C}(26)$ and $\mathrm{Cl}(1)$ occupancy symmetry imposed to 50:50.

The molecular structure of 4.37 shows the complex to lie on a mirror plane which bisects the palladium(II) centre and the $\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{O}_{2}\right) \mathrm{NHCOCH}_{2} \mathrm{~N}$ moiety. As a result the asymmetric unit was found to contain half a molecule of 4.37. The palladium centre was coordinated, within the asymmetric unit, by a phosphorus atom from 4.28 and an auxiliary ligand. The auxiliary ligand site was found to be two fold disordered with the expected methyl and chloride groups being freely interchanged [C(26) and $\mathrm{Cl}(1)$ occupancy symmetry imposed to $50: 50]$. The remaining half of the six membered cis-chelate ring of 4.37 was generated by symmetry [symmetry operations for equivalent atoms, $\left.{ }^{\prime}=x,-y+1 / 2, z\right]$ (Figure 4.15). The geometry with respect to the palladium(II) centre was found to be distorted square planar, $[\mathrm{P}(1)-$ $\operatorname{Pd}(1)-\mathrm{Cl}(1) / \mathrm{C}(26)=173.99(6) \AA]$. The phosphorus atom $\mathrm{P}(1)$ adopts a distorted tetrahedral geometry $[\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pd}(1) 116.5(2), \mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pd}(1) 112.48(17)$ and $\left.\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pd}(1) 115.86(19)^{\circ}\right]$. The nitrogen atom $\mathrm{N}(1)$ was found to adopt a distorted trigonal pyramidal geometry [sum of component angles $=335^{\circ}$ ]. The carbonyl carbons $\mathrm{C}(15)$ and $\mathrm{C}(19)$ were both found to adopt a trigonal planar geometry [sum of component angles $=360^{\circ}$ ]. The bond lengths and angles about the palladium(II) centre and peptide group were broadly as anticipated and similar to those observed for the analogous platinum(II) complexes 4.30, 4.31, 4.32 and 4.34 (Section 4.5.1). ${ }^{274}$ The molecular structure also showed 4.37 to adopt the same "scorpion-like" conformation observed in solid state structures of 4.32 and 4.34 (Section 4.5.1), via formation of an intramolecular hydrogen bond $\mathrm{N}(2)-$ $\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1)\left[\mathrm{N}(2) \cdots \mathrm{N}(1) 2.756(9) \AA, \mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1) 2.27 \AA, \mathrm{~N}(2)-\mathrm{H}(2 \mathrm{~A}) \cdots \mathrm{N}(1) 114^{\circ}\right]$ (Figure 4.14, right).

Table 4.9 Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4.37 .

| $\mathrm{Pd}(1)-\mathrm{P}(1)$ | $2.2963(13)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $173.99(6)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pd}(1)-\mathrm{Cl}(1) / \mathrm{C}(26)$ | $2.3579(19)$ | $\mathrm{P}(1)-\mathrm{Pd}(1)-\mathrm{P}\left(1^{\prime}\right)$ | $95.02(7)$ |
| $\mathrm{P}(1)-\mathrm{C}(1)$ | $1.836(6)$ | $\mathrm{P}\left(1^{\prime}\right)-\mathrm{Pd}(1)-\mathrm{Cl}(1)$ | $88.06(6)$ |
| $\mathrm{P}(1)-\mathrm{C}(7)$ | $1.840(5)$ | $\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{Cl}\left(1^{\prime}\right)$ | $88.43(9)$ |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | $1.868(6)$ | $\mathrm{C}(1)-\mathrm{P}(1)-\mathrm{Pd}(1)$ | $116.5(2)$ |
| $\mathrm{N}(1)-\mathrm{C}(13)$ | $1.475(7)$ | $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{Pd}(1)$ | $112.48(17)$ |
| $\mathrm{N}(1)-\mathrm{C}(14)$ | $1.489(10)$ | $\mathrm{C}(13)-\mathrm{P}(1)-\mathrm{Pd}(1)$ | $115.86(19)$ |
| $\mathrm{N}(1)-\mathrm{C}\left(13^{\prime}\right)$ | $1.475(7)$ | $\mathrm{N}(1)-\mathrm{C}(13)-\mathrm{P}(1)$ | $110.8(4)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.520(11)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}(14)$ | $111.7(4)$ |
| $\mathrm{C}(15)-\mathrm{O}(1)$ | $1.236(9)$ | $\mathrm{C}(13)-\mathrm{N}(1)-\mathrm{C}\left(13^{\prime}\right)$ | $111.6(6)$ |
| $\mathrm{C}(15)-\mathrm{N}(2)$ | $1.365(10)$ | $\mathrm{N}(1)-\mathrm{C}(14)-\mathrm{C}(15)$ | $115.0(7)$ |
| $\mathrm{N}(2)-\mathrm{C}(16)$ | $1.422(9)$ | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{C}(14)$ | $119.4(7)$ |
| $\mathrm{O}(2)-\mathrm{C}(19)$ | $1.380(10)$ | $\mathrm{O}(1)-\mathrm{C}(15)-\mathrm{N}(2)$ | $124.4(7)$ |
| $\mathrm{C}(19)-\mathrm{O}(3)$ | $1.254(12)$ | $\mathrm{N}(2)-\mathrm{C}(15)-\mathrm{C}(14)$ | $116.2(6)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | $1.450(15)$ | $\mathrm{C}(15)-\mathrm{N}(2)-\mathrm{C}(16)$ | $129.7(6)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | $1.367(14)$ | $\mathrm{O}(2)-\mathrm{C}(19)-\mathrm{O}(3)$ | $115.7(10)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | $1.505(15)$ | $\mathrm{O}(3)-\mathrm{C}(19)-\mathrm{C}(20)$ | $126.0(8)$ |
|  |  | $\mathrm{O}(2)-\mathrm{C}(19)-\mathrm{C}(20)$ | $118.3(8)$ |
|  |  | $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $122.9(9)$ |
|  |  | $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(23)$ | $118.2(9)$ |

Symmetry operations for equivalent atoms ' $=x,-y+1 / 2, z$.

### 4.5.3 Ruthenium(II) Coordination Chemistry of 4.22, 4.23, 4.25 and 4.27

Ruthenium piano-stool complexes have also been shown to have biological relevance with regard to cytotoxicity to cancer cell lines. ${ }^{275,276}$ Hence ligands 4.22, 4.23, 4.25 and 4.27 were coordinated to ruthenium(II) centres via the bridge cleavage reaction of $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}$, to form the bimetallic complexes $4.38-4.41$ in good yield (yields ranged between 59 - 89\%) (Equation 4.7).



Equation 4.7

The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of complexes $\mathbf{4 . 3 8} \mathbf{- 4 . 4 1}$ (in $\mathrm{CDCl}_{3}$ ) all showed a new characteristic major singlet ranging between $\delta(\mathrm{P}) 16.5-18.3 \mathrm{ppm}, c a . \delta(\mathrm{P}) 44 \mathrm{ppm}$ downfield compared with that of the free ligand $[c a . \delta(\mathrm{P})-26 \mathrm{ppm}] .{ }^{22,58}$ The ${ }^{1} \mathrm{H}$ NMR spectra of 4.38 - $\mathbf{4 . 4 1}$ all showed well resolved distinct resonances relating to the $p$-cym ancillary ligand, in addition to characteristic $\delta\left(\mathrm{CH}_{2}\right)$ resonances $[c a . \delta(\mathrm{H})$ 4.0 and 2.7 ppm (Table 4.10). ${ }^{22,58}$

Table 4.10 ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\},{ }^{1} \mathrm{H}$ NMR (in $\mathrm{CDCl}_{3}$ ) $\left[\delta(\mathrm{P})\right.$ in ppm] and IR $\left[v\right.$ in $\left.\mathrm{cm}^{-1}\right]$ data ${ }^{\text {a }}$ for 4.38-4.41.

|  | $\delta(\mathrm{P})$ | $\delta\left(\mathrm{CH}_{2} \mathrm{P}\right)$ | $\delta\left(\mathrm{COCH}_{2} \mathrm{~N}\right)$ | $v_{\mathrm{RuCl}}$ | $v_{\mathrm{NH}}$ | $v_{\mathrm{CO}}{ }^{\mathrm{c}}$ | $v_{\mathrm{NH}}{ }^{\mathrm{d}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{4 . 3 8}$ | 16.5 | 3.9 | 2.5 | 291 | 3283 | 1684 | 1522 |
| $\mathbf{4 . 3 9}$ | 18.3 | 4.0 | 2.9 | 290 | 3314 | 1692 | 1509 |
| $\mathbf{4 . 4 0}$ | 16.9 | 3.9 | 2.6 | 291 | 3281 | 1686 | 1520 |
| $\mathbf{4 . 4 1}^{\mathrm{b}}$ | 17.2 | 4.0 | 2.6 | 290 | 3272 | 1676 | 1528 |

${ }^{a}$ Recorded as KBr pellet.
${ }^{\mathrm{b}}$ The complex was found to be impure as judged by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR.
${ }^{\mathrm{c}}$ Amide band I. ${ }^{\mathrm{d}}$ Amide band II.

In the case of 4.41 three minor singlets were also observed in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum $[\delta(\mathrm{P}) 15.6,-26.3$ and $-28.6 \mathrm{ppm}]$. The resonance at $\delta(\mathrm{P})-26.3 \mathrm{ppm}$ was found to correspond to the free ligand $4.27[\delta(\mathrm{P})-26.3 \mathrm{ppm}]$, by direct comparison of the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra. The remaining two species were of similar integration but significantly different chemical shift [ $\Delta \delta(\mathrm{P}) 44.2 \mathrm{ppm}]$. One tentative suggestion towards the assignment of these two resonances, is the presence of the intermediate monometallic complex 4.41a (Figure 4.15) within the isolated solid.


Figure 4.15 Speculated product (4.41a) observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, in addition to 4.41 and 4.27 .

The preparation of 4.41a is in agreement with the seemingly incomplete nature of the reaction (unreacted 4.27 observed by ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy), in addition to the large difference in $\delta(\mathrm{P})$ between the two unassigned resonances and their similar integrals [ratio $\mathrm{P}_{\mathrm{A}}: \mathrm{P}_{\mathrm{B}}=1: 1, \mathrm{P}_{\mathrm{A}}=$ coordinated phosphorus atom, $\mathrm{P}_{\mathrm{B}}=$ uncoordinated phosphorus atom]. However, the occurrence of 4.41a is not supported by the splitting
patterns of the inequivalent phosphorus environments $\mathrm{P}_{\mathrm{A}}$ and $\mathrm{P}_{\mathrm{B}}$, as both appear as singlets. Unfortunately a search of the literature revealed no similar ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR effects or examples of unsymmetrical monometallic ditertiary phosphine complexes.

The infrared spectra of $\mathbf{4 . 3 8} \mathbf{- 4 . 4 1}$ contained the anticipated peptide absorption bands (Table 4.10). ${ }^{194}$ Further support for the preparation of $\mathbf{4 . 3 8} \mathbf{- 4 . 4 1}$ comes from the positive ion FAB mass spectra, which contained the expected fragmentation patterns $\left[\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}=[\mathrm{M}-\mathrm{Cl}]^{+}\right]$. Further characterisation data can be found in the Experimental Section.

### 4.6 Conclusion

In conclusion a range of functionalised tertiary phosphines of the form (R)N(CH2 $\left.\mathrm{PPh}_{2}\right)_{2}$ and (R)NHCOCH $\mathrm{N}_{2}\left(\mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{2} \quad(\mathrm{R}=$ functionalised planar aromatic or ferrocenyl group) have been prepared and characterised. Whilst study into the biological properties of this series of compounds is required, the novel phosphines were coordinated to anticancer relevant transition metals [platinum(II) and ruthenium(II)] to afford examples of $\mathrm{P}, \mathrm{P}$-chelates and bimetallic complexes with "potential" biological applications.

## Chapter 5

## Conclusion

### 5.1 General Conclusions

To date, tertiary phosphines have played important roles in numerous areas of industrial and academic significance ranging from catalysts for a wide range of organic transformations, to reagents used within selective metal extraction and building blocks used in supramolecular chemistry. During the course of this research a wide range of new tertiary phosphines with polyaromatic and ferrocenyl appendages have been prepared via an efficient Mannich-based condensation reaction. The design of these new phosphorus ligands was intentionally tailored towards preparing new compounds that have potential application within some seemingly neglected area of phosphorus based chemistry, such as; photochemical and electrochemical sensors, anticancer drugs and novel coordination compounds such as trans-spanning diphosphines.

Chapter 2 discussed a range of new mono- and bidentate tertiary phosphines with polyaromatic appendages, with the emphasis being on the preparation of new phosphorus based photochemical devices and some novel coordination compounds. In particular the coordination chemistry of $\mathbf{2 . 1} \mathbf{- 2 . 4}$ was extensively studied and revealed this family of ditertary phosphines to be capable of bridging two transition metal centres as well as forming new examples of rare, nine-membered cis- and trans- chelate complexes. Variation of the chemistry used to prepare 2.1 - 2.4 also allowed the synthesis of two analogous monophosphines 2.23 and 2.24. The luminescent properties of selected compounds was also discussed, along with a preliminary investigation into the chemosensor behaviour of the platinum(II) complexes 2.9, 2.10, $\mathbf{2 . 2 6}$ and 2.27. Whilst time did not allow for an extensive study of these compounds against a range of analytes (anions/cations/small molecules), the fluorescent emission spectra of $\mathbf{2 . 2 7}$ was found to be significantly affected by the presence of metal cations $\left(\mathrm{Fe}^{3+}, \mathrm{Na}^{+}\right.$and $\left.\mathrm{Cu}^{2+}\right)$, with both variation of PET and the formation of excimer emitting complexes being observed. Further study into the chemosensory properties of all the tertiary phosphines and coordination compounds reported in this chapter is required, however these preliminary findings show promise towards the potential preparation of rare phosphorus-based molecular devices.

In chapter 3, a series of new mono- and bidentate tertiary phosphines with electrochemically active ferrocenyl appendages were presented. The aim of this chapter was to prepare new examples of phosphorus based electrochemical devices and to explore the coordination chemistry of this family of ligands. In particular, the coordination chemistry of $\mathbf{3 . 1}$ was extensively studied and revealed the phosphine to be capable of bridging two transition metal centres either dimerically or monomerically, as well as showing that the ligand could form new examples of cis and trans chelate complexes. Variations of the chemistry used to prepare 3.1-3.3, allowed the synthesis of a new trimetallo-diphosphine $\mathbf{3 . 1 6}$ in addition to the new monophosphines $\mathbf{3 . 1 4}$ and $\mathbf{3 . 2 0}$ - 3.22. Unfortunately, investigation of the electrochemical properties of the majority of compounds discussed in this chapter, by cyclic voltammetry, revealed no significant change in the Fe (II)/Fe(III) redox couple, suggesting that the $\mathrm{Fe}(\mathrm{II}) /(\mathrm{III})$ centres were unaffected by synthetic variation around the ferrocenyl group. One area of further study would be to introduce an analyte (anion/cation/small molecule) to solutions of some of the compounds reported in this chapter and to investigate any resulting chemosensory behaviour.

Chapter 4 described the preparation of functionalised tertiary phosphines bearing polyaromatic groups and their coordination to anticancer relevant metals $\left(\mathrm{Pt}^{2+}\right.$ and $\left.\mathrm{Ru}^{2+}\right)$. The idea behind this work was to prepare coordination complexes that had the potential of acting as anti-cancer drugs through combination chemotherapy. The successful preparation and characterisation of the ligands, and their subsequent coordination complexes, was accomplished. Future work would involve seeking collaborations for in-vitro or -vivo testing against cancer cell lines.

In closing, this research represents a significant contribution to the library of novel tertiary phosphines, and coordination compounds, that have been prepared using a Mannich-based condensation reaction, and whilst there is clearly further work required in the key areas of photo- / electro-chemical sensing and anticancer drugs, this work clearly provides a strong starting point from which future research can be based.

Chapter 6
Experimental

### 6.1 General Experimental

Unless otherwise stated all preparations of tertiary phosphines were carried out under an inert atmosphere, using standard Schlenk techniques, degassed solvents and freeze-thaw cycles where necessary. All reagents and solvents were purchased from Acros, Aldrich or Alfa Aesar and were used as received. Diethyl ether, toluene and tetrahydrofuran were distilled over sodium / benzophenone under a nitrogen atmosphere, whilst dichloromethane and acetonitrile were distilled over calcium hydride under a nitrogen atmosphere. The metal complexes $\mathrm{PtCl}_{2}(\operatorname{cod}),{ }^{277,278}$ $\mathrm{PtMe}_{2}(\mathrm{cod}),{ }^{279} \quad \mathrm{PdCl}_{2}(\mathrm{cod}),{ }^{277,278} \quad \mathrm{Pd}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod}),{ }^{280} \quad\{\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})\}_{2},{ }^{281}$ $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd}), \mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{nbd})^{282}$ and $\mathrm{AuCl}(\text { tht })^{283}$ were synthesised according to literature methods. The functionalised tertiary phosphine synthon $\mathrm{PRCH}_{2} \mathrm{OH}(\mathrm{PR}=$ $\mathrm{PPh}_{2}, \mathrm{PCy}_{2}$ or PAd ) was preformed from equimolar amounts of the respective secondary phosphine and $\left(\mathrm{CH}_{2} \mathrm{O}\right)_{\mathrm{n}}$ according to literature methods. ${ }^{58,284}$

### 6.2 Instrumental

All ${ }^{1} \mathrm{H}$ NMR spectra were recorded in $\mathrm{CDCl}_{3},\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ or $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ unless otherwise stated on a Bruker DPX-400 FT spectrometer with chemical shifts ( $\delta$ ) in ppm to high frequency of $\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{4}$ and coupling constants $(J)$ in $\mathrm{Hz} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts ( $\delta$ ) in ppm to high frequency of $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$. Infrared spectra were recorded within the range of $4000-200 \mathrm{~cm}^{-1}$ using a Perkin-Elmer 2000 FTIR spectrometer or on a Shimadzu 8300 FTIR spectrometer within the range of $4000-390 \mathrm{~cm}^{-1}$. Elemental analyses were carried out by the Loughborough University Analytical Service on PerkinElmer 2400 CHN or on Exeter Analytical Inc. CE-440 elemental analyzers. Mass spectra were recorded within the Chemistry Department by the Loughborough University Analytical Service or externally by the EPSRC National Mass Spectrometry Service at Swansea University.

### 6.3 Electrochemistry

Cyclic voltammetric measurements were carried out on a EG\&G Model PAR 263A potentiostat / galvanostat using a standard electrochemical cell consisting of a Pt disc working electrode $(\mathrm{d}=1.6 \mathrm{~mm}), \mathrm{Ag} / \mathrm{AgCl}$ reference electrode in a 3 M NaCl solution and a Pt gauze counter electrode at a scan rate of $50 \mathrm{mV} / \mathrm{s}$. All measurements were performed at ambient temperature $\left(22 \pm 1{ }^{\circ} \mathrm{C}\right)$ in dry, nitrogen bubbled $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions containing analyte $(100 \mu \mathrm{M})$ and $\left[\mathrm{NBu}_{4}\right]\left[\mathrm{BF}_{4}\right](0.1 \mathrm{M})$ as the supporting electrolyte. Ferrocene was used as an external standard.

### 6.4 Photochemistry

Ground state absorption spectra were measured using a Hewlett Packard 8453 single beam photodiode array spectrometer. Steady state luminescence measurements were carried out using a Spex FluoroMax spectrofluorophotometer. All absorption and luminescence measurements were performed using a standard quartz fluorescence cell at ambient temperature $\left(22 \pm 2^{\circ} \mathrm{C}\right)$, in dry THF solutions containing analyte (2.5 and $5 \mu \mathrm{M}$ ). All quantum yields ( $\Phi$ ) were calculated using matched absorbance's relative to the integrated emission of an external standard of quinine sulfate (in 0.1 M $\mathrm{H}_{2} \mathrm{SO}_{4}, \Phi=0.58$ ), at room temperature. All quantum yield measurements were conducted using nitrogen bubbled solutions.

### 6.5 X-ray Crystallography

Measurements were made using a variety of diffractometers and radiation sources in the home laboratory, at Daresbury Laboratory SRS and by the EPSRC National Service in Southampton (see Appendix for specific details). The use of synchrotron radiation at Daresbury SRS (stations 9.8 and 16.2 SMX) is of particular note, as the far greater beam flux provided by synchrotron radiation allowed the characterisation of many samples where the crystals would not have been analysed at the home laboratory due to their small size (at least one dimension $<0.05 \mathrm{~mm}$ ) and/or poorly diffracting nature. All data collections were performed at low temperature (120 - 150
K) using a single crystal coated in an inert oil mounted on a glass fibre. Each data collection was conducted in two stages; firstly the determination of the orientation matrix, unit cell and crystal system and secondly a longer data collection to measure either the full sphere or hemisphere of the total diffraction pattern. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. Structures were solved by direct methods or by Patterson synthesis and were refined on $F^{2}$ values for all unique data by full-matrix least squares. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Programs used were COLLECT, ${ }^{285}$ Bruker AXS SMART ${ }^{286}$ or APEX $2^{287}$ for diffractometer control and DENZO or SAINT for frame integration, ${ }^{286,288}$ Bruker SHELXTL ${ }^{250}$ for structure solution, refinement, and molecular graphics and local programs. Platon ${ }^{229}$ was used to model highly disordered molecules as diffuse regions of electron density (SQUEEZE procedure). Cell-now and Twinabs ${ }^{289}$ were used along with SAINT and Bruker SHELXTL to index, integrate, and absorption correct twinned datasets, with the structure being solved and refined with approximately detwinned (SHELXL-97 hklf 4 format reflection data) or multiple diffraction data files (SHELXL-97 hklf 5 format reflection data). See appendix for summarised data tables relating to each molecular structure discussed, in addition to details of individual molecular refinements. See enclosed CD for complete data tables (.rtf files) and .res files relating to each molecular structure.

### 6.6 Chapter 2 Experimental

6.6.1 Preparation of the bidentate ligands 2.1 - 2.4.

The following precursor amines and imines were prepared by slight modification to the known method reported by Zhang et al. ${ }^{187}$
$\left\{\mathbf{P h C} \mathbf{( H ) N C H} \mathbf{N}_{2}\right.$ A solution of ethylenediamine ( $0.300 \mathrm{~g}, 4.943 \mathrm{mmol}$ ) in MeOH ( 5 $\mathrm{cm}^{3}$ ) was added dropwise to a refluxing solution of benzaldehyde ( $1.059 \mathrm{~g}, 9.879$ $\mathrm{mmol})$ in $\mathrm{MeOH}\left(50 \mathrm{~cm}^{3}\right)$. The mixture was stirred at reflux for 4 h to afford a pale yellow solution. The solvent was evaporated under reduced pressure. Yield: 1.147 g , $98 \% .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.21(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CHN}), 7.64-7.28$ (m, 10H, arom. H), 3.90
(s, 4H, $\mathrm{CH}_{2}$ ). $\mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{C}=\mathrm{N}} 1642 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 237[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{~N}_{2}$ requires C, 81.32; H, 6.82; N, 11.85. Found: C, 80.68; H, 6.87; N, 11.79\%.
$\left.\left\{\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{7}} \mathbf{C} \mathbf{C} \mathbf{H}\right) \mathbf{N C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \quad$ 1-Naphthalenecarboxaldehyde ( $\left.1.004 \mathrm{~g}, 6.100 \mathrm{mmol}\right)$, ethylenediamine ( $0.185 \mathrm{~g}, 3.054 \mathrm{mmol})$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ 8.96 (s, 2H, CHN), $8.80-7.35\left(\mathrm{~m}, 14 \mathrm{H}\right.$, arom. H), $4.19\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$. FT-IR ( KBr ): $v_{\mathrm{C}=\mathrm{N}} 1631 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $337[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{~N}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 83.45; H, 6.13; N, 8.11. Found: C, 83.82; H, 5.95; N, 7.91\%.
$\left.\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C} \mathbf{C} \mathbf{H}\right) \mathbf{N C H}_{\mathbf{2}}\right\}_{\mathbf{2}}$ A solution of ethylenediamine $(0.144 \mathrm{~g}, 2.379 \mathrm{mmol})$ in MeOH $\left(5 \mathrm{~cm}^{3}\right)$ was added dropwise to a refluxing solution of anthracene-9-carboxaldehyde $(1.011 \mathrm{~g}, 4.756 \mathrm{mmol})$ in $\mathrm{DMF} / \mathrm{MeOH}\left(1: 5,60 \mathrm{~cm}^{3}\right)$. The resulting yellow suspension was refluxed for 4 h . The yellow precipitate was filtered under reduced pressure and washed with MeOH . Yield: $0.974 \mathrm{~g}, 94 \% .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 9.51$ ( s , 2H, CHN), 8.47 - 7.13 (m, 18H, arom. H), 4.46 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}}$ $1638 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{32} \mathrm{H}_{24} \mathrm{~N}_{2} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 87.14; H, 5.60; N, 6.35 . Found: C, 87.16; H, 5.53; N, 6.26\%.
$\left.\left\{\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}} \mathbf{C} \mathbf{C} \mathbf{H}\right) \mathbf{N C H}_{\mathbf{2}}\right\}_{\mathbf{2}}$ Pyrene-1-carboxaldehyde ( $\left.1.111 \mathrm{~g}, 4.825 \mathrm{mmol}\right)$ and ethylenediamine ( $0.145 \mathrm{~g}, 2.41 \mathrm{mmol}$ ). Yield: $1.101 \mathrm{~g}, 94 \%$. $\mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{C}=\mathrm{N}} 1626$ $\mathrm{cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{36} \mathrm{H}_{24} \mathrm{~N}_{2}$ requires C, 89.23; H, 4.99; N, 5.78. Found: C, 89.50; H, 5.31; N, 5.87\%.
$\left\{\mathbf{P h C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathrm{NaBH}_{4}(0.999 \mathrm{~g}, 25.9 \mathrm{mmol})$ was added in ca. 0.1 g portions to a stirred solution of the respective imine ( $1.002 \mathrm{~g}, 4.240 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{abs}$. EtOH ( $120 \mathrm{~cm}^{3}, 80: 40$ ). The resulting suspension was refluxed for 4 h under a $\mathrm{N}_{2}$ atmosphere before cooling to RT to afford a yellow solution. Concentrated HCl was added dropwise until effervescence subsided, at which point the solvent was evaporated under reduced pressure and a NaOH solution $\left(2.5 \mathrm{~g}, 60 \mathrm{~cm}^{3}\right)$ added. The resulting suspension was stirred briefly before the organic phase was extracted into $\mathrm{CHCl}_{3}\left(60 \mathrm{~cm}^{3}\right)$, dried over anhydrous $\mathrm{MgSO}_{4}$ and the solvent evaporated under reduced pressure. Yield: 1.059 g , Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.29-7.14$ (m,

10 H , arom. H), 3.70 (s, 4H, $\mathrm{NCH}_{2}$ ), 2.69 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{PhCH}_{2} \mathrm{~N}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3301$ $\mathrm{cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $241[\mathrm{M}+\mathrm{H}]^{+}$.
$\left.\left\{\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{7}} \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{N} \mathbf{H}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathrm{NaBH}_{4}(0.655 \mathrm{~g}, 17.0 \mathrm{mmol})$ and the respective imine ( 0.951 $\mathrm{g}, 2.83 \mathrm{mmol})$. Yield: $0.947 \mathrm{~g}, 99 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.04-6.59(\mathrm{~m}, 14 \mathrm{H}$, arom. $\mathrm{H}), 4.13\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 2.83\left(\mathrm{~s}, 4 \mathrm{H},\left(\mathrm{C}_{10} \mathrm{H}_{7}\right) \mathrm{CH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3288 \mathrm{~cm}^{-1}$. MS (FAB ${ }^{+}$): m/z $341[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{~N}_{2} \cdot 1.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 79.41 ; H, 7.36; N, 7.72. Found: C, 79.48; H, 6.99; N, 7.50\%.
$\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathrm{NaBH}_{4}(0.502 \mathrm{~g}, 13.0 \mathrm{mmol})$ and the respective imine ( 0.931 $\mathrm{g}, 2.13 \mathrm{mmol})$. Yield: $0.904 \mathrm{~g}, 96 \%{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.34-7.39(\mathrm{~m}, 18 \mathrm{H}$, arom. $\mathrm{H}), 4.71\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.07\left(\mathrm{~s}, 4 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3326 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $441[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{32} \mathrm{H}_{28} \mathrm{~N}_{2} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$ requires C, 84.64; H, 6.38; N, 6.17. Found: C, 84.46; H, 6.33; N, 6.08\%.
$\left\{\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathrm{NaBH}_{4}(0.491 \mathrm{~g}, 12.7 \mathrm{mmol})$ and the respective imine ( 1.021 $\mathrm{g}, 2.107 \mathrm{mmol})$. Yield: $1.020 \mathrm{~g}, 99 \% .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.42-6.94(\mathrm{~m}, 18 \mathrm{H}$, arom. H), $4.35\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 2.91\left(\mathrm{~s}, 4 \mathrm{H},\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3287$ $\mathrm{cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{36} \mathrm{H}_{28} \mathrm{~N}_{2}$ requires C, 83.13; H, 6.10; N, 5.39. Found: C, 83.23; H, 5.95; N, 4.91\%.
$\left\{\mathbf{P h C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{2 . 1}$ Under a nitrogen atmosphere, a solution of $\left\{\mathrm{PhCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.406 \mathrm{~g}, 1.69 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.795 \mathrm{~g}, 3.38 \mathrm{mmol})$ in degassed $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was refluxed for 17 h . The solvent was evaporated under reduced pressure to afford a viscous oil. Crude yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-27.8 \mathrm{ppm}, 90 \% .{ }^{1} \mathrm{H}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta 7.76$ $-7.10\left(\mathrm{~m}, 30 \mathrm{H}\right.$, arom. H), $3.64\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.21\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{P}\right)$, 2.71 (s, 4H, $\left.\mathrm{PhCH}_{2} \mathrm{~N}\right)$.
$\left\{\mathbf{C}_{10} \mathbf{H}_{7} \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}$ 2.2 Under a nitrogen atmosphere, a solution of $\left\{\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.200 \mathrm{~g}, 0.589 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.268 \mathrm{~g}, 1.18$ mmol ) in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was refluxed for 17 h before cooling to RT to afford a sticky cream solid. The solvent was concentrated under reduced pressure to approximately $10 \mathrm{~cm}^{3}$ and the solid filtered and dried under reduced pressure. Yield:
$0.312 \mathrm{~g}, 72 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-28.2 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta 8.15-6.91(\mathrm{~m}, 34 \mathrm{H}$, arom. H$), 4.00\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.36$ (d, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{P}$ ), 2.78 (s, $4 \mathrm{H}, \mathrm{C}_{10} \mathrm{H}_{7} \mathrm{CH}_{2} \mathrm{~N}$ ). Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{P}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ requires C, 79.56 ; H, 6.41; N, 3.71. Found: C, 79.57; H, 6.29; N, 3.80\%.
6.6.2 Phosphines $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$ were prepared in a similar manner to $\mathbf{2 . 2}$.
$\left\{\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \quad \mathbf{2 . 3} \quad \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.419 \mathrm{~g}, \quad 1.84 \mathrm{mmol})$ and $\left\{\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.406 \mathrm{~g}, 0.921 \mathrm{mmol})$, refluxed for 4 h . Yield: $0.696 \mathrm{~g}, 90 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-28.1 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta 8.33-6.97\left(\mathrm{~m}, 38 \mathrm{H}\right.$, arom. H), $4.41\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.11\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.2\right.$ $\mathrm{Hz}, \mathrm{NCH}_{2} \mathrm{P}$ ), $2.77\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}\right)$. Anal. Calc. for $\mathrm{C}_{58} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 82.35; H, 6.08; N, 3.31. Found: C, 82.33; H, 5.83; N, 3.10\%.
$\left\{\mathbf{C}_{\mathbf{1} 6} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \quad \mathbf{2 . 4} \quad \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.187 \mathrm{~g}, 0.822 \mathrm{mmol})$ and $\left\{\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.201 \mathrm{~g}, 0.411 \mathrm{mmol})$. Yield: $0.293 \mathrm{~g}, 81 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-27.7 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta 8.20-$ $6.95\left(\mathrm{~m}, 38 \mathrm{H}\right.$, arom. H), $4.23\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.26\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.2 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{P}\right), 2.85$ (s, $4 \mathrm{H}, \mathrm{C}_{16} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}$ ). Anal. Calc. for $\mathrm{C}_{62} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ requires C, $78.24 ; \mathrm{H}, 5.77 ; \mathrm{N}$, 2.76. Found: C, 78.18; H, 5.36; N, 3.10\%.
6.6.3 Chemical oxidation of the ditertiary phosphines $\mathbf{2 . 3}$ and $\mathbf{2 . 4}$.
$\left\{\mathbf{C}_{14} \mathbf{H}_{9} \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P}(\mathbf{O}) \mathbf{P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{2 . 5} \mathrm{H}_{2} \mathrm{O}_{2}\left(0.50 \mathrm{~cm}^{3}, 30 \% \mathrm{w} / \mathrm{v}\right)$ was added to a stirred solution of $2.3(0.101 \mathrm{~g}, 0.121 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ and the resulting solution stirred at RT for 1 h . The solvent was evaporated under reduced pressure and the resulting yellow solid dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(2 \mathrm{~cm}^{3}\right)$. Diethyl ether ( $20 \mathrm{~cm}^{3}$ ) was added and the resulting suspended solid stirred for a further 0.5 h . The solid was filtered and dried under reduced pressure. Yield: $0.076 \mathrm{~g}, 72 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 26.7 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR (( $\left.\left.\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 8.82-7.18$ (m, 38H, arom. H$)$, $4.50\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 3.26\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{P}\right), 2.34\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $v_{\mathrm{PO}} 1171 \mathrm{~cm}^{-1}$.
$\left\{\mathbf{C}_{16} \mathbf{H}_{9} \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P}(\mathbf{O}) \mathbf{P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{2 . 6} \mathrm{H}_{2} \mathrm{O}_{2}\left(0.50 \mathrm{~cm}^{3}, 30 \% \mathrm{w} / \mathrm{v}\right)$ was added to a stirred solution of $2.4(0.100 \mathrm{~g}, 0.113 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ and the resulting solution stirred at RT for 1 h . The solvent was removed under reduced pressure and the yellow solid dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(2 \mathrm{~cm}^{3}\right)$. Hexane $\left(20 \mathrm{~cm}^{3}\right)$ was added and the suspension stirred for a further 0.5 h . The solid was filtered and dried under reduced pressure. Yield: Quantitative. FT-IR (KBr): $v_{\mathrm{PO}} 1188 \mathrm{~cm}^{-1}$.

### 6.6.4 Coordination Chemistry of $2.1 \mathbf{- 2 . 4}$.

cis- $\mathbf{P t C l}_{\mathbf{2}}\left[\left\{\mathbf{P h C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2}\right] \mathbf{2 . 7}$ A solution of $\mathbf{2 . 1}(0.115 \mathrm{~g}, 0.163 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.061 \mathrm{~g}, 0.16$ mmol ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred for 0.5 h and concentrated to approximately $2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added, the resulting cream suspension stirred for 0.5 h and the solid filtered under reduced pressure. The filtrate was concentrated under reduced pressure to approximately $2 \mathrm{~cm}^{3}$ and hexane ( $25 \mathrm{~cm}^{3}$ ) added. The resulting suspension was stirred for 0.5 h and the solid filtered and dried under reduced pressure. Yield: 0.063 g, $43 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-1.3\left(\mathrm{~s},{ }^{1} J_{\mathrm{PtP}} 3633 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.79$ $-7.09\left(\mathrm{~m}, 30 \mathrm{H}\right.$, arom. H), $4.02\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{PCH}_{2},{ }^{3} J_{\mathrm{PtH}} 39.2 \mathrm{~Hz}\right), 3.52\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.35$ (s, 4H, CH2). FT-IR (KBr): $v_{\mathrm{PtCl}} 316,290 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 903[\mathrm{M}]^{+}, 867[\mathrm{M}-$ $\mathrm{Cl}]^{+}, 831[\mathrm{M}-2 \mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{42} \mathrm{H}_{42} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PtCl}_{2}$ requires C, $56.23 ; \mathrm{H}, 5.04 ; \mathrm{N}$, 2.98. Found: C, 56.49; H, 4.94; N, 2.83\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left[\left\{\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{7}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2}\right] \mathbf{2 . 8}$ Phosphine $\mathbf{2 . 2}(0.104 \mathrm{~g}, 0.134 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.050 \mathrm{~g}, 0.13 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20$ $\mathrm{cm}^{3}$ ). The resulting solution was stirred for 0.5 h and concentrated to approximately $2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting cream suspension stirred for 0.5 h , and filtered under reduced pressure. The filtrate was concentrated under reduced pressure to approximately $2 \mathrm{~cm}^{3}$ and hexane ( 25 $\mathrm{cm}^{3}$ ) added to afford a cream suspension. The suspension was stirred for 0.5 h and collected by suction filtration. Yield: $0.080 \mathrm{~g}, 60 \%{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-3.6$ (s, ${ }^{1} J_{\text {Ptp }} 3606 \mathrm{~Hz}$ ). ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.88-6.89(\mathrm{~m}, 34 \mathrm{H}$, arom. H), $4.10(\mathrm{~m}, 4 \mathrm{H}$, $\mathrm{PCH}_{2},{ }^{3} J_{\mathrm{PtH}} 40.8 \mathrm{~Hz}$ ), $3.94\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.73\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) . \mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{PtCl}} 317$, $292 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $967[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ requires C, 58.83 ; H, 4.74; N, 2.74. Found: C, 59.01 ; H, 4.95; N, 2.26\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}}\right]$ 2.9 Phosphine $\mathbf{2 . 3}$ ( $0.100 \mathrm{~g}, 0.120 \mathrm{mmol}$ ) was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.045 \mathrm{~g}, 0.12 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20$ $\mathrm{cm}^{3}$ ) and the resulting mixture was stirred for 0.5 h . The solvent was concentrated to approximately $2 \mathrm{~cm}^{3}$ under reduced pressure and $\mathrm{Et}_{2} \mathrm{O}\left(25 \mathrm{~cm}^{3}\right)$ added to afford a cream precipitate. The suspension was stirred for 0.5 h , filtered and dried under reduced pressure. Yield: $0.874 \mathrm{~g}, 87 \%{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-2.7\left(\mathrm{~s},{ }^{1} J_{\mathrm{PtP}} 3593\right.$ $\mathrm{Hz}) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.39-6.81(\mathrm{~m}, 38 \mathrm{H}$, arom. H$), 4.26\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 4.11(\mathrm{~m}$, $4 \mathrm{H}, \mathrm{PCH}_{2},{ }^{3} J_{\mathrm{PtH}} 37.6 \mathrm{~Hz}$ ), $3.92\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) . \mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): \mathrm{v}_{\mathrm{PtCl}} 318,294 \mathrm{~cm}^{-1} . \mathrm{MS}$ $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1103[\mathrm{M}]^{+}, 1067[\mathrm{M}-\mathrm{Cl}]^{+}, 1032[\mathrm{M}-2 \mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{58} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot 0.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $62.24 ; \mathrm{H}, 4.53 ; \mathrm{N}, 2.49$. Found: C, 61.84 ; H, 4.38; N, 2.51\%.

Complex $\mathbf{2 . 1 0}$ was prepared in a similar manner to $\mathbf{2 . 9}$.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left[\left\{\mathbf{C}_{\mathbf{1} \mathbf{6}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2}\right] \mathbf{2 . 1 0} \mathrm{PtCl}_{2}(\operatorname{cod})(0.033 \mathrm{~g}, 0.088 \mathrm{mmol})$ and $2.4(0.078 \mathrm{~g}, 0.088 \mathrm{mmol})$. Yield: $0.086 \mathrm{~g}, 85 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta-3.8$ $\left(\mathrm{s},{ }^{1} J_{\mathrm{PtP}} 3620 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.25-6.78(\mathrm{~m}, 38 \mathrm{H}$, arom. H), $4.11(\mathrm{~m}, 4 \mathrm{H}$, $\mathrm{CH}_{2},{ }^{3} J_{\mathrm{PtH}} 36.0 \mathrm{~Hz}$ ), $3.99\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.95\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) . \mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{PtCl}} 316$, $292 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1151[\mathrm{M}]^{+}$, $1115[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{62} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires C, $63.21 ; \mathrm{H}, 4.53$; N, 2.38. Found: C, $62.78 ; \mathrm{H}$, 4.41; N, 2.37\%.
$\mathbf{P d C l}_{2}\left[\left\{\mathbf{P h C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right] \mathbf{2 . 1 1}$ A solution of $\mathbf{2 . 1}(0.124 \mathrm{~g}, 0.176 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{PdCl}_{2}(\operatorname{cod})(0.050 \mathrm{~g}, 0.18 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred for 0.5 h and concentrated to approximately $2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for 0.5 h , filtered and dried under reduced pressure. Yield: 0.104 g . Attempts to obtain an analytically pure sample of $\mathbf{2 . 1 1}$ were hampered by the slow decomposition of this complex in solution.

Attempts to prepare complexes 2.12 - $\mathbf{2 . 1 4}$ were performed in a similar manner to 2.9. As was the case for $\mathbf{2 . 1 1}$, it was not possible to prepare analytically pure sample of the desired complexes.
$\mathbf{P d C l}_{2}\left[\left\{\mathbf{C}_{10} \mathbf{H}_{7} \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right] 2.12 \mathrm{PdCl}_{2}(\operatorname{cod})(0.037 \mathrm{~g}, 0.13 \mathrm{mmol})$ and 2.2 ( $0.101 \mathrm{~g}, 0.130 \mathrm{mmol})$. Yield: 0.100 g .
$\mathbf{P d C l}_{2}\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{\mathbf{2}}\right] \mathbf{2 . 1 3} \mathrm{PdCl}_{2}($ cod $)(0.038 \mathrm{~g}, 0.13 \mathrm{mmol})$ and 2.3 ( $0.111 \mathrm{~g}, 0.132 \mathrm{mmol})$. Yield: 0.044 g .
$\mathbf{P d C l}_{2}\left[\left\{\mathbf{C}_{\mathbf{1} 6} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right] \mathbf{2 . 1 4} \mathrm{PdCl}_{2}(\operatorname{cod})(0.032 \mathrm{~g}, 0.11 \mathrm{mmol})$ and 2.4 ( $0.099 \mathrm{~g}, 0.11 \mathrm{mmol}$ ). Yield: 0.102 g .

The nickel complex 2.15 was prepared following slight modification to the known method reported by Pringle et al. ${ }^{93}$
$\mathbf{N i C l}_{\mathbf{2}}\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}}\right] \mathbf{2 . 1 5}$ Under a nitrogen atmosphere, a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ / $\mathrm{MeOH}\left(1: 1,20 \mathrm{~cm}^{3}\right)$ solution of $2.3(0.103 \mathrm{~g}, 0.123 \mathrm{mmol})$ and $\mathrm{NiCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.029 \mathrm{~g}$, 0.122 mmol ) was stirred at reflux for 1 h . The solvent was evaporated under reduced pressure to yield a green solid. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 15.3$ ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.28-6.60(\mathrm{~m}, 38 \mathrm{H}$, arom. H$), 4.75\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 4.19$ (d, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{P}$ ), 3.42 (s, $4 \mathrm{H}, \mathrm{C}_{14} \mathrm{H}_{9} \mathrm{CH}_{2} \mathrm{~N}$ ). Anal. Calc. for $\mathrm{C}_{58} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{NiCl}_{2} \cdot 1.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, 66.33; H, 4.93; N, 2.61. Found: C, 66.63; H, 5.24; N, 2.94\%.
trans- $\mathbf{P d}(\mathbf{M e}) \mathbf{C l}\left[\left\{\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{7} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right] \mathbf{2 . 1 6}$ A solution of $\mathbf{2 . 2}(0.099 \mathrm{~g}$, $0.135 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{Pd}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod})$ ( $0.035 \mathrm{~g}, 0.132 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred for 0.5 h , and the solvent concentrated to approximately $2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting suspension stirred for 0.5 h , before the white precipitate was filtered and dried under reduced pressure. Yield: $0.042 \mathrm{~g}, 35 \%$. FT-IR (KBr): $v_{\text {PdCl }} 262 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z 857 [M-Cl] ${ }^{+}$. Anal. Calc. for $\mathrm{C}_{51} \mathrm{H}_{49} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PdCl} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, $66.01 ; \mathrm{H}, 5.38 ; \mathrm{N}, 2.99$. Found: C , 65.73; H, 5.31; N, 3.19\%.
trans- $\mathbf{P d}(\mathbf{M e}) \mathbf{C l}\left[\left\{\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right] \mathbf{2 . 1 7}$ Phosphine $\mathbf{2 . 3}$ (0.101 g, $0.115 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{Pd}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod})(0.030 \mathrm{~g}, 0.113$
$\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred at RT for 0.5 h before being concentrated under reduced pressure to approximately $2 \mathrm{~cm}^{3}$. Diethyl ether ( 25 $\mathrm{cm}^{3}$ ) was added and the precipitate stirred for a further 0.5 h , filtered and dried under reduced pressure. Yield: $0.067 \mathrm{~g}, 60 \%$. FT-IR (KBr): $v_{\text {PdCl }} 261$ (b) $\mathrm{cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{59} \mathrm{H}_{53} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PdCl} \cdot 0.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, $70.10 ; \mathrm{H}, 5.31 ; \mathrm{N}, 2.76$. Found: C, 70.40; H, 5.42; N, 2.62\%.

Complex $\mathbf{2 . 1 8}$ was prepared in a similar manner to 2.17.
trans- $\mathbf{P d}(\mathbf{M e}) \mathbf{C l}\left[\left\{\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}}\right] \mathbf{2 . 1 8} \mathbf{P d}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod})(0.029 \mathrm{~g}$, $0.11 \mathrm{mmol})$ and $2.4(0.100 \mathrm{~g}, 0.113 \mathrm{mmol})$. Yield $0.084 \mathrm{~g}, 73 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 14.2 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.26-6.56(\mathrm{~m}, 38 \mathrm{H}$, arom. H$), 4.42(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 4.16 (bs, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.94 (bs, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), -0.07 ( $\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{PH}} 6.0 \mathrm{~Hz}, \mathrm{CH}_{3}$ ). FT-IR (KBr): $v_{\text {PdCl }} 263 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $1005[\mathrm{M}-\mathrm{Cl}]^{+}$and $990\left[\mathrm{M}-\mathrm{Cl}-\mathrm{CH}_{3}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{63} \mathrm{H}_{53} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{PdCl}$ requires C , 72.62; H, 5.13; N, 2.69. Found: C, 72.43; H, 5.08; N, 2.74\%.
trans- $\mathbf{R h C l}(\mathbf{C O})\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}}\right] \mathbf{2 . 1 9}$ Phosphine $\mathbf{2 . 3}$ (0.106 g, $0.126 \mathrm{mmol})$ was added to a stirred solution of $\left\{\mathrm{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}(0.025 \mathrm{~g}, 0.063$ mmol) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The mixture was stirred for 1 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting suspension stirred for a further 0.5 h , filtered and dried under reduced pressure. Yield: Quantitative. FT-IR (KBr): $v_{\mathrm{CO}} 1969 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{59} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{RhCl} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, 68.33; H, 4.93; N, 2.68. Found: C, 68.21; H, 4.92; N, 3.04\%.
$\left\{\mathbf{R u C l}_{\mathbf{2}}(\boldsymbol{p}-\mathbf{c y m})\right\}_{2}\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}}\right] \mathbf{2 . 2 0}$ Phosphine 2.3 ( 0.101 g , $0.121 \mathrm{mmol})$ was added to a stirred solution of $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.038 \mathrm{~g}$, $0.062 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(25 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred for 0.5 h and the solvent was concentrated under reduced pressure to $c a .2 \mathrm{~cm}^{3}$. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for 0.5 h , filtered and dried under reduced pressure. Yield: $0.086 \mathrm{~g}, 97 \%$. Anal. Calc. for $\mathrm{C}_{78} \mathrm{H}_{78} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Cl}_{4} \mathrm{Ru}_{2}$ requires: C, $64.54 ; \mathrm{H}, 5.42$, N, 1.93. Found: C, $64.54 ; \mathrm{H}, 5.12 ; \mathrm{N}, 2.11 \%$.

Complex 2.21 was prepared in a similar manner to $\mathbf{2 . 2 0}$, however due to the light sensitive nature of $\mathrm{Au}^{+}$the reaction was conducted in the dark.
$\left\{\mathbf{A u C l}_{2}\left[\left\{\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2}\right] \mathbf{2 . 2 1} \mathrm{AuCl}(\right.$ tht $)(0.050 \mathrm{~g}, 0.16 \mathrm{mmol}), \mathbf{2 . 3}$ ( $0.065 \mathrm{~g}, 0.077 \mathrm{mmol}$ ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right.$ ). Yield: $0.087 \mathrm{~g}, 87 \%$. FT-IR ( KBr ): $v_{\text {Aucl }} 331 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{58} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Au}_{2} \mathrm{Cl}_{2}$ requires: C, $53.51 ; \mathrm{H}, 3.87 ; \mathrm{N}$, 2.15. Found: C, 53.51 ; H, 3.85; N, 2.22\%.
cis- $\mathbf{M o}(\mathbf{C O})_{4}\left[\left\{\mathbf{C}_{14} \mathbf{H}_{9} \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right]$ 2.22 Under a nitrogen atmosphere, a solution of $2.3(0.104 \mathrm{~g}, 0.063 \mathrm{mmol})$ and $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd})(0.019 \mathrm{~g}, 0.063 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at reflux for 33 h . The solvent was concentrated under reduced pressure to approximately $2 \mathrm{~cm}^{3}$ and degassed $\mathrm{Et}_{2} \mathrm{O}\left(15 \mathrm{~cm}^{3}\right)$ added. The resulting cream suspension was stirred for 1 h , filtered and dried under reduced pressure. Yield: $0.071 \mathrm{~g}, 55 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 19.1 \mathrm{ppm}$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.17-7.06\left(\mathrm{~m}, 38 \mathrm{H}\right.$, arom. H), $3.94\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.65\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.12$ (s, 4H, CH 2 ). FT-IR (KBr): $v_{\text {CO }}$ 2017, $1893 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1045[\mathrm{M}]^{+}, 989$ [M-2CO] ${ }^{+}$. Anal. Calc. for $\mathrm{C}_{62} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Mo} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ requires C, 67.76; $\mathrm{H}, 5.14 ; \mathrm{N}, 2.55$. Found: C, 67.41; H, 4.49; N, 2.56\%.
6.6.5 Preparation of the monophosphines $\mathbf{2 . 2 3}-\mathbf{2 . 2 5}$.

The precursor amines and imines below were prepared following slight modification to the known method reported by Zhang et al. ${ }^{187}$
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{C H}_{3}$ Ice chilled ethylamine $\left(0.90 \mathrm{~cm}^{3}, 14 \mathrm{mmol}\right)$ was added to a chilled solution of 9-anthracenecarboxaldehyde ( $1.270 \mathrm{~g}, 5.973 \mathrm{mmol}$ ) in MeOH $\left(100 \mathrm{~cm}^{3}\right)$. The resulting suspension was stirred for 0.25 h at $c a .0^{\circ} \mathrm{C}$ before stirring for a further 4 h at RT. The solvent was evaporated under reduced pressure. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 9.36(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CHN}), 8.42-7.39(\mathrm{~m}, 9 \mathrm{H}$, arom. H$)$, $3.90\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.46\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1636 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $233[\mathrm{M}]^{+}$and $234[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{17} \mathrm{H}_{15} \mathrm{~N}$ requires C, 87.52; H, 6.48; N, 6.00. Found: C, 87.20; H, 6.67; N, 6.20\%.


#### Abstract

$\left(\mathrm{C}_{16} \mathbf{H}_{9}\right) \mathbf{C}(\mathbf{H}) \mathrm{NCH}_{2} \mathrm{CH}_{3}$ was prepared in a similar manner to $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2} \mathrm{CH}_{3}$.


$\left(\mathbf{C}_{16} \mathbf{H}_{9}\right) \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{C H}_{3} \quad$ Ethylamine $\left(0.5 \mathrm{~cm}^{3}, 7.652 \mathrm{mmol}\right)$ and $1-$ pyrenecarboxaldehyde $(0.797 \mathrm{~g}, 3.43 \mathrm{mmol})$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 9.32(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CHN}), 8.89-7.97\left(\mathrm{~m}, 9 \mathrm{H}\right.$, arom. H), $3.85\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.4 \mathrm{~Hz}\right.$, $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 1.46 ( $\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ). FT-IR ( KBr ): $v_{\mathrm{C}=\mathrm{N}} 1624 \mathrm{~cm}^{-1} . \mathrm{MS}$ $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 257[\mathrm{M}]^{+}$and $258[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{19} \mathrm{H}_{15} \mathrm{~N}$ requires C, 88.68; H, 5.88; N, 5.44. Found: C, 88.49; H, 5.65; N, 4.85\%.
$\left(\mathbf{C}_{16} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C}(\mathbf{H}) \mathbf{N P h}$ Aniline $(0.208 \mathrm{~g}, 2.21 \mathrm{mmol})$ in $\mathrm{MeOH}\left(30 \mathrm{~cm}^{3}\right)$ was added dropwise to a refluxing suspension of $1-$ pyrenecarboxaldehyde ( $0.514 \mathrm{~g}, 2.21 \mathrm{mmol}$ ) in $\mathrm{MeOH}\left(70 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred at reflux for 4 h to afford a yellow solution. The solvent was evaporated under reduced pressure to give a yellow product. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 9.38(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CHN}), 8.93-6.16(\mathrm{~m}$, 14 H , arom. H). FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1577 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{15} \mathrm{~N} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 89.15; H, 5.04; N, 4.52. Found: C, 89.66; H, 5.14; N, 4.31\%.
$\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{3}} \quad \mathrm{NaBH}_{4} \quad\left(\begin{array}{lllll}1.143 & \mathrm{~g}, & 29.61 & \mathrm{mmol}) & \text { and }\end{array}\right.$ $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2} \mathrm{CH}_{3}(1.161 \mathrm{~g}, 4.976 \mathrm{mmol})$. Yield: $1.089 \mathrm{~g}, 93 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.46-7.37\left(\mathrm{~m}, 9 \mathrm{H}\right.$, arom. H), $4.67\left(\mathrm{~s}, 2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 2.86(\mathrm{q}, 2 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $1.14\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3318$ $\mathrm{cm}^{-1}$. MS (FAB ${ }^{+}$): m/z $235[\mathrm{M}]^{+}, 234[\mathrm{M}-\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{~N} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 83.57; H, 7.43; N, 5.73. Found: C, 83.18; H, 7.32; N, 5.72\%.
$\left(\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )}\left(\mathbf{C}_{2} \mathbf{H}_{\mathbf{5}}\right) \mathrm{NaBH}_{4}(0.697 \mathrm{~g}, 18.06 \mathrm{mmol})$ and $\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2} \mathrm{CH}_{3}$ $(0.768 \mathrm{~g}, 2.98 \mathrm{mmol})$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.29-7.82(\mathrm{~m}, 9 \mathrm{H}$, arom. H), $4.42\left(\mathrm{~s}, 2 \mathrm{H},\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 2.78\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.13(\mathrm{t}$, $3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ). FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3300 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 259[\mathrm{M}]^{+}$, $258[\mathrm{M}-\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{19} \mathrm{H}_{17} \mathrm{~N} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 85.04; H, 6.76; N, 5.22. Found: C, 84.59; H, 6.39; N, 5.11\%.
$\left(\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{P h} \mathrm{NaBH}_{4}(0.458 \mathrm{~g}, 11.7 \mathrm{mmol})$ and $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NPh}(0.602 \mathrm{~g}$, $1.97 \mathrm{mmol})$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.45-6.17(\mathrm{~m}, 14 \mathrm{H}$, arom. H ),
$4.90\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 4.02(\mathrm{bs}, 1 \mathrm{H}, \mathrm{NH})$. FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3405 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}$ $307[\mathrm{M}+\mathrm{H}]^{+}, 306[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{17} \mathrm{~N} \cdot 0.5 \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ requires C, 87.24; H, 6.10; N, 4.24. Found: C, 86.93; H, 5.56; N, 3.70\%.
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C}_{2} \mathbf{H}_{\mathbf{5}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2} \mathbf{2 . 2 3}$ Under a nitrogen atmosphere, a solution of $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{C}_{2} \mathrm{H}_{5}(0.228 \mathrm{~g}, 0.969 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.227 \mathrm{~g}, 0.976$ $\mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at RT for 3 d to yield a yellow suspension. The solvent was concentrated to approximately $5 \mathrm{~cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield: $0.280 \mathrm{~g}, 67 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-27.6 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta 8.45-7.06(\mathrm{~m}, 19 \mathrm{H}$, arom. H), $4.66\left(\mathrm{~s}, 2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.35\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right), 2.74(\mathrm{q}, 2 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.99\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. MS (FAB ${ }^{+}$): m/z 432 $[\mathrm{M}]^{+}$
$\left(\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C}_{\mathbf{2}} \mathbf{H}_{\mathbf{5}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}} \mathbf{2 . 2 4}$ Under a nitrogen atmosphere, a solution of $\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{C}_{2} \mathrm{H}_{5}(0.216 \mathrm{~g}, 0.833 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.196 \mathrm{~g}, 0.843$ mmol ) in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at RT for 3 d to yield a clear solution containing a small amount of oily solid. The solvent was evaporated under reduced pressure to yield a viscous oil. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-27.7 \mathrm{ppm}$. ${ }^{1} \mathrm{H}$ NMR (freeze-thawed $\left.\mathrm{CDCl}_{3}\right): \delta 8.41-7.05(\mathrm{~m}, 19 \mathrm{H}$, arom. H$), 4.36(\mathrm{~s}, 2 \mathrm{H}$, $\left.\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.34\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right), 2.75\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $1.02\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. MS ( $\mathrm{FAB}^{+}$): m/z $456[\mathrm{M}-\mathrm{H}]^{+}, 215$ $\left[\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2}\right]^{+}$.
6.6.6 Coordination chemistry of $\mathbf{2 . 2 3}$ and $\mathbf{2 . 2 4}$

Complex 2.26 was prepared in a similar manner to $\mathbf{2 . 7}$.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{3}}\right\}_{\mathbf{2}} \quad \mathbf{2 . 2 6} \mathrm{PtCl}_{2}(\operatorname{cod}) \quad\left(\begin{array}{llll}0.082 & \mathrm{~g}, & 0.22\end{array}\right.$ $\mathrm{mmol}), 2.23(0.199 \mathrm{~g}, 0.441 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.227 \mathrm{~g}, 92 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 2.6 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3636 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.02-6.39$ (m, 58 H , arom. H), $4.23\left(\mathrm{~s}, 4 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right.$ ), 3.94 (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $2.58(\mathrm{q}, 4 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.95\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1097$ $[\mathrm{M}-\mathrm{Cl}]^{+}$.
cis- $\left.\mathbf{P t C l}_{2}\left\{\mathbf{C}_{\mathbf{1}} \mathbf{6} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{3}\right\}_{2} \mathbf{2} .27 \mathrm{~A}$ solution of $\mathbf{2 . 2 4}(0.330 \mathrm{~g}$, $0.584 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.108$ $\mathrm{g}, 0.289 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred for 1 h to yield a yellow solution. The solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure and $\mathrm{Et}_{2} \mathrm{O}\left(25 \mathrm{~cm}^{3}\right)$ was added to give a yellow suspension. The suspension was stirred for a further 0.5 h , and the solid filtered and dried under reduced pressure. Yield: $0.213 \mathrm{~g}, 62 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 3.7 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3628 \mathrm{~Hz}, 71 \% .{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 8.12-6.56\left(\mathrm{~m}, 58 \mathrm{H}\right.$, arom. H), $4.04\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.99(\mathrm{~s}, 4 \mathrm{H}$, $\mathrm{CH}_{2}$ ), $2.26\left(\mathrm{q}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.75\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. FT-IR $(\mathrm{KBr}): v_{\mathrm{PtCl}} 304,282 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1145[\mathrm{M}-\mathrm{Cl}]^{+}$.
$\mathbf{A u C l}\left\{\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{3}}\right\} \mathbf{2} \mathbf{2 8}$ A solution of $\mathbf{2 . 2 3}$ (0.199 g, 0.404 $\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of AuCl (tht) $(0.129 \mathrm{~g}$, $0.402 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred, in the dark, for 0.5 h before the solvent was evaporated under reduced pressure to yield a viscous oil. Hexane $\left(10 \mathrm{~cm}^{3}\right)$ was added and the resulting yellow suspension vigorously triturated to yield a yellow suspension which was filtered and dried under reduced pressure. Yield: $0.185 \mathrm{~g}, 69 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 18.9 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.31-$ 7.05 ( $\mathrm{m}, 19 \mathrm{H}$, arom. H), 4.67 (s, $2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}$ ), 3.73 (bs, $2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.23(\mathrm{q}$, $2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $1.19\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 630$ $[\mathrm{M}-\mathrm{Cl}]^{+}, 191\left[\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{30} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{PAuCl} \cdot 0.25 \mathrm{C}_{6} \mathrm{H}_{14}$ requires: C, 55.03; H, 4.62; N, 2.04. Found: C, 54.77; H, 4.47; N, 1.85\%.
$\mathbf{A u C l}\left\{\left(\mathbf{C}_{\mathbf{1 6}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{\mathbf{3}}\right\} \mathbf{2 . 2 9}$ Ligand $\mathbf{2 . 2 4}$ ( $0.224 \mathrm{~g}, 0.426 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of AuCl (tht) $(0.136 \mathrm{~g}, 0.424$ $\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred, in the dark, for 0.5 h before the solvent was evaporated under reduced pressure to yield a viscous oil. The oil was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(2 \mathrm{~cm}^{3}\right)$ and hexane $\left(10 \mathrm{~cm}^{3}\right)$ added, the resulting yellow solution was vigorously triturated to yield a sticky yellow suspension, which over 0.5 h of vigorous stirring, congealed into a "gummy" solid. The solid was removed and dried under reduced pressure to afford a yellow crystalline solid. Yield: 0.183 g , $63 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 18.5 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.21-6.91(\mathrm{~m}, 19 \mathrm{H}$, arom. H), 4.41 (bs, $\left.2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.73\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right), 3.17\left(\mathrm{bd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8\right.$
$\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $1.20\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right) . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 688[\mathrm{M}-2 \mathrm{H}]^{+}$, $654[\mathrm{M}-\mathrm{Cl}]^{+}, 215\left[\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{32} \mathrm{H}_{28} \mathrm{NPAuCl} \cdot 0.25 \mathrm{C}_{6} \mathrm{H}_{14}$ requires: C, 56.55; H, 4.46; N, 1.97. Found: C, 56.24; H, 4.33; N, 1.80\%.
6.6.7 Preparation of the monophosphine $\mathbf{2 . 3 0}$.

The precursor amine and imine below were prepared following slight modification to the known method reported by Zhang et al. ${ }^{187}$
$\left\{\left(\mathbf{C}_{\mathbf{1}} \mathbf{(} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{\mathbf{2}} \mathbf{\}}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}}\right.$ A solution of 1,3-diaminopropane ( $0.254 \mathrm{~g}, 3.39 \mathrm{mmol}$ ) in $\mathrm{MeOH}\left(5 \mathrm{~cm}^{3}\right)$ was added dropwise to a refluxing solution of $1-$ pyrenecarboxaldehyde $(1.562 \mathrm{~g}, 6.716 \mathrm{mmol})$ in $\mathrm{MeOH}\left(50 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred at reflux for 4 h to afford a suspended yellow solid which was filtered and dried under reduced pressure. Yield: $1.185 \mathrm{~g}, 70 \%$. FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}}$ $1623 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{26} \mathrm{~N}_{2} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 88.33; H, 5.31; N, 5.57. Found: C, 88.25; H, 5.19; N, 5.61\%.
$\left\{\left(\mathbf{C}_{\mathbf{1} \mathbf{6}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \quad \mathrm{NaBH}_{4} \quad\left(\begin{array}{lllll}0.323 & \mathrm{~g}, & 8.37 & \mathrm{mmol}\end{array}\right)$ and $\left\{\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2} \mathrm{CH}_{2}(0.696 \mathrm{~g}, 1.40 \mathrm{mmol})$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.27-7.81(\mathrm{~m}, 18 \mathrm{H}$, arom. H$), 4.35\left(\mathrm{~s}, 4 \mathrm{H},\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 2.82(\mathrm{t}, 4 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{CH}_{2}$ ), $1.76\left(\mathrm{~m}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{CH}_{2}\right)$. FT-IR (KBr): $v_{\mathrm{NH}}$ $3289 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right)$: m/z $503[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{30} \mathrm{~N}_{2} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 83.90; H, 6.27; N, 5.29. Found: C, 83.62; H, 5.99; N, 5.15\%.
$\left\{\left(\mathbf{C}_{16} \mathbf{H}_{9}\right) \mathbf{C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{C H}_{2} \mathbf{2 . 3 0}$ Under a nitrogen atmosphere, a solution of $\left\{\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}(0.101 \mathrm{~g}, 0.201 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.093 \mathrm{~g}$, $0.41 \mathrm{mmol})$ in MeOH :toluene $\left(1: 1,20 \mathrm{~cm}^{3}\right)$ was refluxed for 3 d . The solvent was removed under reduced pressure to yield a viscous yellow oil. $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was added and the resulting solid stirred for 2 h , filtered and dried under reduced pressure. Yield: $0.124 \mathrm{~g}, 69 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (freeze-thawed $\mathrm{CDCl}_{3}$ ): $\delta-28.1 \mathrm{ppm}$. ${ }^{1} \mathrm{H}$ NMR (freeze-thawed $\left.\mathrm{CDCl}_{3}\right): \delta 8.43-6.99(\mathrm{~m}, 38 \mathrm{H}$, arom. H$), 4.22(\mathrm{~s}, 4 \mathrm{H}$, $\left.\left(\mathrm{C}_{16} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.24\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{PH}} 4.0 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{PPh}_{2}\right), 2.56\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}\right.$, $\mathrm{NCH}_{2} \mathrm{CH}_{2}$ ), $1.61\left(\mathrm{~m}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{CH}_{2}\right)$.

### 6.7 Chapter 3 Experimental

### 6.7.1 Preparation of 3.1-3.3.

The precursor imine $\left\{\mathbf{F c C}(\mathbf{H}) \mathbf{N C H}_{\mathbf{2}}\right\}_{2}$ and the parent amine $\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{2}$ were prepared following slight modification to the known method reported by Benito et $a l .{ }^{218}$
$\left\{\mathbf{F c C} \mathbf{( H )} \mathbf{N C H}_{\mathbf{2}}\right\}_{\mathbf{2}}$ Ethylenediamine ( $0.165 \mathrm{~g}, 2.72 \mathrm{mmol}$ ), ferrocenealdehyde ( 1.186 $\mathrm{g}, 5.430 \mathrm{mmol})$ and $\mathrm{MeOH}\left(50 \mathrm{~cm}^{3}\right)$. Yield: $1.218 \mathrm{~g}, 99 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.08$ ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CHN}$ ), $4.54\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.25\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.06\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.68(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH} \mathrm{H}_{2} \mathrm{~N}$ ). $\mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{C}=\mathrm{N}} 1639 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 452[\mathrm{M}]^{+}, 453[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{Fe}_{2}$ requires C, $63.75 ; \mathrm{H}, 5.35 ; \mathrm{N}, 6.20$. Found C, $63.51 ; \mathrm{H}$, 5.27; N, 6.14\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathrm{NaBH}_{4}(0.470 \mathrm{~g}, 12.2 \mathrm{mmol}),\left\{\mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2}(0.913 \mathrm{~g}, 2.02$ $\mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(120 \mathrm{~cm}^{3}, 2: 1\right)$. Yield: $0.911 \mathrm{~g}, 99 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ $4.11\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.06\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.02\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.43\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NH}\right)$, $2.68\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right) . v_{\mathrm{NH}} 3334 \mathrm{~cm}^{-1}$. FAB mass spectrum: $\mathrm{m} / \mathrm{z} 456[\mathrm{M}]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{Fe}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 59.10 ; \mathrm{H}, 6.35 ; \mathrm{N}, 5.74$. Found C, 59.41; H, 6.28; N, 5.54\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2}$ 3.1 Under a nitrogen atmosphere, an orange suspension of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.496 \mathrm{~g}, 1.09 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.495 \mathrm{~g}, 2.18 \mathrm{mmol})$ in degassed $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at room temperature for 72 h . The yellow suspension was concentrated under reduced pressure to $c a .10 \mathrm{~cm}^{3}$ and the solid filtered and dried under reduced pressure. Yield: $0.663 \mathrm{~g}, 72 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-27.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.52-7.19(\mathrm{~m}, 20 \mathrm{H}$, arom. H), $4.01(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.98\left(\mathrm{~s}, 14 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.54\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right), 3.11\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6\right.$ $\left.\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{P}\right), 2.58\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right)$. MS ( $\mathrm{FAB}^{+}$): m/z $667\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$ requires: C, $69.35 ; \mathrm{H}, 6.00$; N, 3.25. Found: C, 69.25; H, 5.95; N, 3.35\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P C y}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{3 . 2}$ Under a nitrogen atmosphere, an orange solution of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.139 \mathrm{~g}, 0.305 \mathrm{mmol})$ and $\mathrm{Cy}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.175 \mathrm{~g}, 0.613 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right.$, freeze-thawed) was stirred at RT for 6 d . The resulting yellow suspension was concentrated to $c a .2 \mathrm{~cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield: $0.093 \mathrm{~g}, 34 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right):-18.1 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.08\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.04\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.02\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.52(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}$ ), $2.49\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right), 2.46\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 1.67$ - $1.12(\mathrm{~m}, 44 \mathrm{H}$, cyclohexyl H). MS (FAB ${ }^{+}$): m/z $875[\mathrm{M}-\mathrm{H}]^{+}, 678\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{74} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \cdot 1.25 \mathrm{H}_{2} \mathrm{O}$ requires: C, $66.78 ; \mathrm{H}, 8.29$; N, 3.12. Found: C, 66.80; H, 8.46; N, 3.17\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P A d}\right) \mathbf{C H}_{2}\right\}_{2}$ 3.3 Under a nitrogen atmosphere, an orange suspension of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}(0.108 \mathrm{~g}, 0.238 \mathrm{mmol})$ and $\mathrm{PAdCH}_{2} \mathrm{OH}(0.141 \mathrm{~g}, 0.476$ mmol ) in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right.$, freeze-thawed) was stirred at reflux for 44 h to yield a dark orange solution. Upon standing for 2 h at RT an orange solid precipitated. The suspension was concentrated to approximately $10 \mathrm{~cm}^{3}$ under reduced pressure and the precipitate filtered and dried under reduced pressure. Yield: $0.081 \mathrm{~g}, 37 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right):-42.8 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.08-4.02\left(\mathrm{~m}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\mathrm{C}_{5} \mathrm{H}_{5}$ ), $3.59\left(\mathrm{bm}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right.$, enantiomer A), $3.42\left(\mathrm{bm}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right.$, enantiomer B), $2.71\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{PCH}_{2}\right.$, enantiomer A), $2.54\left(\mathrm{bm}, 4 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2}\right), 2.31(\mathrm{~m}, 2 \mathrm{H}$, $\mathrm{PCH}_{2}$, enantiomer B), $1.89-1.24(\mathrm{~m}, 32 \mathrm{H}$, Ad. cage H). Anal. Calc. for $\mathrm{C}_{46} \mathrm{H}_{62} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{O}_{6} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, 59.94; H, 6.90; N, 3.04. Found: C, 59.99; H, 6.88; N, 3.11\%.
6.7.2 Coordination Chemistry of $\mathbf{3 . 1} \mathbf{- 3 . 3}$.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{3 . 4}$ Ligand $\mathbf{3 . 1}(0.075 \mathrm{~g}, 0.088 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.033 \mathrm{~g}, 0.087 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for a further 0.5 h . The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.085 \mathrm{~g}, 86 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): 2.6 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}}$ $3666 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.59-7.19\left(\mathrm{~m}, 20 \mathrm{H}\right.$, arom. H), $4.11\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $4.01\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.98\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.76$ (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.09\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right)$,
3.02 (s, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ). FT-IR (KBr): $\mathrm{v}_{\mathrm{PtCl}} 318,294 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1118$ $[\mathrm{M}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{Cl}_{2} \mathrm{Pt} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, 51.61; H, 4.76; N, 2.41. Found: C, 51.67; H, 4.59; N, 2.31\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\mathbf{F C C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P C y}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{3 . 5}$. A solution of $\mathbf{3 . 2}$ ( $\left.0.069 \mathrm{~g}, 0.079 \mathrm{mmol}\right)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.029 \mathrm{~g}, 0.078 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting yellow suspension stirred for a further 0.5 h . The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.032 \mathrm{~g}, 36 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : 18.8 (s, ${ }^{1} J_{\mathrm{PtP}} 3586 \mathrm{~Hz}$ ), $17.9\left(\mathrm{~s},{ }^{1} J_{\mathrm{PtP}} 3402 \mathrm{~Hz}\right) . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1071[\mathrm{M}-\mathrm{Cl}]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{74} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot 2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, $47.58 ; \mathrm{H}, 5.99$; N, 2.13. Found: C, 47.94; H, 5.94; N, 2.16\%.

Complex 3.6 was prepared in a similar manner to 3.5 unless otherwise stated.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{F C C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P A d}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{3 . 6}$ A solution of $\mathbf{3 . 3}(0.051 \mathrm{~g}, 0.056 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\mathrm{cod})(0.021 \mathrm{~g}, 0.056 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. Following the addition of $\mathrm{Et}_{2} \mathrm{O}$ no precipitation was observed and the solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$. Hexane $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting yellow suspension refrigerated overnight to yield further solid. The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.026 \mathrm{~g}, 39 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 2.9\left(\mathrm{~s},{ }^{1} J_{\text {PtP }} 3411 \mathrm{~Hz}\right),-27.5\left(\mathrm{~s},{ }^{1} J_{\text {PtP }} 3397 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.19-4.13\left(\mathrm{~m}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{4}\right), 4.03\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.70(\mathrm{bs}, 4 \mathrm{H}$, $\mathrm{CH}_{2}$ ), 2.96 (bs, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 2.37 - $1.12(\mathrm{~m}, 32 \mathrm{H}$, Ad. cage H$)$. FT-IR (KBr): $\mathrm{v}_{\mathrm{PtCl}} 316$, $290 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1071[\mathrm{M}-2 \mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{46} \mathrm{H}_{62} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{O}_{6} \mathrm{Fe}_{2} \mathrm{PtCl}_{2}$ requires: C, 46.88; H, 5.30; N, 2.38. Found: C, 47.03; H, 4.87, N, 2.82\%.
cis- $\mathbf{P d C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{3 . 7}$ Ligand $\mathbf{3 . 1}(0.011 \mathrm{~g}, 0.12 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PdCl}_{2}(\operatorname{cod})(0.034 \mathrm{~g}, 0.12 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting cream suspension stirred for a further 0.5 h . The cream precipitate was filtered and dried
under reduced pressure. Yield: 0.089 g . Attempts to obtain an analytically pure sample of $\mathbf{3 . 7}$ were hampered by slow decomposition to $\mathrm{PdCl}_{2}\left(\mathrm{Ph}_{2} \mathrm{POCH}_{2} \mathrm{PPh}_{2}\right)$.
cis- $\mathbf{P d C l}_{2}\left(\mathbf{P h}_{2} \mathbf{P O C H} \mathbf{P P h}_{2}\right) \mathbf{3 . 7 A}$ Ligand $\mathbf{3 . 1}(0.158 \mathrm{~g}, 0.176 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PdCl}_{2}(\operatorname{cod})(0.050 \mathrm{~g}, 0.175 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred for 4 d and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting suspension stirred for a further 0.5 h . The precipitate was filtered and dried under reduced pressure (Yield: 0.128 g ). The complex 3.7A was recrystallised from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $\mathrm{Et}_{2} \mathrm{O}$ using 0.050 g of crude product. Yield: 0.019 g . ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : 159.9 ( $\mathrm{d},{ }^{2} J_{\mathrm{PP}} 17.0 \mathrm{~Hz}$ ), $79.9\left(\mathrm{~d},{ }^{2} \mathrm{~J}_{\mathrm{PP}} 17.0 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.87-7.45(\mathrm{~m}, 20 \mathrm{H}$, arom. H), $3.41(\mathrm{~d}$, $2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 6.8 \mathrm{~Hz} \mathrm{CH} 2 \mathrm{P}$ ). FT-IR (KBr): $v_{\mathrm{PdCl}} 308,289 \mathrm{~cm}^{-1}$. MS (FAB ${ }^{+}$): m/z $542[\mathrm{M}-$ $\mathrm{Cl}]^{+}, 199\left[\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{Fe}\right]^{+}$.
cis- $\mathbf{P t M e}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathbf{3 . 8}$ Ligand $\mathbf{3 . 1}(0.090 \mathrm{~g}, 0.11 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PtMe}_{2}(\operatorname{cod})(0.035 \mathrm{~g}, 0.11 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(20 \mathrm{~cm}^{3}\right)$ and hexane $\left(15 \mathrm{~cm}^{3}\right)$ were added and the resulting orange suspension stirred for a further 0.5 h . The orange precipitate was filtered and dried under reduced pressure. Yield: $0.037 \mathrm{~g}, 33 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 19.7$, (s, $\left.{ }^{1} J_{\mathrm{PtP}} 1866 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.55-7.07(\mathrm{~m}, 20 \mathrm{H}$, arom. H ), 3.95 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.88\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.80\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.55\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$, $2.85\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right), 2.56\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 0.25\left(\mathrm{~m}, 6 \mathrm{H},{ }^{2} J_{\mathrm{PtH}} 69.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{PH}} 13.2 \mathrm{~Hz}\right.$, $\left.{ }^{2} J_{\mathrm{PtH}}{ }^{3} J_{\mathrm{PH}} 12.8 \mathrm{~Hz}, \mathrm{PtCH}_{3}\right)$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1062\left[\mathrm{M}-\mathrm{CH}_{3}\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{52} \mathrm{H}_{56} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{Cl}_{2} \mathrm{Pt} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$ requires: C, $57.23 ; \mathrm{H}, 5.31 ; \mathrm{N}, 2.58$. Found: C, 57.25; H, 5.16; N, 2.43\%.

Trans, trans- $\left\{\mathbf{P d}\left(\mathbf{C H}_{3}\right) \mathbf{C l}\left\{\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right\}_{2} \mathbf{3 . 9}$ Ligand 3.1 ( 0.111 g , $0.121 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{Pd}\left(\mathrm{CH}_{3}\right) \mathrm{Cl}(\mathrm{cod})(0.032 \mathrm{~g}, 0.12 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to ca. $2 \mathrm{~cm}^{3}$ under reduced pressure. Hexane $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting cream suspension stirred for a further 0.5 h . The cream precipitate was filtered and dried under reduced pressure. Yield: $0.074 \mathrm{~g}, 61 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): 13.0$ ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.82-7.36\left(\mathrm{~m}, 20 \mathrm{H}\right.$, arom. H), $4.29\left(\mathrm{t}, 4 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz}\right.$,
$\left.\mathrm{C}_{5} \mathrm{H}_{4}\right), 4.24\left(\mathrm{t}, 4 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.20\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.81\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.67(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.59 (br, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), $0.00\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{PH}} 12 \mathrm{~Hz}, \mathrm{CH}_{3}\right.$ ). FT-IR (KBr): $v_{\mathrm{PdCl}} 263$ $\mathrm{cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 973[0.5 \mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{51} \mathrm{H}_{53} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{PdCl} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, $58.09 ; \mathrm{H}, 5.07$; N, 2.72. Found: C, $58.03 ; \mathrm{H}$, 5.10; N, 2.72\%.

Trans, trans- $\left\{\mathbf{R h}(\mathbf{C O}) \mathbf{C l}\left\{\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}\right\} \mathbf{3 . 1 0}$ Ligand 3.1 ( 0.098 g , $0.11 \mathrm{mmol})$ was added to a stirred solution of $\left\{\operatorname{Rh}(\mu-\mathrm{Cl})(\mathrm{CO})_{2}\right\}_{2}(0.023 \mathrm{~g}, 0.056$ $\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to ca. $2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting orange suspension stirred for a further 0.5 h . The orange precipitate was filtered and dried under reduced pressure. Yield: $0.033 \mathrm{~g}, 29 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 16.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{RhP}} 130 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.73-7.29(\mathrm{~m}, 20 \mathrm{H}$, arom. H$)$, 4.19 (s, 4H, C ${ }_{5} \mathrm{H}_{4}$ ), 4.16 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 4.11 ( $\mathrm{s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.94 (s, 4H, $\mathrm{CH}_{2}$ ), 3.76 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.57 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{CO}} 1969 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 983$ $[0.5 \mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{102} \mathrm{H}_{100} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Fe}_{4} \mathrm{P}_{4} \mathrm{Rh}_{2} \mathrm{Cl}_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, 58.81; H, 5.08; N, 2.69. Found: C, 58.37; H, 4.79; N, 3.22\%.
$\boldsymbol{c i s}-\mathbf{M o}(\mathbf{C O})_{4}\left\{\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2}$ 3.11 Under a nitrogen atmosphere, a solution of $3.1(0.096 \mathrm{~g}, 0.11 \mathrm{mmol})$ and $\mathrm{Mo}(\mathrm{CO})_{4}(\mathrm{nbd})(0.032 \mathrm{~g}, 0.11 \mathrm{mmol})$ in degassed $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was stirred at RT for 10 d . The solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting orange suspension stirred for a further 0.5 h . The orange precipitate was filtered and dried under reduced pressure. Yield: $0.065 \mathrm{~g}, 58 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 29.0 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.44-7.32(\mathrm{~m}, 20 \mathrm{H}$, arom. H$), 3.99(\mathrm{~s}, 4 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.85\left(\mathrm{bs}, 14 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\mathrm{C}_{5} \mathrm{H}_{5}$ ), $3.29\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 2.78\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 1.97(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{CO}}$ 2018, 1918, 1898, $1870 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1061$ $[\mathrm{M}]^{+}, 1005[\mathrm{M}-2 \mathrm{CO}]^{+}$. Anal. Calc. for $\mathrm{C}_{54} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{Mo} \cdot 1.75 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, 55.37; H, 4.46; N, 2.32. Found: C, 55.40; H, 4.25; N, 2.45\%.
$\left\{\mathbf{R u C l}_{\mathbf{2}}(\boldsymbol{p} \text { - } \mathbf{c y m})\right\}_{\mathbf{2}}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathbf{3 . 1 2}$ Phosphine $\mathbf{3 . 1}$ ( $0.038 \mathrm{~g}, 0.043$ $\mathrm{mmol})$ was added to a stirred solution of $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.026 \mathrm{~g}, 0.043$ $\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred for 0.5 h before concentrating the solvent under reduced pressure to $c a .2 \mathrm{~cm}^{3}$. Hexane $\left(25 \mathrm{~cm}^{3}\right)$ was
added and the resulting orange suspension stirred for a further 0.5 h . The orange precipitate was filtered and dried under reduced pressure. Yield: $0.054 \mathrm{~g}, 86 \%$. ${ }^{31} \mathrm{P}\{1 \mathrm{H}\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): 25.2 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 7.94-7.46(\mathrm{~m}, 20 \mathrm{H}$, arom. H), $5.37\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right), 5.20\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.2 \mathrm{~Hz}, \mathrm{CH}\right), 5.12\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6 \mathrm{~Hz}\right.$, $\mathrm{CH}), 3.99\left(\mathrm{t}, 4 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.88\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.74\left(\mathrm{t}, 4 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz}\right.$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.64\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right.$ ), $2.52\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.39$ (sept, ${ }^{3} J_{\mathrm{HH}} 6.8$ $\mathrm{Hz}, 2 \mathrm{H}, \mathrm{CH}), 1.79\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 0.96\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{3}\right)$. FT-IR (KBr): $\mathrm{v}_{\mathrm{RuCl}}$ $295 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 973\left[\mathrm{M}-\mathrm{RuCl}_{2}(p-\mathrm{cym}) \mathrm{PPh}_{2}\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{78} \mathrm{H}_{78} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{Cl}_{4} \mathrm{Ru}_{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, $55.01 ; \mathrm{H}, 5.21$; N, 1.81. Found: C, 54.93; H, 5.26; N, 2.17\%.
$\left\{\mathbf{A u C l}_{\mathbf{2}}\left\{\mathbf{F C C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{3 . 1 3}\right.$ Ligand $3.1(0.108 \mathrm{~g}, 0.118 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{AuCl}($ tht $)(0.076 \mathrm{~g}, 0.24 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred in the dark for 0.5 h and concentrated under reduced pressure to $c a .2 \mathrm{~cm}^{3}$. Hexane ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for a further 0.5 h . The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.130 \mathrm{~g}, 84 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 19.4 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.68-7.40(\mathrm{~m}, 20 \mathrm{H}$, arom. H$), 4.03\left(\mathrm{~s}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right), 3.64$ (d, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 1.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.51\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right.$ ), $2.60\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right)$. FT-IR (KBr): $v_{\text {AuCl }} 330 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $1317[\mathrm{M}]^{+}, 1316[\mathrm{M}-\mathrm{H}]^{+}, 1281[\mathrm{M}-\mathrm{H}-\mathrm{Cl}]^{+}$, $199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{~N}_{2} \mathrm{Fe}_{2} \mathrm{P}_{2} \mathrm{Au}_{2} \mathrm{Cl}_{2}$ requires: $\mathrm{C}, 45.58 ; \mathrm{H}, 3.83 ; \mathrm{N}$, 2.13. Found: C, 45.45 ; H, 3.84; N, 2.02\%.

### 6.7.3 Preparation of $\mathbf{3 . 1 4}$

$\mathbf{F c C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{C H}_{3}$ Ice chilled ethylamine $\left(0.50 \mathrm{~cm}^{3}, 7.6 \mathrm{mmol}\right)$ was added to an ice chilled solution of ferrocenecarboxaldehyde $(0.575 \mathrm{~g}, 2.63 \mathrm{mmol})$ in MeOH ( 100 $\mathrm{cm}^{3}$ ). The resulting solution was stirred for 0.25 h at $c a .0^{\circ} \mathrm{C}$ before stirring for a further 6.5 h at RT. The solvent was removed under reduced pressure. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): ~ \delta 8.15(\mathrm{bs}, 1 \mathrm{H}, \mathrm{CHN}), 4.66\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.38$ (bs, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 4.20 (bs, $5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.51 (bs, $2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 1.28 (bs, $3 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ). FTIR ( KBr ): $\mathrm{v}_{\mathrm{C}=\mathrm{N}}$ 1644. MS ( $\mathrm{FAB}^{+}$): m/z $241[\mathrm{M}]^{+}, 240[\mathrm{M}-\mathrm{H}]^{+}, 242[\mathrm{M}+\mathrm{H}]^{+}$.

Amine $\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3}$ was prepared in a similar manner to amine $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{3} \quad \mathrm{NaBH}_{4}(0.585 \mathrm{~g}, 15.2 \mathrm{mmol}), \mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2} \mathrm{CH}_{3}(0.615 \mathrm{~g}$, 2.55 mmol ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(120 \mathrm{~cm}^{3} ; 2: 1\right)$.Yield: $0.568 \mathrm{~g}, 92 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.12\left(\mathrm{t}, 2 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.05\left(\mathrm{bs}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.03\left(\mathrm{t}, 2 \mathrm{H}, J_{\mathrm{HH}} 1.6\right.$ $\mathrm{Hz}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.45\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.61\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.04(\mathrm{t}, 3 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ). FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3310$. MS ( $\mathrm{FAB}^{+}$): m/z $243[\mathrm{M}]^{+}, 242[\mathrm{M}-$ $\mathrm{H}]^{+}, 244[\mathrm{M}+\mathrm{H}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{NFe} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C , 61.93; H, 7.20; N, 5.56. Found C, 62.48; H, 6.87; N, 5.27\%.
$\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2} \mathbf{C H}_{3} \mathbf{3 . 1 4}$ Under a nitrogen atmosphere, an orange solution of $\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2} \mathrm{CH}_{3}(0.615 \mathrm{~g}, 2.55 \mathrm{mmol})(0.173 \mathrm{~g}, 0.712 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.165 \mathrm{~g}, 0.714 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at RT for 5 d . The solvent was removed under reduced pressure. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-27.7 \mathrm{ppm} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 7.43-7.23(\mathrm{~m}, 10 \mathrm{H}$, arom. H), 4.07 (bs, $\left.2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.02\left(\mathrm{bs}, 7 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right), 3.62\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.16\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}}\right.$ $3.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}$ ), $2.54\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.93\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 457[\mathrm{M}+\mathrm{O}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.

### 6.7.4 Coordination chemistry of $\mathbf{3 . 1 4}$.

$\mathbf{A u C l}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{C H}_{3}\right\} \mathbf{3 . 1 5}$ A solution of $\mathbf{3 . 1 4}(0.101 \mathrm{~g}, 0.181 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathrm{AuCl}(\mathrm{tht})(0.057 \mathrm{~g}, 0.18 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$. The mixture was stirred in the dark for 0.5 h before the solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Hexane $\left(15 \mathrm{~cm}^{3}\right)$ was added to precipitate an orange solid which dissolved after a brief period of stirring. Hexane $\left(10 \mathrm{~cm}^{3}\right)$ was added and the resulting cream suspension stirred for 1 d in the dark. The orange precipitate was filtered and dried under reduced pressure. Yield: 0.068 g , $56 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 50.1-29.9(\mathrm{bm}), 17.4$ (s) ppm. Anal. Calc. for $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{NPFeAuCl} \cdot 0.75 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires $\mathrm{C}, 43.57 ; \mathrm{H}, 4.03 ; \mathrm{N}, 1.90$. Found $\mathrm{C}, 43.54$; H, 3.93; N, 1.57\%.

### 6.7.5 Preparation of $\mathbf{3 . 1 6}$ and $\mathbf{3 . 1 7}$

The precursor imines $\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}, \quad\left\{\mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2} \mathrm{CH}_{2}$ and amines $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$, $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}$ were prepared in a similar manner to their ethylenediamine analogues, ${ }^{218}$ and their polyaromatic analogues discussed in Chapter 2. ${ }^{187}$
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N C}(\mathbf{H})\right\}_{2} \mathbf{F c}\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CHO}\right)_{2} \mathrm{Fe}(0.205 \mathrm{~g}, 0.847 \mathrm{mmol}), \mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.364 \mathrm{~g}$, $1.69 \mathrm{mmol})$ and $\mathrm{MeOH}\left(50 \mathrm{~cm}^{3}\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.93(\mathrm{~s}$, $2 \mathrm{H}, \mathrm{CHN}$ ), $4.52\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.35-4.09\left(\mathrm{~m}, 26 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right)$. FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1636 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $636[\mathrm{M}]^{+}, 437\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{Fe}_{3} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, 63.29 ; H, 5.16; N, 4.34. Found: C, 63.05; H, 5.21; N, 4.23\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{F c} \mathrm{NaBH}_{4}(0.183 \mathrm{~g}, 4.74 \mathrm{mmol}),\left\{\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H})\right\}_{2} \mathrm{Fc}(0.498 \mathrm{~g}$, 0.783 mmol ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(60 \mathrm{~cm}^{3}, 2: 1\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.12\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.04\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.99\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.45(\mathrm{bs}, 8 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3091 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 640[\mathrm{M}]^{+}, 639[\mathrm{M}-\mathrm{H}]^{+}$, $243\left[\mathrm{M}-2\left(\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{Fe}\right)\right]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{34} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{Fe}_{3} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires: C, 61.20; H, 5.89; N, 4.20. Found: C, 61.14; H, 5.88; N, 3.90\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{F c} \mathbf{3 . 1 6}$ Under a nitrogen atmosphere, a solution of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}(0.309 \mathrm{~g}, 0.483 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.223 \mathrm{~g}, 0.959$ $\mathrm{mmol})$ in toluene: $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}, 2: 1\right)$ was stirred for 44 h at RT. The solvent was removed under reduced pressure. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right):-27.8$ (s) ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.42-7.07(\mathrm{~m}, 20 \mathrm{H}$, arom. H$), 4.08\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $4.04\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.00\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.98\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.55\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $3.51\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.02\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right.$ ). MS ( $\mathrm{FAB}^{+}$): m/z 199 $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.

Imine $\left\{\mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2} \mathrm{CH}_{2}$ and amine $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}$ were prepared in a similar manner to their ethylene diamine counterparts, ${ }^{218}$ and their polyaromatic analogues discussed in Chapter 2. ${ }^{187}$
$\left\{\mathbf{F c C}(\mathbf{H}) \mathbf{N C H}_{\mathbf{2}} \mathbf{\}}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}}\right.$ 1,3-diaminopropane ( $0.185 \mathrm{~g}, 2.47 \mathrm{mmol}$ ), ferrocenealdehyde $(1.079 \mathrm{~g}, 4.942 \mathrm{mmol})$ and $\mathrm{MeOH}\left(60 \mathrm{~cm}^{3}\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 8.15(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CHN}), 4.64\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.36\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.18\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right)$, $3.53\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}\right), 2.00\left(\mathrm{~m}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1637 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{Fe}_{2} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, $63.79 ; \mathrm{H}$, 5.67; N, 5.95. Found C, 63.88; H, 5.71; N, 5.83\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}}\right\}_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \mathrm{NaBH}_{4}(0.581 \mathrm{~g}, 15.1 \mathrm{mmol}),\left\{\mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2} \mathrm{CH}_{2}(1.125$ $\mathrm{g}, 2.413 \mathrm{mmol}$ ) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(120 \mathrm{~cm}^{3}, 2: 1\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.10\left(\mathrm{t}, 4 \mathrm{H}, J_{\mathrm{HH}} 1.6 \mathrm{~Hz} \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.05\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.03\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 1.6\right.$ $\mathrm{Hz}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.44\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.63\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}\right), 1.62(\mathrm{~m}, 2 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3302 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 470[\mathrm{M}]^{+}$, $471[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{25} \mathrm{H}_{30} \mathrm{~N}_{2} \mathrm{Fe}_{2} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 60.39 ; \mathrm{H}, 6.69 ; \mathrm{N}$, 5.63. Found C, 60.37; H, 6.44; N, 5.35\%.
$\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{C H}_{\mathbf{2}} \mathbf{3 . 1 7}$ Under a nitrogen atmosphere, an orange suspension of $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{CH}_{2}(0.126 \mathrm{~g}, 0.268 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ ( $0.122 \mathrm{~g}, 0.536 \mathrm{mmol}$ ) in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred at RT for 14 d . The solvent was slowly removed under reduced pressure to afford a viscous oil. Yield: 0.198 g , $85 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-26.9$ (bs), -27.6 (bs), -28.5 (bs); respective \% ratio ca. 1:5:1. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.00\left(\mathrm{bs}, 18 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\mathrm{C}_{5} \mathrm{H}_{4}$ 's), $3.56(\mathrm{~s}, 4 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.08 (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{PPh}_{2}$ ), 2.89 (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}$ ), 1.43 (bs, 2 H , $\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}$ ). MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 681\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}, 483\left[\mathrm{M}-\mathrm{PPh}_{2}-\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{Fe}\right]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.

### 6.7.6 Coordination chemistry of $\mathbf{3 . 1 6}$

$\left\{\mathbf{A u C l}_{2}\left\{\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right\}_{2} \mathbf{F c} \mathbf{3 . 1 8} \mathrm{~A}\right.$ colourless solution of $\mathrm{AuCl}(\mathrm{tht})$ $(0.118 \mathrm{~g}, 0.368 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $\mathbf{3 . 1 6}$ ( $0.222 \mathrm{~g}, 0.186 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred, in the dark, for 1 h and concentrated under reduced pressure to $c a .2 \mathrm{~cm}^{3}$. Hexane ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for a further 0.5 h . The precipitate was filtered and dried under reduced pressure. Yield: $0.239 \mathrm{~g}, 87 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 17.4$ (s) ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.71-7.25(\mathrm{~m}, 20 \mathrm{H}$,
arom. H), $4.02\left(\mathrm{bm}, 26 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.81 (bs, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.56 (bs, $4 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.44 (bs, 4H, CH2 ). MS ( $\mathrm{FAB}^{+}$): m/z $1233\left[\mathrm{M}-\mathrm{AuCl}_{2}\right]^{+}, 1615\left[\mathrm{M}-2 \mathrm{Cl}+\mathrm{PPh}_{2}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{60} \mathrm{H}_{58} \mathrm{~N}_{2} \mathrm{Fe}_{3} \mathrm{P}_{2} \mathrm{Au}_{2} \mathrm{Cl}_{2} \cdot 0.75 \mathrm{C}_{6} \mathrm{H}_{14}$ requires: C , $49.47 ; \mathrm{H}, 4.41 ; \mathrm{N}, 1.79$. Found: C, 49.40; H, 4.43; N, 1.79\%.

The ruthenium complex $\mathbf{3 . 1 9}$ was prepared in a similar manner to $\mathbf{3 . 1 8}$.
$\left.\left\{\mathbf{R u C l}_{\mathbf{2}} \mathbf{( p - c y m}\right)\right\}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{F c} \mathbf{3 . 1 9}[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.083$ $\mathrm{g}, 0.14 \mathrm{mmol})$, $3.16(0.162 \mathrm{~g}, 0.136 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. Yield: 0.136 g , $61 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 26.1$ (s) ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.93-7.36(\mathrm{~m}$, 20 H , arom. H), $5.13\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.2 \mathrm{~Hz}, \mathrm{CH}\right), 5.06\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.2 \mathrm{~Hz}, \mathrm{CH}\right), 3.92(\mathrm{~s}$, $\left.4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.82\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.77\left(\mathrm{bs}, 14 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{4}\right), 3.62\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, 3.42 (bs, 4H, CH ${ }_{2} \mathrm{P}$ ), 2.59 (s, 4H, CH2 $\mathrm{C}_{5} \mathrm{H}_{4}$ ), 2.49 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 2.35 (sept, 2 H , $\left.{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}\right), 1.71\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 0.85\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{3}\right) . \mathrm{MS}\left(\mathrm{FAB}^{+}\right)$: $\mathrm{m} / \mathrm{z} 1651[\mathrm{M}]^{+}, 1615[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{80} \mathrm{H}_{86} \mathrm{~N}_{2} \mathrm{Fe}_{3} \mathrm{P}_{2} \mathrm{Ru}_{2} \mathrm{Cl}_{4}$ requires: C, 58.20; H, 5.25; N, 1.70. Found: C, 57.80; H, 5.26; N, 1.78\%.
cis- $\left.\mathbf{P t C l}_{\mathbf{2}}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right) \mathbf{C H}_{\mathbf{2}}\right\}_{2} \mathbf{F c}\right\} \mathrm{PtCl}_{2}(\mathrm{cod})(0.075 \mathrm{~g}, 0.20 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $\left(5 \mathrm{~cm}^{3}\right)$ and $3.16(0.239 \mathrm{~g}, 0.201 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(5 \mathrm{~cm}^{3}\right)$. Yield: $0.178 \mathrm{~g}, 68 \%$. FTIR ( KBr ): $\mathrm{v}_{\mathrm{PtCl}} 313,288 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $1266[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{60} \mathrm{H}_{58} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Fe}_{3} \mathrm{PtCl}_{2} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires C, $54.20 ; \mathrm{H}, 4.62$; N, 2.11. Found: C, $54.13 ; \mathrm{H}$, 4.57; N, 1.95\%.
6.7.7 Preparation of $\mathbf{3 . 2 0} \mathbf{- 3 . 2 2}$.

The precursor imine $\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H}) \mathrm{Fc}$ and amine $\left(\mathrm{FcCH}_{2}\right)_{2} \mathrm{NH}$ were prepared in a similar manner to $\left\{\mathrm{FcC}(\mathrm{H}) \mathrm{NCH}_{2}\right\}_{2}$ and $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2}$.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N C} \mathbf{( H )} \mathbf{F c}$ Ferrocenecarboxaldehyde ( $\left.0.366 \mathrm{~g}, 1.68 \mathrm{mmol}\right), \mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.360$ $\mathrm{g}, 1.67 \mathrm{mmol})$ and $\mathrm{MeOH}\left(35 \mathrm{~cm}^{3}\right)$. Yield $0.666 \mathrm{~g}, 97 \%$. Attempts to obtain an analytically pure sample of $\mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H}) \mathrm{Fc}$ were hampered by hydrolysis and the incomplete nature of the reaction. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.04$ (s, $1 \mathrm{H}, \mathrm{CHN}$ ). FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1635 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 411[\mathrm{M}]^{+}, 412[\mathrm{M}+\mathrm{H}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.
$\left.\mathbf{( F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N H ~ N a B H} 4$ ( $\left.0.241 \mathrm{~g}, 6.24 \mathrm{mmol}\right), \mathrm{FcCH}_{2} \mathrm{NC}(\mathrm{H}) \mathrm{Fc}(0.614 \mathrm{~g}, 1.08 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(60 \mathrm{~cm}^{3}, 2: 1\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.13(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.11\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.04\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.47\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NH}\right) . \mathrm{FT}-\mathrm{IR}$ (KBr): $v_{\mathrm{NH}} 3331 \mathrm{~cm}^{-1}$. FAB mass spectrum: m/z $413[\mathrm{M}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{22} \mathrm{H}_{23} \mathrm{NFe}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, $62.60 ; \mathrm{H}, 5.73$; N, 3.32. Found C, 62.74; H, 5.81; N, 3.08\%.

The tertiary phosphines $\mathbf{3 . 2 0}$ - $\mathbf{3 . 2 2}$ were prepared in a similar manner to $\mathbf{3 . 4} \mathbf{- 3 . 6}$.
$\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}} \mathbf{3 . 2 0} \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.227 \mathrm{~g}, 0.976 \mathrm{mmol})$, $\left(\mathrm{FcCH}_{2}\right)_{2} \mathrm{NH}(0.404$ $\mathrm{g}, 0.978 \mathrm{mmol})$ and $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.345 \mathrm{~g}, 58 \% \cdot{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ $-27.9 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.27-7.19(\mathrm{~m}, 10 \mathrm{H}$, arom. H$), 4.09\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $4.05\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.01\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.55\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.04\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 4.0\right.$ $\left.\mathrm{Hz}, \quad \mathrm{CH}_{2} \mathrm{P}\right)$. MS (FAB+$+\mathrm{m} / \mathrm{z} 413 \quad\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{35} \mathrm{H}_{34} \mathrm{NPFe}_{2} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, $68.26 ; \mathrm{H}, 5.65$; N, 2.27. Found C, 68.05 ; H, 5.71; N, 2.40\%.
$\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P C y}_{\mathbf{2}} \mathbf{3 . 2 1} \mathrm{An}$ orange solution of $\left(\mathrm{FcCH}_{2}\right)_{2} \mathrm{NH}(0.397 \mathrm{~g}, 0.961$ $\mathrm{mmol})$ and $\mathrm{Cy}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.274 \mathrm{~g}, 0.960 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right.$, freeze-thawed) was stirred at RT for 6 d . The resulting yellow suspension was concentrated to $c a .2$ $\mathrm{cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield: 0.352 g , $59 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-19.3 \mathrm{ppm} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 4.10\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $4.04\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.02\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.44\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.41\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 1.6\right.$ $\left.\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{P}\right), 1.61-1.10(\mathrm{~m}, 22 \mathrm{H}, \mathrm{Cy} H)$. MS ( $\mathrm{FAB}^{+}$): m/z $639[\mathrm{M}+\mathrm{O}]^{+}, 623[\mathrm{M}]^{+}$, $622[\mathrm{M}-\mathrm{H}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{35} \mathrm{H}_{46} \mathrm{NPFe}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 66.47$; H, 7.49; N, 2.21. Found C, 66.11; H, 7.44; N, 2.12\%.
$\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P A d} \mathbf{3 . 2 2}$ An orange solution of $\left(\mathrm{FcCH}_{2}\right)_{2} \mathrm{NH}(0.150 \mathrm{~g}, 0.363 \mathrm{mmol})$ and $\mathrm{PAdCH}_{2} \mathrm{OH}(0.113 \mathrm{~g}, 0.367 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right.$, freeze-thawed) was stirred at RT for 7 d . The resulting yellow suspension was concentrated to $c a .2 \mathrm{~cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield: $0.109 \mathrm{~g}, 47 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-44.5 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.10\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.08$ (bs, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.06\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.03\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.56\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{HH}} 13.2 \mathrm{~Hz}\right.$, $\mathrm{CH}_{A} \mathrm{H}_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.31\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{HH}} 13.6 \mathrm{~Hz}, \mathrm{CH}_{\mathrm{A}} H_{B} \mathrm{C}_{5} \mathrm{H}_{4} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.49\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$,
$1.83-1.19\left(\mathrm{~m}, 16 \mathrm{H}\right.$, Ad. cage H). MS ( $\mathrm{FAB}^{+}$): m/z $641[\mathrm{M}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{33} \mathrm{H}_{40} \mathrm{NO}_{3} \mathrm{PFe}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 60.95 ; \mathrm{H}, 6.35 ; \mathrm{N}, 2.15$. Found C , 60.96; H, 6.35; N, 2.23\%.
6.7.8 Coordination chemistry of $\mathbf{3 . 2 0}-\mathbf{3 . 2 2}$.
$\mathbf{R u C l}_{\mathbf{2}} \mathbf{( \boldsymbol { p } - \mathbf { c y m } )}\left\{\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right\} \mathbf{3 . 2 3}[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.051 \mathrm{~g}, 0.083$ mmol), $3.20\left(0.103 \mathrm{~g}, 0.168 \mathrm{mmol}\right.$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. Yield: $0.135 \mathrm{~g}, 88 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 26.1 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.99-7.39(\mathrm{~m}, 10 \mathrm{H}$, arom. H), $5.14\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.6 \mathrm{~Hz}, \mathrm{CH}\right), 5.06\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6 \mathrm{~Hz}, \mathrm{CH}\right), 3.89\left(\mathrm{bs}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, 3.64 (bs, $12 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ and $\mathrm{CH}_{2} \mathrm{P}$ ), 2.73 (s, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 2.38 (sept, ${ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{CHCH}_{3}$ ), $1.72\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 0.85\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{CHCH}_{3}\right)$. MS ( $\mathrm{FAB}{ }^{+}$): m/z 917 $[\mathrm{M}]^{+}, 918[\mathrm{M}+\mathrm{H}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{45} \mathrm{H}_{48} \mathrm{NPFe}_{2} \mathrm{Cl}_{2} \mathrm{Ru} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: C, 56.92 ; H, 5.14; N, 1.46. Found: C, 57.16; H, 5.34; N, 1.43\%.

The complex $\mathbf{3 . 2 4}$ was prepared in a similar manner to $\mathbf{3 . 2 3}$.
$\left.\mathbf{R u C l}_{\mathbf{2}} \mathbf{( p - c y m}\right)\left\{\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P C y}_{\mathbf{2}}\right\} \mathbf{3 . 2 4}[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.062 \mathrm{~g}, 0.10$ $\mathrm{mmol})$, $3.21(0.128 \mathrm{~g}, 0.205 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. Yield: $0.156 \mathrm{~g}, 83 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 32.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 5.50(\mathrm{bs}, 4 \mathrm{H}, \mathrm{CH}), 4.18(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 4.03 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.96 ( $\mathrm{s}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.39 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), 3.27 ( $\mathrm{s}, 4 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 2.74 ( $\left.\mathrm{sept},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.03$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ), $1.23(\mathrm{~d}, 6 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right) . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 894[\mathrm{M}-\mathrm{Cl}]^{+}, 859[\mathrm{M}-2 \mathrm{Cl}]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{45} \mathrm{H}_{60} \mathrm{NPFe}_{2} \mathrm{Cl}_{2} \mathrm{Ru} \cdot 0.75 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires: $\mathrm{C}, 55.32 ; \mathrm{H}$, 6.24; N, 1.41. Found: C, 55.81; H, 6.47; N, 1.44\%.

The complex $\mathbf{3 . 2 5}$ was prepared in a similar manner to 3.12.
$\left.\mathbf{R u C l}_{\mathbf{2}} \mathbf{( p - c y m}\right)\left\{\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P A d}\right\} \mathbf{3 . 2 5}$ Ligand 3.22 ( $\left.0.099 \mathrm{~g}, 0.15 \mathrm{mmol}\right)$ and $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.047 \mathrm{~g}, 0.076 \mathrm{mmol})$. Yield: $0.121 \mathrm{~g}, 83 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 20.7 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 5.75\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{CH}\right.$, enantiomer A and B), $5.58\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{CH}\right.$, enantiomer A), $5.12\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.2 \mathrm{~Hz}, \mathrm{CH}\right.$, enantiomer B), $4.15\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.01\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.97\left(\mathrm{bs}, 10 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.40$ $\left(\mathrm{m}, 6 \mathrm{H}, \mathrm{CH}_{2}\right.$, enantiomer A and B), $2.85\left(\mathrm{~m},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right.$, enantiomer

A and B), 2.06 (s, $3 \mathrm{H}, \mathrm{CH}_{3}$, enantiomer A and B), $1.68-1.15$ (m, 22H, Ad. cage H and $\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$, enantiomer A and B). MS $\left(\mathrm{FAB}^{+}\right)$: m/z $948[\mathrm{M}]^{+}, 947[\mathrm{M}-\mathrm{H}]^{+}, 912$ $[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{43} \mathrm{H}_{54} \mathrm{NO}_{3} \mathrm{PFe}_{2} \mathrm{Cl}_{2} \mathrm{Ru} \cdot 0.5 \mathrm{C}_{4} \mathrm{H}_{10} \mathrm{O}$ requires: C, 54.89; H, 6.04; N, 1.42. Found: C, 55.09; H, 6.14; N, 1.40\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\left(\mathbf{F c C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{N C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right\}_{2} \mathbf{3 . 2 6}$ Ligand $\mathbf{3 . 2 0}(0.064 \mathrm{~g}, 0.11 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{PtCl}_{2}(\mathrm{cod})(0.020 \mathrm{~g}, 0.052 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Hexane ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for a further 0.5 h . The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.032 \mathrm{~g}, 41 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): 4.9\left(\mathrm{~s},{ }^{1} J_{\mathrm{PtP}} 3625 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.62-6.63\left(\mathrm{~m}, 20 \mathrm{H}\right.$, arom. H), $4.20\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.95\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $3.82\left(\mathrm{~s}, 20 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 2.90\left(\mathrm{~s}, 8 \mathrm{H}, \mathrm{CH}_{2} \mathrm{~N}\right), 2.77\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{PPh}_{2}\right) . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z}$ $1453[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.
6.7.9 Preparation of $\mathbf{3 . 2 7 - 3 . 2 9}$.

The synthesis for the precursor aldoxime and amine are described as follows.
$\mathbf{F c C}(\mathbf{H}) \mathbf{N O H}$ was prepared following a slight modification to the procedure previously reported by Schlögl. ${ }^{290}$ Sodium acetate ( $4.780 \mathrm{~g}, 57.69 \mathrm{mmol}$ ) and hydroxylammonium hydrochloride $(2.700 \mathrm{~g}, 38.47 \mathrm{mmol})$ were dissolved separately in the minimum amount of deionised water and were added to a stirred solution of ferrocenealdehyde ( $4.199 \mathrm{~g}, 19.23 \mathrm{mmol}$ ) in EtOH ( $100 \mathrm{~cm}^{3}$ ). The resulting suspension was stirred at $60^{\circ} \mathrm{C}$ for 6 h before being reduced to dryness. EtOH (20 $\left.\mathrm{cm}^{3}\right)$ and $\mathrm{Et}_{2} \mathrm{O}\left(120 \mathrm{~cm}^{3}\right)$ were added and the resulting suspension stirred for 0.5 h before the suspended inorganic solid was filtered and washed with $\mathrm{Et}_{2} \mathrm{O}$. The combined filtrate and washes were reduced to dryness. Yield: 4.490 g , Quantitative. ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 7.91$ (bs, 1H, CHN), 7.16 (bs, $1 \mathrm{H}, \mathrm{OH}$ ), 4.74 (t, $2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 2 \mathrm{~Hz}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.46\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 2 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.30\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 2 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.28\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 2\right.$ $\mathrm{Hz}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.16\left(\mathrm{~s}, 5 \mathrm{H} \mathrm{C}_{5} \mathrm{H}_{5}\right.$ ), $4.13\left(\mathrm{~s}, 5 \mathrm{H} \mathrm{C}_{5} \mathrm{H}_{5}\right.$ ). FT-IR (KBr): $v_{\text {OH }} 3448$, $v_{\mathrm{C}=\mathrm{N}} 1636$ $\mathrm{cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $229[\mathrm{M}]^{+}$.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}}$ was prepared via a modified procedure to that reported by Beer. ${ }^{247}$ An excess of lithium aluminum hydride ( $1.453 \mathrm{~g}, 37.14 \mathrm{mmol}$ ) was added portion wise with care to a solution of $\mathrm{FcC}(\mathrm{H}) \mathrm{NOH}(1.838 \mathrm{~g}, 8.024 \mathrm{mmol})$ in dry THF $\left(80 \mathrm{~cm}^{3}\right)$. The resulting mixture was stirred under a nitrogen atmosphere for 6 h before dry toluene $\left(80 \mathrm{~cm}^{3}\right)$ was added followed by ethyl acetate $\left(15 \mathrm{~cm}^{3}\right)$, with caution. NaOH solution ( 5 M ) was added dropwise until precipitation of inorganic solids was complete. The resulting mixture was filtered to yield an orange filtrate and a "gummy" solid residue. The residue was washed with copious amounts of toluene$\mathrm{MeOH}(80: 20)$ and the combined filtrate and washes evaporated to dryness. Further inorganic impurities were removed by dissolution of the organic phase in dichloromethane followed by filtration and evaporation of the filtrate. The product was further purified by column chromatography on silica using $\mathrm{MeOH}-\mathrm{NH}_{4} \mathrm{OH}$ (95:5) as eluent. Yield: $1.012 \mathrm{~g}, 59 \%{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 4.10\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.07$ (s, $5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ ), 4.04 (bs, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.48 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 1.42 (bs, 2H, NH2). FTIR (KBr): $v_{\mathrm{NH}} 3430 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $215[\mathrm{M}]^{+}, 199\left[\mathrm{M}_{\left.-\mathrm{NH}_{2}\right]^{+} \text {. Anal. Calc. for }}\right.$ $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{NFe} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 58.96; H, 6.07; N, 6.25. Found: C, 59.11; H, 6.05; N, 6.12\%.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{3 . 2 7}$ Under a nitrogen atmosphere, a freeze-thawed solution of $\mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.203 \mathrm{~g}, 0.944 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was cannulated onto $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.430 \mathrm{~g}, 1.89 \mathrm{mmol})$ and the orange solution stirred for 72 h . The resulting suspension was concentrated to $c a .2 \mathrm{~cm}^{3}$ and the solid filtered and dried under reduced pressure. Yield: $0.419 \mathrm{~g}, 73 \%{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-28.1 \mathrm{ppm}$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.30-7.15\left(\mathrm{~m}, 20 \mathrm{H}\right.$, arom. H), $4.07\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.02(\mathrm{bs}, 7 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ and $\left.\mathrm{C}_{5} \mathrm{H}_{5}\right), 3.86\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.35\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 644[\mathrm{M}+2 \mathrm{O}]^{+}, 611[\mathrm{M}-\mathrm{H}]^{+}, 426\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{Fe}$ requires C, 72.68; H, 5.77; N, 2.29. Found C, 72.40; H, 5.87; N, 2.38\%.

Phosphine 3.28 and $\mathbf{3 . 2 9}$ were prepared in a similar manner to 3.27.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P C y}_{2}\right)_{\mathbf{2}} 3.28 \mathrm{Cy}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.293 \mathrm{~g}, 1.04 \mathrm{mmol}), \mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.112 \mathrm{~g}$, $0.521 \mathrm{mmol})$ and $\mathrm{MeOH}\left(10 \mathrm{~cm}^{3}\right)$. Yield: $0.239 \mathrm{~g}, 73 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta-$ $18.3 \mathrm{ppm} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 4.11\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 1.6, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.06\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.01$ $\left(\mathrm{t}, 2 \mathrm{H}, \mathrm{J}_{\mathrm{HH}} 1.6, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.64\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.57\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right), 1.66-1.14(\mathrm{~m}$,

44H, Cy $H$ ). MS ( $\mathrm{FAB}^{+}$): m/z $635[\mathrm{M}]^{+}, 634[\mathrm{M}-\mathrm{H}]^{+}, 438\left[\mathrm{M}-\mathrm{PCy}_{2}\right]^{+}, 199[\mathrm{M}-$ $\left.\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{59} \mathrm{NP}_{2} \mathrm{Fe}$ requires C, $69.91 ; \mathrm{H}, 9.35 ; \mathrm{N}, 2.20$. Found C, 70.17; H, 9.53; N, 2.37\%.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P A d}\right)_{\mathbf{2}} \mathbf{3 . 2 9} \mathrm{PAdCH}_{2} \mathrm{OH}(0.313 \mathrm{~g}, 1.09 \mathrm{mmol})$ and $\mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.117$ $\mathrm{g}, 0.544 \mathrm{mmol}$ ). Yield: $0.227 \mathrm{~g}, 62 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-42.9(\mathrm{~s})$ and -43.1 (s) ppm; respective \% ratio ca. 1:2. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.11$ (bs, $\left.2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.05$ (bs, $7 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ and $\mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.69 (bs, $2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), $2.82\left(\mathrm{~m}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right.$, enantiomer A), 2.79 (m, 2H, ${ }^{2} J_{\mathrm{PH}} 4.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}$, enantiomer B), $2.50-1.22$ (m, Ad. cage H). MS ( $\mathrm{FAB}^{+}$): $\mathrm{m} / \mathrm{z} 472\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{33} \mathrm{H}_{47} \mathrm{NP}_{2} \mathrm{O}_{6} \mathrm{Fe}$ requires C, 59.02; H, 7.05; N, 2.09. Found C, 58.88; H, 6.82; N, 2.11\%.
6.7.10 Coordination chemistry of $3.27-3.29$.

Complexes 3.30-3.32 were prepared in a similar manner to 3.4.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 0}$ Phosphine 3.27 ( $\left.0.246 \mathrm{~g}, 0.382 \mathrm{mmol}\right)$, $\mathrm{PtCl}_{2}(\mathrm{cod})(0.143 \mathrm{~g}, 0.382 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.320 \mathrm{~g}, 96 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-9.1 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3389 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.67-7.25$ (m, 20H, arom. H), $4.09\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.02\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.95\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.45$ (s, 2H, CH ${ }_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.23\left(\mathrm{~d}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P},{ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz}\right.$ ). FT-IR (KBr): $v_{\mathrm{PtCl}} 312,292$ $\mathrm{cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 877 \quad[\mathrm{M}]^{+}, 875 \quad[\mathrm{M}-2 \mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{FePtCl}_{2} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$ requires C, $49.88 ; \mathrm{H}, 4.13 ; \mathrm{N}, 1.57$. Found C, $49.51 ; \mathrm{H}$, 4.08; N, 1.46\%.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P C y}_{2}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 1}$ Phosphine $\mathbf{3 . 2 8}$ ( $\left.0.151 \mathrm{~g}, 0.239 \mathrm{mmol}\right)$, $\mathrm{PtCl}_{2}$ (cod) $(0.089 \mathrm{~g}, 0.24 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.211 \mathrm{~g}, 99 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 5.5 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3473 \mathrm{~Hz} .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 4.14\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, $4.09\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.07\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.36\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.60\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{PH}} 2.4\right.$ Hz). FT-IR (KBr): $v_{\mathrm{PtCl}} 302,279 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 901[\mathrm{M}]^{+}, 866[\mathrm{M}-\mathrm{Cl}]^{+}, 199$ $\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{59} \mathrm{NP}_{2} \mathrm{FePtCl}_{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, 46.26; $\mathrm{H}, 6.23$; N, 1.42. Found C, 46.61 ; H, 6.33; N, 1.57\%.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P A d}\right)_{2}\right\}$ 3.32 Phosphine 3.29 ( $\left.0.150 \mathrm{~g}, 0.223 \mathrm{mmol}\right)$, $\mathrm{PtCl}_{2}(\operatorname{cod})(0.084 \mathrm{~g}, 0.23 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.198 \mathrm{~g}, 95 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta-16.4\left({ }^{1} J_{\mathrm{PtP}} 3390 \mathrm{~Hz}\right)$ and $-17.9\left({ }^{1} J_{\mathrm{PtP}} 3377 \mathrm{~Hz}\right)$; respective $\%$ ratio ca. 1:2. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 3.69-3.59\left(\mathrm{~m}, 11 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ and $\left.\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.20-2.82$ $\left(\mathrm{m}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right), 1.22-0.60\left(\mathrm{~m}, 32 \mathrm{H}\right.$, Ad. cage H). FT-IR (KBr): $v_{\mathrm{PtCl}} 320,296 \mathrm{~cm}^{-1}$. MS (FAB $\left.{ }^{+}\right): \mathrm{m} / \mathrm{z} 938 \quad[\mathrm{M}]^{+}, 937 \quad[\mathrm{M}-\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{33} \mathrm{H}_{47} \mathrm{NP}_{2} \mathrm{O}_{6} \mathrm{FePtCl}_{2} \cdot 0.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires $\mathrm{C}, 41.65 ; \mathrm{H}, 4.99$; N, 1.46. Found C , 41.63; H, 4.97; N, 1.48\%.
cis- $\mathbf{P d C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 3}$ Compound $\mathbf{3 . 2 7}$ ( $\left.0.121 \mathrm{~g}, 0.198 \mathrm{mmol}\right)$, $\mathrm{PdCl}_{2}($ cod $)(0.056 \mathrm{~g}, 0.20 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.144 \mathrm{~g}, 93 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 7.6$ (s) ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.71-7.26$ (m, 20H, arom. H), $4.09\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.03\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.96\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.52\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right)$, 3.18 (bs, 4H, $\mathrm{CH}_{2} \mathrm{P}$ ). FT-IR (KBr): $v_{\text {PdCl }} 303$ and $294 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 788$ $[\mathrm{M}]^{+}, \quad 753 \quad[\mathrm{M}-\mathrm{Cl}]^{+}, \quad 199 \quad\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{FePdCl}_{2} \cdot 1.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires $\mathrm{C}, 51.34 ; \mathrm{H}, 4.22$; $\mathrm{N}, 1.57$. Found C, 51.38 ; H, 4.29; N, 1.68\%.
cis- $\mathbf{P d C l}_{2}\left\{\mathbf{F c C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P C y}_{2}\right)_{2}\right\} \mathbf{3 . 3 4}$ Phosphine $\mathbf{3 . 2 8}(0.127 \mathrm{~g}, 0.200 \mathrm{mmol})$, $\mathrm{PdCl}_{2}(\operatorname{cod})(0.057 \mathrm{~g}, 0.20 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.135 \mathrm{~g}, 83 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 29.6 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.16\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.10(\mathrm{~s}, 5 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{5}$ ), $4.08\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.43\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.57\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$. FT-IR ( KBr ): $v_{\text {PdCl }} 301,277 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 812[\mathrm{M}-\mathrm{H}]^{+}, 778[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{37} \mathrm{H}_{59} \mathrm{NP}_{2} \mathrm{FePdCl}_{2} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires $\mathrm{C}, 52.65 ; \mathrm{H}, 7.07 ; \mathrm{N}, 1.63$. Found C, 52.66; H, 7.04; N, 1.79\%.
cis- $\mathbf{P d C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P A d}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 5}$ Phosphine $\mathbf{3 . 2 9}$ ( $\left.0.135 \mathrm{~g}, 0.201 \mathrm{mmol}\right)$, $\mathrm{PdCl}_{2}(\mathrm{cod})(0.057 \mathrm{~g}, 0.20 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.146 \mathrm{~g}, 86 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 1.7(\mathrm{~s}), 0.0(\mathrm{~s}) ;$ respective $\%$ ratio $c a .1: 2 .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 4.32$ (s, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.28\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 4.26\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.69\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 2.69(\mathrm{~s}$, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $2.25-1.26(\mathrm{~m}, 32 \mathrm{H}$, Ad. cage H$)$. FT-IR ( KBr ): $v_{\text {PdCl }} 314$ and $292 \mathrm{~cm}^{-1}$. MS $\quad\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 813 \quad[\mathrm{M}-\mathrm{Cl}]^{+}, 199 \quad\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{33} \mathrm{H}_{47} \mathrm{NP}_{2} \mathrm{O}_{6} \mathrm{FePdCl}_{2}$ requires C, 46.69; H, 5.58; N, 1.65. Found C, 46.32; H, 5.51; N, 1.83\%.
cis- $\mathbf{C r C O}_{4}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2}\right\} \mathbf{3 . 3 6}$ Under a nitrogen atmosphere, THF $\left(15 \mathrm{~cm}^{3}\right.$, freeze-thawed) was added to $3.27(0.094 \mathrm{~g}, 0.15 \mathrm{mmol})$ and $\mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{nbd})(0.040 \mathrm{~g}$, $0.15 \mathrm{mmol})$. The resulting yellow solution was stirred at $60^{\circ} \mathrm{C}$ for 1 h before being reduced to dryness under vacuum. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ 38.9 ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.46-7.19\left(\mathrm{~m}, 20 \mathrm{H}\right.$, arom. H), $4.10\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$, 4.05 (bs, $7 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ and $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.55\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.18\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$. FT-IR (KBr): $v_{\mathrm{CO}} 2014$ (s), 1921 ( $\mathrm{s}, \mathrm{b}$ ), 1875 ( $\left.\mathrm{s}, \mathrm{b}\right) \mathrm{cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 775$ [M] ${ }^{+}, 663$ $[\mathrm{M}-4 \mathrm{CO}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{41} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{FeCrO}_{4}$ requires $\mathrm{C}, 63.50$; H, 4.55; N, 1.81. Found C, 63.29; H, 4.62; N, 1.77\%.
$\boldsymbol{c i s}-\mathbf{C r C O}_{\mathbf{4}}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P C y}_{2}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 7}$ Under a nitrogen atmosphere, THF ( $15 \mathrm{~cm}^{3}$, freeze-thawed) was added to $3.28(0.074 \mathrm{~g}, 0.12 \mathrm{mmol})$ and $\mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{nbd})(0.030 \mathrm{~g}$, $0.12 \mathrm{mmol})$. The resulting yellow solution was stirred at $60^{\circ} \mathrm{C}$ for 5 h before being reduced to dryness under vacuum. Yield: $0.076 \mathrm{~g}, 82 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ 37.2 (s), -18.3 (s) ppm; respective $\%$ ratio $c a .1: 2 . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 780[\mathrm{M}]^{+}, 687$ $[\mathrm{M}-4 \mathrm{CO}]^{+}, 635\left[\mathrm{FcCH}_{2} \mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{PCy}_{2}\right)_{2}\right]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.

Complex $\mathbf{3 . 3 8}$ was prepared in a similar manner to $\mathbf{3 . 3 7}$.
cis- $\mathbf{C r C O}_{\mathbf{4}}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P A d}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 8}$ Phosphine $\mathbf{3 . 2 9}$ ( $\left.0.055 \mathrm{~g}, 0.082 \mathrm{mmol}\right)$ and $\mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{nbd})(0.021 \mathrm{~g}, 0.083 \mathrm{mmol})$. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta$ 31.7 (s), 29.9 (s) ppm; respective \% ratio ca. 2:1. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.13$ ( $\mathrm{s}, 2 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), 4.08 ( $\mathrm{s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ ), $4.00\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right.$ ), 3.68 (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), 3.48 (bs, 2 H , $\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 2.87 - 1.12 (m, 32H, Ad. cage H). FT-IR (KBr): $v_{\mathrm{CO}} 2006$ ( s ), 1883 ( s , b) $\mathrm{cm}^{-1} \cdot \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 835[\mathrm{M}]^{+}, 723[\mathrm{M}-4 \mathrm{CO}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.
$\left\{\mathbf{A u C l}_{\mathbf{2}}\left\{\mathbf{F C C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{3 . 3 9}\right.$ Phosphine $\mathbf{3 . 2 7}(0.102 \mathrm{~g}, 0.167 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{AuCl}(\mathrm{tht})(0.107 \mathrm{~g}, 0.334 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. The solution was stirred in the dark for 0.5 h before the solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether $\left(25 \mathrm{~cm}^{3}\right)$ was added to yield some cream precipitate. Hexane $\left(25 \mathrm{~cm}^{3}\right)$ was added and the resulting cream suspension stirred for a further 0.5 h in the dark. The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.122 \mathrm{~g}, 68 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 16.7$ (s) ppm. MS ( $\mathrm{FAB}^{+}$): m/z $1076[\mathrm{M}]^{+}, 1075[\mathrm{M}-\mathrm{H}]^{+}, 1040[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal.

Calc. for $\mathrm{C}_{37} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{FeAu}_{2} \mathrm{Cl}_{2} \cdot 0.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $40.76 ; \mathrm{H}, 3.26$; $\mathrm{N}, 1.28$. Found C, 40.82; H, 3.21; N, 1.25\%.
6.7.11 Preparation of $\mathbf{3 . 4 0 - 3 . 4 2 .}$
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C O}_{\mathbf{2}} \mathbf{C}\left(\mathbf{C H}_{3}\right)_{3} \mathbf{3 . 4 0}$ Under a flow of nitrogen, $\mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.208 \mathrm{~g}, 0.967$ mmol) in degassed EtOH ( $15 \mathrm{~cm}^{3}$ ) was added dropwise to ice cooled di-tertbutyldicarbonate ( $0.220 \mathrm{~g}, 0.978 \mathrm{mmol}$ ) over 10 min , the ensuing solution was stirred for a further 10 min at $c a .0^{\circ} \mathrm{C}$ before warming back to RT, where stirring was continued for a further 1 d . The resulting orange solution was reduced to dryness under vacuum, re-dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$ and washed with NaOH solution (1 $\mathrm{M}, 20 \mathrm{~cm}^{3}$ ). The organic layer was dried over $\mathrm{MgSO}_{4}$, filtered under gravity and reduced to dryness. The product was further purified by column chromatography on silica using petroleum ether and ethyl acetate (20:1) as eluent. Yield: $0.285 \mathrm{~g}, 93 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 4.62(\mathrm{bs}, 1 \mathrm{H}, \mathrm{NH}), 4.11\left(\mathrm{bs}, 7 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{4}\right), 4.07(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.93 (d, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 4.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 1.39 (s, $9 \mathrm{H}, \mathrm{CH}_{3}$ ). FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}}$ $3325,1528, v_{\mathrm{CO}} 1686 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 315[\mathrm{M}]^{+}, 259\left[\mathrm{M}-\mathrm{C}_{4} \mathrm{H}_{10}\right]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{16} \mathrm{H}_{21} \mathrm{O}_{2} \mathrm{NFe}$ requires $\mathrm{C}, 60.97 ; \mathrm{H}, 6.72 ; \mathrm{N}, 4.44$. Found C, 60.86; H, 7.04; N, 4.41\%.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{3 . 4 2}$ Under a nitrogen atmosphere, triethylamine $\left(0.300 \mathrm{~cm}^{3}, 2.13\right.$ mmol , freeze-thawed) was added to a stirred solution of $\mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.146 \mathrm{~g}, 0.679$ mmol ) in THF ( $15 \mathrm{~cm}^{3}$, freeze-thawed). The orange solution was cooled to $0^{\circ} \mathrm{C}$ and $\mathrm{ClPPh}_{2}\left(0.250 \mathrm{~cm}^{3}, 1.36 \mathrm{mmol}\right)$ added. The resulting suspension was stirred for 5 $\min$. at $0^{\circ} \mathrm{C}$ before stirring for a further 18 h at RT. The suspension was filtered under nitrogen and the filtrate evaporated to dryness. Hexane $\left(10 \mathrm{~cm}^{3}\right)$ was added and the resulting suspended orange solid stirred for 2 h . before being filtered in air, washed was $\operatorname{EtOH}\left(2 \mathrm{~cm}^{3}\right)$ and dried under reduced pressure. Yield: $0.106 \mathrm{~g}, 27 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 59.4 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.34-7.19(\mathrm{~m}, 20 \mathrm{H}$, arom. $\mathrm{H}), 4.18\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{PH}} 20.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{~N}\right), 3.85\left(\mathrm{~s}, 5 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right), 3.80\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.33(\mathrm{~s}$, $\left.2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right)$. $\mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 584[\mathrm{M}]^{+}, 384\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{35} \mathrm{H}_{31} \mathrm{NP}_{2} \mathrm{Fe} \cdot 0.75 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 70.42 ; \mathrm{H}, 5.44 ; \mathrm{N}, 2.35$. Found C, 70.37; H, 5.46; N, 2.38\%.
6.7.12 Coordination chemistry of $\mathbf{3 . 4 2}$.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{F c C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\}$ 3.43. Phosphinoamine 3.42 ( $0.065 \mathrm{~g}, 0.11 \mathrm{mmol}$ ) was added to a stirred solution of $\mathrm{PtCl}_{2}(\operatorname{cod})(0.036 \mathrm{~g}, 0.096 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension stirred for a further 0.5 h . The yellow precipitate was filtered and dried under reduced pressure. Yield: $0.061 \mathrm{~g}, 75 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \delta 17.8 \mathrm{ppm}$, ${ }^{1} J_{\mathrm{PtP}} 3290 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \delta 7.69-7.45(\mathrm{~m}, 20 \mathrm{H}$, arom. H), $3.84(\mathrm{~s}, 5 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{5}$ ), 3.80 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.76 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.33 (s, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ). MS ( $\mathrm{FAB}^{+}$): $\mathrm{m} / \mathrm{z} 849[\mathrm{M}]^{+}, 814[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{35} \mathrm{H}_{31} \mathrm{NP}_{2} \mathrm{FePtCl}_{2} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, 48.63; H, 3.65; N, 1.61. Found C, 48.43; H, 3.68; N, 1.64\%.

### 6.7.13 Preparation of 3.44.

$\mathbf{P h}_{2} \mathbf{P C H}(\mathbf{P h}) \mathbf{C H}_{\mathbf{2}} \mathbf{C H O}$ The tertiary phosphine $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO}$ was prepared following slight modification of a known method reported by Moiseev. ${ }^{264}$ Under a nitrogen atmosphere, diphenylphosphine $\left(0.840 \mathrm{~cm}^{3}, 4.83 \mathrm{mmol}\right)$ was added dropwise to cinnamaldehyde ( $0.709 \mathrm{~g}, 5.31 \mathrm{mmol}$, freeze-thawed) at room temperature with vigorous stirring. The resulting mixture was heated briefly to $50^{\circ} \mathrm{C}$ to give a pink solid which was triturated with degassed $\mathrm{Et}_{2} \mathrm{O}\left(5 \mathrm{~cm}^{3}\right)$, filtered, and washed with further degassed $\mathrm{Et}_{2} \mathrm{O}$ before drying under vacuum. Yield: $1.31 \mathrm{~g}, 85 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 0.0 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 9.48$ (s, $\left.\mathrm{H}, \mathrm{CHO}\right), 7.58-$ $6.95\left(\mathrm{~m}, 15 \mathrm{H}\right.$, arom. H), $4.01(\mathrm{~m}, \mathrm{H}, \mathrm{PCH}), 2.97\left(\mathrm{~m}, \mathrm{H}, \mathrm{CH}_{A} \mathrm{H}_{\mathrm{B}}\right), 2.62(\mathrm{~m}, \mathrm{H}$, $\left.\mathrm{CH}_{\mathrm{A}} H_{B}\right) . \mathrm{FT}-\mathrm{IR}(\mathrm{KBr}): v_{\mathrm{C}=\mathrm{o}} 1711 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $318[\mathrm{M}]^{+}, 319[\mathrm{M}+\mathrm{H}]^{+}$, $335[\mathrm{M}+\mathrm{O}]^{+}$. Anal. Calc. for $\mathrm{C}_{21} \mathrm{H}_{19} \mathrm{OP}$ requires C, $79.23 ; \mathrm{H}, 6.02 ; \mathrm{N}, 0.00$. Found C, 79.21; H, 6.15; N, 0.11\%.
$\mathbf{P h}_{2} \mathbf{P C H}(\mathbf{P h}) \mathbf{C H}_{2} \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{F c} 3.44$ Under a nitrogen atmosphere, an orange suspension of $\mathrm{Ph}_{2} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}_{2} \mathrm{CHO}(0.517 \mathrm{~g}, 1.62 \mathrm{mmol})$ and $\mathrm{FcCH}_{2} \mathrm{NH}_{2}(0.350 \mathrm{~g}$, $1.63 \mathrm{mmol})$ in $\mathrm{MeOH}\left(40 \mathrm{~cm}^{3}\right.$, freeze-thawed) was refluxed for 4 h . The solvent was removed under reduced pressure. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 1.1$ ppm. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.57-7.02\left(\mathrm{~m}, 15 \mathrm{H}\right.$, arom. H), $7.36\left(\mathrm{t},{ }^{3} J_{\mathrm{HH}} 4.4 \mathrm{~Hz}, 1 \mathrm{H}\right.$, CHN), 4.01 (bs, $2 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.96 (bs, $7 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}$ and $\mathrm{CH}_{2} \mathrm{Fc}$ ), 3.89 (bs, $1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ),
$3.84\left(\mathrm{bs}, 1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.74(\mathrm{~m}, 1 \mathrm{H}, \mathrm{PCH}), 2.73\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{A} \mathrm{H}_{\mathrm{B}}\right), 2.57(\mathrm{~m}, 1 \mathrm{H}$, $\mathrm{CH}_{\mathrm{A}} H_{B}$ ). FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1667$ (s) $\mathrm{cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 516[\mathrm{M}+\mathrm{H}]^{+}, 531$ $[\mathrm{M}+\mathrm{O}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.
6.7.14 Coordination chemistry of $\mathbf{3 . 4 4}$.

Complex $\mathbf{3 . 4 5}$ was prepared in a similar manner to $\mathbf{3 . 4 3}$.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{P h}_{2} \mathbf{P C H}(\mathbf{P h}) \mathbf{C H}_{\mathbf{2}} \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{F c}\right\} \mathbf{3 . 4 5} \mathrm{PtCl}_{2}(\operatorname{cod})(0.092 \mathrm{~g}, 0.25 \mathrm{mmol})$, $3.44(0.200 \mathrm{~g}, 0.244 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.182 \mathrm{~g}, 95 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 12.3 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3745 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.37$ (bs, $\left.1 \mathrm{H}, \mathrm{CHN}\right)$, $7.61-6.24\left(15 \mathrm{H}\right.$, arom. H), $5.77\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}} 13.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{\mathrm{A}} \mathrm{H}_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.94\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}\right.$ $13.6 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH}_{\mathrm{A}} \mathrm{CH}_{\mathrm{B}} \mathrm{C}_{5} \mathrm{H}_{4}$ ), $4.54\left(\mathrm{bs}, 1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.21\left(\mathrm{bs}, 1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.17(\mathrm{bs}, 5 \mathrm{H}$ , $\mathrm{C}_{5} \mathrm{H}_{5}$ ), $4.12\left(\mathrm{bs}, 1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.04\left(\mathrm{bs}, 1 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.25\left(\mathrm{bt},{ }^{2} J_{\mathrm{PH}} 10.4 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{PCH}\right)$, $3.04\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{A} \mathrm{H}_{\mathrm{B}}\right), 2.74\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{CH}_{\mathrm{A}} H_{B}\right)$. FT-IR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1640(\mathrm{w}) \mathrm{cm}^{-1} . \mathrm{MS}$ $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 746[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{32} \mathrm{H}_{30} \mathrm{NPFePtCl}_{2}$ requires C, 49.19; H, 3.87; N, 1.79. Found C, 48.91; H, 4.20; N, 1.68\%.
$\mathbf{A u C l}\left\{\mathbf{P h}_{2} \mathbf{P C H}(\mathbf{P h}) \mathbf{C H}_{\mathbf{2}} \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{2} \mathbf{F c}\right\} \mathbf{3 . 4 6}$ Phosphine $\mathbf{3 . 4 4}(0.069 \mathrm{~g}, 0.13 \mathrm{mmol})$ was added to a stirred solution of $\mathrm{AuCl}($ tht $)(0.042 \mathrm{~g}, 0.13 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10$ $\mathrm{cm}^{3}$ ). The solution was stirred in the dark for 0.5 h before the solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Hexane ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting yellow suspension was stirred for a further 0.5 h . The precipitate was filtered and dried under reduced pressure. Yield: $0.034 \mathrm{~g}, 34 \%$. Characterisation by NMR eluded that $\mathbf{3 . 4 6}$ adopted a number of isomers in solution, as a result only regions for specific resonances have been suggested for the ${ }^{1} \mathrm{H}$ NMR data. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 45.2$ (bs), 44.8 (s) ppm, respective $\%$ ratio 4.5:1. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 7.90-7.15(\mathrm{~m}$, arom. H and CHN$), 4.41-4.35(\mathrm{~m}, \mathrm{PCH}), 4.15-3.83\left(\mathrm{~m}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$, $\mathrm{C}_{5} \mathrm{H}_{4}$ and $\left.\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.12\left(\mathrm{~m}, \mathrm{CH}_{\mathrm{A}} H_{B}\right), 2.75\left(\mathrm{~m}, \mathrm{CH}_{\mathrm{A}} H_{B}\right)$. FT-IR $(\mathrm{KBr}): v_{\mathrm{C}=\mathrm{N}} 1643$ (w) $\mathrm{cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $747[\mathrm{M}]^{+}, 712[\mathrm{M}-\mathrm{Cl}]^{+}, 199\left[\mathrm{M}-\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{32} \mathrm{H}_{30} \mathrm{NPFeAuCl} \cdot 1.5 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 49.60 ; \mathrm{H}, 4.29$; $\mathrm{N}, 1.81$. Found $\mathrm{C}, 49.63 ; \mathrm{H}$, 3.95; N, 1.63\%.
$\left.\mathbf{R u C l}_{\mathbf{2}} \mathbf{( p - c y m}\right)\left\{\mathbf{P h}_{2} \mathbf{P C H}(\mathbf{P h}) \mathbf{C H}_{\mathbf{2}} \mathbf{C}(\mathbf{H}) \mathbf{N C H}_{\mathbf{2}} \mathbf{F c}\right\} \mathbf{3 . 4 7}$ Phosphine $\mathbf{3 . 4 4}$ ( 0.125 g , $0.243 \mathrm{mmol})$ was added to a stirred solution of $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.075 \mathrm{~g}, 0.12$ $\mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The solution was stirred for 0.5 h and the solvent concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Hexane ( $25 \mathrm{~cm}^{3}$ ) was added and the resulting orange suspension stirred for a further 0.5 h . The precipitate was filtered and dried under reduced pressure. Yield: $0.058 \mathrm{~g}, 29 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ $23.6(\mathrm{~s}), 23.1(\mathrm{~s})$ and $21.0 \mathrm{ppm}(\mathrm{s})$; respective $\%$ ratio $c a .4: 3: 1$. FT-IR ( KBr ): $v_{\mathrm{C}=\mathrm{N}}$ $1636(\mathrm{w}) \mathrm{cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 822[\mathrm{M}]^{+}, 823[\mathrm{M}-\mathrm{H}]^{+}, 786[\mathrm{M}-\mathrm{Cl}]^{+}, 199[\mathrm{M}-$ $\left.\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{42} \mathrm{H}_{44} \mathrm{NPFeRuCl}_{2} \cdot 1.25 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $55.99 ; \mathrm{H}, 5.05$; N, 1.51. Found C, 55.72 ; H, 5.22 ; N, 1.63\%.
6.7.15 Preparation of $\mathbf{3 . 4 8}$ - This involved a four step synthesis, as outlined below.
$\left(\mathbf{C}_{5} \mathbf{H}_{\mathbf{4}} \mathbf{C H O}\right)_{\mathbf{2}} \mathbf{F e}$ was prepared following slight modification to the known method. ${ }^{291}$ Under a nitrogen atmosphere, a freeze-thawed solution of ferrocene (5.005 g, 26.37 $\mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}\left(60 \mathrm{~cm}^{3}\right)$ was cooled to $-78{ }^{\circ} \mathrm{C}$ and treated with $22.70 \mathrm{~cm}^{3}$ of 2.5 M $\mathrm{n}-\mathrm{BuLi}(56.75 \mathrm{mmol})$ in hexane. The reaction mixture was stirred for 0.5 h at $-78^{\circ} \mathrm{C}$ before freeze-thawed tetramethylethylenediamine (TMEDA) ( $8.60 \mathrm{~cm}^{3}, 56.7 \mathrm{mmol}$ ) was added dropwise. The subsequent suspension was stirred at $-78^{\circ} \mathrm{C}$ for a further 0.5 h before stirring for an additional 20 h at RT. DMF $\left(6.50 \mathrm{~cm}^{3}, 84.0 \mathrm{mmol}\right.$, previously freeze-thawed and dried over $\mathrm{CaH}_{2}$ ) was added dropwise to the reaction mixture at $-78{ }^{\circ} \mathrm{C}$. The resulting yellow suspension was stirred at $-78{ }^{\circ} \mathrm{C}$ for a further 0.5 h before stirring for a subsequent 1.5 h at RT. The mixture was hydrolysed at $-78{ }^{\circ} \mathrm{C}$ by the addition of $\mathrm{H}_{2} \mathrm{O}\left(20 \mathrm{~cm}^{3}\right)$. The organic phase was extracted into $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(60 \mathrm{~cm}^{3}\right)$, dried over $\mathrm{MgSO}_{4}$, and the solvent removed under reduced pressure. The product was purified by column chromatography, on silica using hexane : ethyl acetate (10:1) as eluent, to give shiny red crystals. Yield: 2.138 $\mathrm{g}, 34 \%{ }^{1}{ }^{\mathrm{H}} \mathrm{NMR}\left(\mathrm{CDCl}_{3}\right): \delta 9.88(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CHO}), 4.82\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.61(\mathrm{~s}, 4 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ). FT-IR (KBr): $v_{\mathrm{C}=\mathrm{O}} 1679 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 242[\mathrm{M}]^{+}, 265[\mathrm{M}+\mathrm{Na}]^{+}$. Anal. Calc. for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{O}_{2} \mathrm{Fe}$ requires: C, 59.54; H, 4.16; N, 0.00. Found: C, 59.41 ; H, 4.42; N, 0.12\%.

The imine, $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Fe}$, was prepared following a slight modification to the known preparation. ${ }^{265}$
$\left(\mathbf{C}_{5} \mathbf{H}_{\mathbf{4}} \mathbf{C} \mathbf{( H )} \mathbf{N C H}_{\mathbf{2}}\right)_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \mathbf{F e}$ 1,3-diaminopropane ( $0.21 \mathrm{~cm}^{3}, 2.5 \mathrm{mmol}$ ) was added to a stirred solution of $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CHO}\right)_{2} \mathrm{Fe}(0.600 \mathrm{~g}, 2.48 \mathrm{mmol})$ in absolute $\mathrm{EtOH}\left(50 \mathrm{~cm}^{3}\right)$. The resulting solution was refluxed for 2 h and allowed to cool to RT to afford a deep red solution. The solution was concentrated to approximately $10 \mathrm{~cm}^{3}$ and hexane $\left(20 \mathrm{~cm}^{3}\right)$ added to give an orange precipitate. The resulting suspension was filtered and dried under reduced pressure to give an orange-brown solid. The organic product then extracted into $\mathrm{CHCl}_{3}\left(30 \mathrm{~cm}^{3}\right)$ and the solvent removed under reduced pressure. Yield: $0.333 \mathrm{~g}, 48 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.21$ (s, $2 \mathrm{H}, \mathrm{CHN}$ ), 4.51 (bs, 4 H , $\mathrm{C}_{5} \mathrm{H}_{4}$ ), 4.33 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.53 (vbs, $4 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2}$ ), 2.54 (bs, $2 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2}$ ). FTIR (KBr): $v_{\mathrm{C}=\mathrm{N}} 1631 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $280[\mathrm{M}]^{+}, 281[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{15} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{Fe} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 63.29; H, 5.84; N, 9.84. Found C, 63.20; H, 5.67; N, 9.74\%.

The amine, $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Fe}$, was prepared in a similar manner $\left\{\mathrm{FcCH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right\}_{2} \mathrm{Fc}$.
$\left(\mathbf{C}_{5} \mathbf{H}_{\mathbf{4}}^{\left.\mathbf{4} \mathbf{C H}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{2}\right)_{\mathbf{2}} \mathbf{C H}_{\mathbf{2}} \mathbf{F e} \quad \mathrm{NaBH}_{4} \quad(0.227 \quad \mathrm{~g}, \quad 5.88 \quad \mathrm{mmol}), ~}\right.$ $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{C}(\mathrm{H}) \mathrm{NCH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Fe}(0.274 \mathrm{~g}, 0.978 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{EtOH}\left(50 \mathrm{~cm}^{3}, 30: 20\right)$. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta 4.12\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 4.02\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.32$ (s, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), $2.98\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 11 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{CH}_{2}\right.$ ), 2.51 (bs, $2 \mathrm{H}, \mathrm{NH}$ ), $1.66(\mathrm{bm}$, $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 10 \mathrm{~Hz}, \mathrm{NCH}_{2} \mathrm{CH}_{2}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3334,3293 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $284[\mathrm{M}]^{+}, 285[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{15} \mathrm{H}_{20} \mathrm{~N} 2 \mathrm{Fe} \cdot 0.33\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ requires C, 58.93; H, 6.67; N, 8.96. Found C, 59.26; H, 7.17; N, 8.63\%.
$\mathbf{C}_{10} \mathbf{H}_{8} \mathrm{Fe}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right) \mathbf{C H}_{2}\right)_{2} \mathbf{C H}_{\mathbf{2}} \mathbf{3 . 4 8}$ Under a nitrogen atmosphere, an orange solution of $\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{CH}_{2} \mathrm{~N}(\mathrm{H}) \mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{Fe}(0.083 \mathrm{~g}, 0.29 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ ( $0.132 \mathrm{~g}, 0.586 \mathrm{mmol}$ ) in $\mathrm{MeOH}\left(10 \mathrm{~cm}^{3}\right)$ was refluxed for 4 d to yield an orange suspension upon cooling. The suspension was stirred for a further 18 h at RT before being concentrated under reduced pressure to $c a .2 \mathrm{~cm}^{3}$ and stirred for an additional 4 h to afford an oily solid. The remaining solution was cannulated off, before the oily brown solid was dried under reduced pressure. Yield $0.146 \mathrm{~g}, 73 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right):-27.0 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.42-7.22(\mathrm{~m}, 20 \mathrm{H}$, arom. H$), 3.93(\mathrm{~s}, 4 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{H}_{4}$ ), $3.86\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.49\left(\mathrm{bs}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}\right), 3.30\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{PH}} 2.8 \mathrm{~Hz}\right.$,
$\mathrm{NCH}_{2} \mathrm{P}$ ), 2.92 (bs, $4 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2}$ ), 1.42 (bs, $2 \mathrm{H}, \mathrm{NCH}_{2} \mathrm{CH}_{2}$ ). MS ( $\mathrm{FAB}^{+}$): m/z 681 $[\mathrm{M}]^{+}, 495\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}$.

### 6.8 Chapter 4 Experimental

6.8.1 Preparation of the precursor aldoxime, amine and 4.1.
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C}(\mathbf{H}) \mathbf{N O H}$ was prepared following a slight modification to the procedure previously reported by Schlögl for the preparation of $\mathrm{FcC}(\mathrm{H}) \mathrm{NOH} .{ }^{290}$ Sodium acetate $(5.462 \mathrm{~g}, 65.92 \mathrm{mmol})$ and hydroxylammonium hydrochloride ( $3.088 \mathrm{~g}, 43.99 \mathrm{mmol}$ ) were dissolved separately in the minimum amount of deionised water and were added to a stirred solution of 9-anthracenecarboxaldehyde ( $4.672 \mathrm{~g}, 21.974 \mathrm{mmol}$ ) in EtOH $\left(100 \mathrm{~cm}^{3}\right)$. The resulting suspension was stirred at $60{ }^{\circ} \mathrm{C}$ for 6 h before the solvent was concentrated to $c a .10 \mathrm{~cm}^{3}$ under reduced pressure. EtOH ( $60 \mathrm{~cm}^{3}$ ) and $\mathrm{Et}_{2} \mathrm{O}\left(200 \mathrm{~cm}^{3}\right)$ were added and the resulting suspension stirred for a further 0.5 h before the suspended inorganic solid was filtered and washed with $\mathrm{Et}_{2} \mathrm{O}$. The combined filtrate and washes were combined and the solvent removed under reduced pressure. Yield: Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 9.89(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CHN}), 8.72-7.58$ (m, 9H, arom. H), $8.19(\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH})$. FT-IR (KBr): $v_{\mathrm{OH}} 3271, v_{\mathrm{C}=\mathrm{N}} 1562 \mathrm{~cm}^{-1} . \mathrm{MS}$ $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 221[\mathrm{M}]^{+}$.
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}}$ was prepared via a modified procedure to that reported by Beer for the preparation of $\mathrm{FcCH}_{2} \mathrm{NH}_{2} .{ }^{247}$ The aldoxime $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{C}(\mathrm{H}) \mathrm{NOH}(4.008 \mathrm{~g}, 18.12$ mmol ) was dissolved in dry THF ( $160 \mathrm{~cm}^{3}$ ) and an excess of lithium aluminum hydride ( $3.270 \mathrm{~g}, 83.58 \mathrm{mmol}$ ) added, portionwise with care. The resulting mixture was stirred under nitrogen for 6 h before dry toluene $\left(160 \mathrm{~cm}^{3}\right)$ was added followed by ethyl acetate ( $30 \mathrm{~cm}^{3}$ ) with caution. NaOH solution ( 5 M ) was added dropwise until precipitation of inorganic solids was complete. The resulting mixture was filtered to yield an orange filtrate and a gummy solid residue. The residue was washed with copious amounts of toluene- $\mathrm{MeOH}\left(200 \mathrm{~cm}^{3}, 80: 20\right)$ and the combined filtrate and washes evaporated to dryness. Further inorganic impurities were removed by dissolution of the organic phase in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ followed by filtration and evaporation of the solvent. Attempts to obtain an analytically pure sample of $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{NH}_{2}$ by column chromatography were hampered by the lack of any suitable solvent system.

Crude yield: $2.649 \mathrm{~g}, 71 \%$. FT-IR ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ mull): $v_{\mathrm{NH}} 3360$ and $v_{\mathrm{CH}} 2963 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 207[\mathrm{M}]^{+}, 191\left[\mathrm{M}-\mathrm{NH}_{2}\right]^{+}$.
$\left(\mathbf{C}_{14} \mathbf{H}_{9}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2}$ 4.1 Under a nitrogen atmosphere, a solution of $\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{NH}_{2}(0.224 \mathrm{~g}, 1.08 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.502 \mathrm{~g}, 2.16 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was refluxed for 3 d to yield a small amount of suspended yellow solid. The solvent was concentrated to approximately $2 \mathrm{~cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield: $0.145 \mathrm{~g}, 22 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-28.1 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.60-6.97(\mathrm{~m}, 29 \mathrm{H}$, arom. H$), 4.88(\mathrm{~s}$, $\left.2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.59\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} \mathrm{~J}_{\mathrm{PH}} 2.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$. MS (FAB ${ }^{+}$): m/z $601[\mathrm{M}-3 \mathrm{H}]^{+}$, $418\left[\mathrm{M}-\mathrm{PPh}_{2}\right]^{+}$and $191\left[\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2}\right]^{+}$.

### 6.8.2 Preparation of 4.2a.

$\mathbf{C}_{10} \mathbf{H}_{8} \mathbf{O}_{\mathbf{2}} \mathbf{N}(\mathbf{H}) \mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}$ 4.2a Under a nitrogen atmosphere, a pale yellow solution of 4-methyl-7-amino-coumarin ( $0.101 \mathrm{~g}, 0.565 \mathrm{mmol}$ ) and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.256 \mathrm{~g}, 1.14$ mmol ) in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right.$ ) was refluxed for 4 d to yield a pale yellow suspension. The suspension was stirred for a further 2 d at RT to give further precipitate. The solvent was concentrated to $c a .2 \mathrm{~cm}^{3}$ and the precipitate filtered and dried under reduced pressure. Yield $0.049 \mathrm{~g}, 23 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-19.6 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta 7.40-6.40(\mathrm{~m}, 13 \mathrm{H}$, arom. H), $5.92(\mathrm{~s}, 1 \mathrm{H}, \mathrm{COCH}), 4.20(\mathrm{bs}, 1 \mathrm{H}$, NH), 3.81 (bs, 2H, $\mathrm{CH}_{2} \mathrm{P}$ ), 2.27 (s, 3H, CH3 ). FT-IR (KBr): $v_{\mathrm{NH}} 3311$, $v_{\mathrm{CO}} 1697$. Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{NO}_{2} \mathrm{P} \cdot \mathrm{H}_{2} \mathrm{O}$ requires C, 70.58; H, 5.67; N, 3.58. Found: C, 70.86; H, 5.56; N, 3.86\%.

### 6.8.3 Coordination chemistry of 4.1 and 4.2a.

Complex 4.3 and 4.4 were both prepared in a similar manner to $\mathbf{3 . 4 2}$.
cis- $\mathbf{P t C l}_{2}\left\{\left(\mathbf{C}_{14} \mathbf{H}_{9}\right) \mathbf{C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2}\right\} \quad 4.3 \quad \mathrm{PtCl}_{2}($ cod $)(0.045 \mathrm{~g}, 0.12 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ and $4.1(0.104 \mathrm{~g}, 0.124 \mathrm{mmol})$. Yield: $0.104 \mathrm{~g}, 99 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-7.0 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3416 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.38-7.00(\mathrm{~m}, 19 \mathrm{H}$, arom. H), $4.45\left(\mathrm{~s}, 2 \mathrm{H},\left(\mathrm{C}_{14} \mathrm{H}_{9}\right) \mathrm{CH}_{2} \mathrm{~N}\right), 3.53\left(\mathrm{~m}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{PtH}} 36.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$. MS
$\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 834[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{41} \mathrm{H}_{35} \mathrm{NP}_{2} \mathrm{PtCl}_{2}$ requires C, $56.62 ; \mathrm{H}$, 4.06; N, 1.61. Found: C, 56.96; H, 4.27; N, 1.65\%.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{8}} \mathbf{O}_{\mathbf{2}} \mathbf{N} \mathbf{( H )} \mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right\}_{2} \mathbf{4 . 4} \mathrm{PtCl}_{2}(\operatorname{cod})(0.013 \mathrm{~g}, 0.035 \mathrm{mmol})$ and $\mathbf{4 . 2 a}$ ( $0.026 \mathrm{~g}, 0.070 \mathrm{mmol})$. Yield: $0.024 \mathrm{~g}, 68 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 6.3 \mathrm{ppm}$, ${ }^{1} J_{\mathrm{PtP}}$ $3709 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.88-6.46(\mathrm{~m}, 26 \mathrm{H}$, arom. H), $5.95(\mathrm{~s}, 2 \mathrm{H}, \mathrm{NH}$ or $\mathrm{COCH}), 5.90(\mathrm{~s}, 2 \mathrm{H}, \mathrm{NH}$ or COCH$), 4.24\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 6.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right), 2.25(\mathrm{~s}, 6 \mathrm{H}$, $\mathrm{CH}_{3}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3355, v_{\mathrm{CO}} 1711, v_{\mathrm{PtCl}} 318,282 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1013$ $[\mathrm{M}]^{+}, 977[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{46} \mathrm{H}_{40} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ requires C, $52.68 ; \mathrm{H}$, 4.22; N, 2.67. Found: C, 52.24; H, 3.90; N, 2.55\%.
6.8.4 Preparation of the ditertiary phosphines 4.22 - 4.29.

The synthesis of the precursor benzyl methylcarbamates and the 2-aminoacetamides are described as follows. The benzyl methylcarbamates $\mathbf{4 . 5 - 4 . 1 3}$ were prepared following the known procedure, ${ }^{271}$ unless otherwise stated.
$\mathbf{P h N H C O C H}_{\mathbf{2}} \mathbf{N H C O O C H}_{\mathbf{2}} \mathbf{P h} \mathbf{4 . 5}$ Aniline ( $\left.\begin{array}{l}1.510 \\ \mathrm{~g}, \\ 16.21\end{array} \mathrm{mmol}\right)$, dicyclohexylcarbodiimide ( $3.677 \mathrm{~g}, 17.82 \mathrm{mmol}$ ) and n -carbobenzyloxyglycine ( $3.392 \mathrm{~g}, 16.21 \mathrm{mmol}$ ). Yield: $3.098 \mathrm{~g}, 67 \% .{ }^{1} \mathrm{H}$ NMR ( $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 9.96(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{NHCO}$ ), $7.60-7.03\left(\mathrm{~m}, 10 \mathrm{H}\right.$, arom. H), $7.55\left(\mathrm{t}, 1 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{PhNHCO}\right)$, 5.06 (s, $2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}$ ), 3.81 (d, $2 \mathrm{H},{ }^{4} \mathrm{~J}_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH}$ ). FT-IR (KBr): $v_{\mathrm{NH}}$ 3341, 1536, $v_{\text {CO }} 1673 \mathrm{~cm}^{-1}$. EI-MS: m/z 284 [M] ${ }^{+}$. Anal. Calc. for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{3}$ requires C, 67.59; H, 5.67; N, 9.85. Found C, 67.16; H, 5.67; N, 9.41\%.
$\left(\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{7}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H C O O C H}_{\mathbf{2}} \mathbf{P h}$ 4.6 Naphthylamine ( $3.001 \mathrm{~g}, 20.96 \mathrm{mmol}$ ), dicyclohexylcarbodiimide ( $4.671 \mathrm{~g}, 22.64 \mathrm{mmol}$ ) and n -carbobenzyloxyglycine $(4.391 \mathrm{~g}, 20.99 \mathrm{mmol})$. Yield: $6.459 \mathrm{~g}, 92 \% .{ }^{1} \mathrm{H}$ NMR ( $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 9.96(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{NHCO}$ ), $8.09-7.31\left(\mathrm{~m}, 13 \mathrm{H}\right.$, arom. H and NH ), $5.09\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right), 4.00$ (d, $\left.2 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3252,1544, v_{\mathrm{CO}} 1656 \mathrm{~cm}^{-1}$. MS (FAB ${ }^{+}$): m/z $334[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{20} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{3} \cdot 0.25 \mathrm{H}_{2} \mathrm{O}$ requires C, $70.89 ; \mathrm{H}$, 5.50; N, 8.27. Found C, 71.12; H, 5.49; N, 8.54\%.
$\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N H C O O C H} \mathbf{2} \mathbf{P h} 4.7$ Dicyclohexylcarbodiimide (1.176 g, 5.700 mmol ) and n -carbobenzyloxyglycine $(1.084 \mathrm{~g}, 5.181 \mathrm{mmol})$ were added to a stirred solution of 2 -aminoanthracene $(1.001 \mathrm{~g}, 5.180 \mathrm{mmol})$ in THF $\left(100 \mathrm{~cm}^{3}\right)$. The solution was refluxed at $85{ }^{\circ} \mathrm{C}$ for $c a .23 \mathrm{~h}$ before cooling to RT. The resulting precipitate was filtered under gravity and the filtrate taken to dryness under reduced pressure to yield a dark green solid. The solid was recrystallised by addition of ethyl acetate $\left(100 \mathrm{~cm}^{3}\right)$ followed by addition of light petroleum $\left(100 \mathrm{~cm}^{3}\right)$ and stirred for 30 min . The suspension was filtered and dried under reduced pressure to yield a dark green solid. Yield: $0.431 \mathrm{~g}, 22 \%{ }^{1}{ }^{1} \mathrm{H}$ NMR ( $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 10.25\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NHCO}\right)$, $8.50-7.32\left(\mathrm{~m}, 14 \mathrm{H}\right.$, arom. H), $7.63\left(\mathrm{t}, 1 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{C}_{14} \mathrm{H}_{9} \mathrm{NHCO}\right), 5.09(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}$ ), $3.91\left(\mathrm{~d}, 2 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3319,1540$, $v_{\mathrm{CO}} 1672 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 384[\mathrm{M}]^{+}$.
$\left(\mathbf{C}_{\mathbf{1 3}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H C O O C H}_{\mathbf{2}} \mathbf{P h} 4.8$ 2-aminofluorene ( 1.009 g , 5.567 mmol ), dicyclohexylcarbodiimide ( $1.264 \mathrm{~g}, 6.126 \mathrm{mmol}$ ) and n -carbobenzyloxyglycine ( $1.165 \mathrm{~g}, 5.569 \mathrm{mmol}$ ). The resulting deep red solution was stirred for 7 h . Yield: $2.209 \mathrm{~g}, 60 \% .{ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 10.09\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NHCO}\right), 7.92-7.25(\mathrm{~m}\right.$, 12 H , arom. H), $7.61\left(\mathrm{t}, 1 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz},\left(\mathrm{C}_{13} \mathrm{H}_{9}\right) \mathrm{NHCO}\right), 5.07\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right)$, 3.91 (s, 2H, CH ${ }_{2}$ ), $3.85\left(\mathrm{~d},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH} H\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3338,1541$, $v_{\mathrm{CO}} 1675 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 372[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{3} \cdot \mathrm{H}_{2} \mathrm{O}$ requires C, 73.39; H, 5.89; N, 7.44. Found C, 73.02; H, 5.73; N, 7.85\%.
$\left(\mathbf{C}_{\mathbf{1 2}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N H C O O C H} \mathbf{2} \mathbf{P h} 4.9 \mathrm{~N}$-carbobenzyloxyglycine ( $1.858 \mathrm{~g}, 8.882$ mmol ) and dicyclohexylcarbodiimide ( $2.015 \mathrm{~g}, 9.781 \mathrm{mmol}$ ) were added to a stirred solution of 2-aminobiphenyl ( $1.503 \mathrm{~g}, 8.884 \mathrm{mmol}$ ) in THF $\left(100 \mathrm{~cm}^{3}\right)$. The resulting deep red solution was stirred at RT for 4 h to yield a white suspension. The suspension was filtered under gravity and the resulting filtrate evaporated to dryness under reduced pressure, to yield a brown solid. Ethyl acetate ( $100 \mathrm{~cm}^{3}$ ) and light petroleum $\left(100 \mathrm{~cm}^{3}\right)$ were added and the resulting suspension was stirred for 0.5 h to yield a fine solid. The solid was filtered under gravity and the filtrate taken to dryness under reduced pressure to yield a viscous orange oil. The solid was characterised by ${ }^{1} \mathrm{H}$ NMR and IR to be $N, N$ '-dicyclohexylurea, the known byproduct of the peptide coupling. Compound 4.9 was recrystallised from the viscous orange oil by addition of ethyl acetate $\left(10 \mathrm{~cm}^{3}\right)$ and petroleumether $\left(50 \mathrm{~cm}^{3}\right)$. The resulting
suspension was filtered and dried under reduced pressure. Yield $2.429 \mathrm{~g}, 76 \%$. ${ }^{1} \mathrm{H}$ NMR (( $\left.\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 9.10\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NHCO}\right), 7.71-7.26$ (m, 10H, arom. H), 7.51 (bs, $\left.1 \mathrm{H}\left(\mathrm{C}_{12} \mathrm{H}_{9}\right) \mathrm{N} H \mathrm{CO}\right), 5.03\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right), 3.66\left(\mathrm{~d}, 2 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 5.6 \mathrm{~Hz}\right.$, $\mathrm{COCH}_{2} \mathrm{NH}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3371,3317,1518, v_{\mathrm{CO}} 1674 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $360[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{3}$ requires C, 72.11; H, 5.59; N, 7.65. Found C, 72.04; H, 5.99; N, 8.25\%.
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{1 2}} \mathbf{N}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N H C O O C H} \mathbf{2} \mathbf{P h} 4.10$ 3-amino-9-ethylcarbazole (2.507 g, $11.92 \mathrm{mmol})$, dicyclohexylcarbodiimide $(2.701 \mathrm{~g}, 13.09 \mathrm{mmol})$ and $\mathrm{n}-$ carbobenzyloxyglycine ( $2.495 \mathrm{~g}, 11.93 \mathrm{mmol}$ ). Yield: $3.644 \mathrm{~g}, 76 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 9.98\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NHCO}\right), 8.46-7.05(\mathrm{~m}, 12 \mathrm{H}\right.$, arom. H), $7.45(\mathrm{t}, 1 \mathrm{H}$, $\left.{ }^{4} J_{\mathrm{HH}} 7.2 \mathrm{~Hz},\left(\mathrm{C}_{14} \mathrm{H}_{12}\right) \mathrm{N} H \mathrm{CO}\right), 5.08\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right), 4.41\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}\right.$, $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $3.87\left(\mathrm{~d},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{~N} H\right), 1.30\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3317,1561, v_{\mathrm{CO}} 1678 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 401[\mathrm{M}]^{+}$. Anal. Calc. for $\mathrm{C}_{24} \mathrm{H}_{23} \mathrm{~N}_{3} \mathrm{O}_{3} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, $70.23 ; \mathrm{H}, 5.89 ; \mathrm{N}, 10.24$. Found C, 70.62; H, 5.47; N, 10.03\%.
$\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{O}_{2}\right) \mathbf{N H C O C H}_{2} \mathbf{N H C O O C H}_{2} \mathbf{P h} 4.11$ 7-amino-4-methylcoumarin (3.001 g, $18.74 \mathrm{mmol})$, dicyclohexylcarbodiimide ( $4.670 \mathrm{~g}, 22.63 \mathrm{mmol}$ ) and $\mathrm{n}-$ carbobenzyloxyglycine ( $4.380 \mathrm{~g}, 20.94 \mathrm{mmol}$ ). Yield: $2.020 \mathrm{~g}, 32 \%$. ${ }^{1} \mathrm{H}$ NMR (( $\left.\mathrm{CD}_{3}\right)_{2}$ SO: $\delta 10.56\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2} \mathrm{NHCO}\right), 8.06-7.07(\mathrm{~m}, 8 \mathrm{H}$, arom. H), $7.67(\mathrm{t}, 1 \mathrm{H}$, $\left.{ }^{4} J_{\mathrm{HH}} 5.6 \mathrm{~Hz},\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{O}_{2}\right) \mathrm{N} H \mathrm{CO}\right), 6.32(\mathrm{~s}, 1 \mathrm{H}, \mathrm{COCH}), 5.17\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right), 3.92$ (d, $\left.{ }^{4} J_{\mathrm{HH}} 5.6 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{~N} H\right)$, $2.46\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3324,1583$, $v_{\mathrm{CO}}$ 1694, $1625 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $367[\mathrm{M}+\mathrm{H}]^{+}, 366[\mathrm{M}]^{+}$.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H C O O C H}_{\mathbf{2}} \mathbf{P h} 4.12$ To a solution of aminomethylferrocene $(0.190 \mathrm{~g}, 0.883 \mathrm{mmol})$ in THF $\left(10 \mathrm{~cm}^{3}\right)$ was added dicyclohexylcarbodiimide ( 0.203 $\mathrm{g}, 0.974 \mathrm{mmol}$ ) and n -carbobenzyloxyglycine ( $0.188 \mathrm{~g}, 0.885 \mathrm{mmol}$ ) both in THF ( 5 $\mathrm{cm}^{3}$ each). The mixture was stirred at RT for 4 h . The insoluble $N, N^{\prime}-$ dicyclohexylurea was removed by filtration and the solvent replaced by dichloromethane $\left(5 \mathrm{~cm}^{3}\right)$. Addition of hexane afforded a yellow suspension which was stirred for 0.5 h . The suspended solid was filtered and dried under reduced pressure. Yield: $0.263 \mathrm{~g}, 73 \% .{ }^{1} \mathrm{H}$ NMR $\mathrm{CDCl}_{3}: \delta 7.28-7.26(\mathrm{~m}, 5 \mathrm{H}$, arom. H ), 6.21 (bs, $1 \mathrm{H}, \mathrm{NH}$ ), 5.38 (bs, $1 \mathrm{H}, \mathrm{NH}$ ), 5.06 (s, $2 \mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}$ ), 4.09 - 4.07 (m, 11H,
$\mathrm{C}_{5} \mathrm{H}_{5}, \mathrm{C}_{5} \mathrm{H}_{4}$ and $\mathrm{CH}_{2} \mathrm{C}_{5} \mathrm{H}_{4}$ ), 3.81 (d, $2 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 5.2 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH}$ ). FT-IR (KBr): $v_{\mathrm{NH}}$ 3426, 3341, 1539, $v_{\mathrm{CO}} 1670 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 407[\mathrm{M}]^{+}, 406[\mathrm{M}-\mathrm{H}]^{+}, 199$ $\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.
$\left(\mathbf{C}_{\mathbf{1 3}} \mathbf{H}_{\mathbf{8}} \mathbf{N}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N H C O O C H} \mathbf{2} \mathbf{P h} 4.13$ 9-fluorenone hydrazone (1.194 g, 6.145 mmol), dicyclohexylcarbodiimide ( $1.395 \mathrm{~g}, 6.760 \mathrm{mmol}$ ) and $\mathrm{n}-$ carbobenzyloxyglycine ( $1.286 \mathrm{~g}, 6.149 \mathrm{mmol}$ ). Following the second addition of ethyl acetate and petroleumether and subsequent filtration, 4.13 was obtained as an orange solid upon evaporation of the filtrate. Yield: $1.829 \mathrm{~g}, 77 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}: \delta 8.79-7.30\left(\mathrm{~m}, 14 \mathrm{H}\right.\right.$, arom. H and $\left.\left(\mathrm{C}_{13} \mathrm{H}_{8} \mathrm{~N}\right) \mathrm{NHCO}\right)$, $5.08(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{Ph}$ ), $3.86\left(\mathrm{~d}, 2 \mathrm{H},{ }^{4} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{COCH}_{2} \mathrm{NH}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3326,1551$, $v_{\mathrm{CO}} 1695 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $386[\mathrm{M}+\mathrm{H}]^{+}$.

The substituted 2-aminoacetamide 4.14 was prepared following a slight modification to the known procedure. ${ }^{271}$

PhNHCOCH $\mathbf{N H H}_{2}$ 4.14 Cyclohexene ( $2.6 \mathrm{~cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.252 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ) were added to a stirred suspension of 4.5 ( $1.003 \mathrm{~g}, 3.528 \mathrm{mmol}$ ) in absolute EtOH ( 50 $\mathrm{cm}^{3}$ ). The resulting black suspension was refluxed for 6 h at $120^{\circ} \mathrm{C}$, filtered hot under gravity and the filtrate evaporated under reduced pressure. Yield $0.521 \mathrm{~g}, 98 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 7.58-6.68\left(\mathrm{~m}, 5 \mathrm{H}\right.$, arom. H), 3.33 (bs, $2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{NH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3341,3322,1561, v_{\mathrm{CO}} 1655 \mathrm{~cm}^{-1}$. EI-MS: m/z 150 [M].

The substituted 2-aminoacetamides $\mathbf{4 . 1 5} \mathbf{- 4 . 2 1}$ were prepared in a similar manner to 4.14 unless otherwise stated.
$\left(\mathbf{C}_{10} \mathbf{H}_{7}\right) \mathbf{N H C O C H}_{2} \mathbf{N H}_{\mathbf{2}} \mathbf{4 . 1 5}$ Compound 4.6 ( $1.001 \mathrm{~g}, 2.994 \mathrm{mmol}$ ), cyclohexene ( $2.6 \mathrm{~cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.248 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). Yield $0.547 \mathrm{~g}, 91 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)$ : $\delta$ 8.11 - 7.53 (m, 7 H , arom. H), $3.60\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{NH}_{2}\right.$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3350$, 3264, 1553, $v_{\mathrm{CO}} 1696 \mathrm{~cm}^{-1}$. MS (FAB $)$ : m/z $200[\mathrm{M}]^{+}$and $201[\mathrm{M}+\mathrm{H}]^{+}$.
$\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}} \mathbf{4 . 1 6}$ Compound $\mathbf{4 . 7}(0.394 \mathrm{~g}, 1.03 \mathrm{mmol})$, cyclohexene ( 2.6 $\mathrm{cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.250 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). The resulting black suspension was refluxed for 19 h $\left(118^{\circ} \mathrm{C}\right)$. Yield: 0.265 g , Quantitative. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): ~ \delta 8.53-7.45(\mathrm{~m}, 10 \mathrm{H}$, arom. H), 3.30 (bs, $2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{NH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3326,1574, v_{\mathrm{CO}} 1626 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $250[\mathrm{M}]^{+}$.
$\left(\mathbf{C}_{\mathbf{1 3}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N H}_{\mathbf{2}} \mathbf{4 . 1 7}$ Compound $\mathbf{4 . 8}(0.998 \mathrm{~g}, 2.69 \mathrm{mmol})$, cyclohexene ( 2.6 $\mathrm{cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.252 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). The resulting black suspension was refluxed for 17 h $\left(118{ }^{\circ} \mathrm{C}\right)$. Yield: $0.565 \mathrm{~g}, 88 \% .{ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 7.97-7.24(\mathrm{~m}, 7 \mathrm{H}$, arom. H$)$, 3.90 (s, 2H, CH2 ), 3.30 (bs, 2H, $\mathrm{COCH}_{2} \mathrm{NH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3395,3255,1531$, $v_{\mathrm{CO}} 1668 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 238[\mathrm{M}]^{+}, 239[\mathrm{M}+\mathrm{H}]^{+}$. Anal. Calc. for $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{~N}_{2} \mathrm{O} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 72.86; H, 6.11; N, 11.33. Found C, 73.40; H, 6.11; N, $11.32 \%$.
$\left(\mathbf{C}_{\mathbf{1 2}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}} \mathbf{4 . 1 8}$ Compound $4.9(1.002 \mathrm{~g}, 2.779 \mathrm{mmol})$, cyclohexene ( $2.6 \mathrm{~cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.250 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). Yield: $0.599 \mathrm{~g}, 95 \%$. ${ }^{1} \mathrm{H}$ NMR ( $\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)$ : $\delta 8.35-7.13\left(\mathrm{~m}, 9 \mathrm{H}\right.$, arom. H), $3.14\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{NH}_{2}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3393$, 3226, 1521, $v_{\mathrm{CO}} 1656 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $227[\mathrm{M}+\mathrm{H}]^{+}$
$\left(\mathbf{C}_{14} \mathbf{H}_{12} \mathbf{N}\right) \mathbf{N H C O C H N H} \mathbf{2} \mathbf{4 . 1 9}$ Compound $4.10(1.009 \mathrm{~g}, 2.513 \mathrm{mmol})$, cyclohexene ( $2.6 \mathrm{~cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.252 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). Yield: $0.623 \mathrm{~g}, 93 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right)$ : $\delta 8.45-7.16\left(\mathrm{~m}, 7 \mathrm{H}\right.$, arom. H), $4.41\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.30(\mathrm{bs}, 2 \mathrm{H}$, $\mathrm{COCH}_{2} \mathrm{NH}_{2}$ ), $1.27\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ). FT-IR ( KBr ): $v_{\mathrm{NH}} 3385,3278$, $1590, v_{\mathrm{CO}} 1658 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $267[\mathrm{M}]^{+}$.
$\left(\mathbf{C}_{10} \mathbf{H}_{7} \mathrm{O}_{2}\right) \mathbf{N H C O C H}_{2} \mathbf{N H}_{\mathbf{2}}$ 4.20 Cyclohexene $\left(1.3 \mathrm{~cm}^{3}\right)$, activated palladium on charcoal ( 0.125 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ) and 4.11 ( $0.502 \mathrm{~g}, 2.161 \mathrm{mmol}$ ). The resulting black suspension was refluxed for $1 \mathrm{~h}\left(118^{\circ} \mathrm{C}\right)$. Yield: $0.258 \mathrm{~g}, 83 \%{ }^{1} \mathrm{H}$ NMR (( $\left.\left.\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 7.89-7.61(\mathrm{~m}, 3 \mathrm{H}$, arom. H$), 6.31(\mathrm{~s}, 1 \mathrm{H}, \mathrm{COCH}), 3.40(\mathrm{~s}, 2 \mathrm{H}$,
$\left.\mathrm{COCH}_{2} \mathrm{~N}\right), 2.45\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3325,1589$, $\mathrm{v}_{\mathrm{CO}} 1686,1624 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $233[\mathrm{M}+\mathrm{H}]^{+}$.
$\mathbf{F c C H}_{\mathbf{2}} \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}} \mathbf{4 . 2 1}$ Compound $4.12(0.518 \mathrm{~g}, 1.272 \mathrm{mmol})$, cyclohexene ( $1.6 \mathrm{~cm}^{3}$, in excess of the molar proportion required) and activated palladium on charcoal ( 0.157 g , palladium $10 \% \mathrm{w} / \mathrm{w}$ ). The resulting black suspension was refluxed for $1 \mathrm{~h}\left(110^{\circ} \mathrm{C}\right)$, under a nitrogen atmosphere. Yield: $0.223 \mathrm{~g}, 92 \%$. ${ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 7.49(\mathrm{bs}, 1 \mathrm{H}, \mathrm{NH}), 4.12-4.05\left(\mathrm{bm}, 9 \mathrm{H}, \mathrm{C}_{5} \mathrm{H}_{5}\right.$ and $\left.\mathrm{C}_{5} \mathrm{H}_{4}\right), 3.51-3.41$ (bm, 4H, CH ${ }_{2}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3325,1574, v_{\mathrm{CO}} 1628 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z 272 $[\mathrm{M}]^{+}$.

PhNHCOCH $\mathbf{2}^{\mathbf{N}}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2} \mathbf{4 . 2 2}$ Under a nitrogen atmosphere, a solution of 4.14 $(0.108 \mathrm{~g}, 0.719 \mathrm{mmol})$ and $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.365 \mathrm{~g}, 1.52 \mathrm{mmol})$ in $\mathrm{MeOH}\left(20 \mathrm{~cm}^{3}\right)$ was stirred for 23 h . The solution was concentrated to $c a .5 \mathrm{~cm}^{3}$ under reduced pressure and the resulting cream precipitate filtered and dried under reduced pressure. Yield: $0.252 \mathrm{~g}, 64 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-26.4 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.13(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.47-6.83\left(\mathrm{~m}, 25 \mathrm{H}\right.$, arom. H), $3.67\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right)$, $3.66\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3300,1519, v_{\mathrm{CO}} 1677 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{OP}_{2}$ requires C, 74.71; H, 5.90; N, 5.12. Found C, 74.76; H, 5.86; N, 4.90\%.

Unless otherwise stated phosphines 4.23 - $\mathbf{4 . 2 9}$ were prepared in a similar manner to 4.22 .
$\left(\mathbf{C}_{10} \mathbf{H}_{7}\right) \mathbf{N H C O C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2} \mathbf{4 . 2 3}$ Compound 4.15 ( $\left.0.157 \mathrm{~g}, 0.786 \mathrm{mmol}\right)$, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.355 \mathrm{~g}, 1.48 \mathrm{mmol})$ and stirred for 21 h . Yield: 0.337 g , Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-26.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.67$ (s, $\left.1 \mathrm{H}, \mathrm{NH}\right), 7.92-$ $6.91\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $3.84\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right), 3.74\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3319,1522, v_{\mathrm{CO}} 1684 \mathrm{~cm}^{-1}$.
$\left(\mathbf{C}_{14} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N H C H}_{2} \mathbf{P P h}_{\mathbf{2}} \mathbf{4 . 2 4 a}$ Under a nitrogen atmosphere, a solution of $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}$ in $\mathrm{MeOH}\left(10 \mathrm{~cm}^{3}\right)$ was added dropwise, over a period of 40 min via a pressure equalizing dropping funnel, to a stirred solution of 4.16 in $\mathrm{MeOH}\left(10 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred at RT for 2 h to yield a white precipitate which was
filtered and dried under reduced pressure. Yield: $0.025 \mathrm{~g}, 15 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta-21.6 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 10.06(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.55-7.45$ (m, 20H, arom. H and NH), $3.61\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right), 3.55\left(\mathrm{~d}, 2 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 3.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3317,3222,1513, v_{\mathrm{CO}} 1664 \mathrm{~cm}^{-1}$. Attempts to obtain an ideal elemental analysis result were unsuccessful: Anal. Calc. for $\mathrm{C}_{29} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{OP} \cdot 1.25 \mathrm{H}_{2} \mathrm{O}$ requires C, 73.95 ; H, 5.88; N, 5.95. Found C, 73.94; H, 5.37; N, 5.69\%.
$\left(\mathbf{C}_{13} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{4 . 2 5}$ Compound 4.17 ( $\left.0.334 \mathrm{~g}, 1.40 \mathrm{mmol}\right)$, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.675 \mathrm{~g}, 2.81 \mathrm{mmol})$ and stirred for 17 h . Yield: $0.654 \mathrm{~g}, 75 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-26.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.17(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.63-6.60(\mathrm{~m}$, 27 H , arom. H), 3.72 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.62 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), 3.61 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3314,1500, v_{\mathrm{CO}} 1687 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{41} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{OP}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, 76.50; H, 5.79; N, 4.35. Found C, 76.88; H, 5.41; N, 4.16\%.
$\left(\mathbf{C}_{12} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H}_{2} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{4 . 2 6}$ Compound 4.18 ( $\left.0.101 \mathrm{~g}, 0.445 \mathrm{mmol}\right)$, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.209 \mathrm{~g}, 0.888 \mathrm{mmol})$, stirred for 22 h . Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta-28.6 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.31(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.86-6.94(\mathrm{~m}$, 29 H , arom. H), 3.47 (s, $2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}$ ), 3.32 (d, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 2.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3312,1519, v_{\mathrm{CO}} 1651 \mathrm{~cm}^{-1}$.
$\left(\mathbf{C}_{14} \mathbf{H}_{12} \mathbf{N}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2} \mathbf{4 . 2 7}$ Compound 4.19 ( $\left.0.203 \mathrm{~g}, 0.801 \mathrm{mmol}\right)$, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.398 \mathrm{~g}, 1.66 \mathrm{mmol})$, stirred for 17 h . Yield: $0.410 \mathrm{~g}, 77 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta-26.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.24(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.04-7.14(\mathrm{~m}$, 27 H , arom. H), 4.32 (q, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 3.73 (s, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 3.72 (s, 2 H , $\mathrm{CH}_{2}$ ), $3.71\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.40\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ). FT-IR (KBr): $\mathrm{v}_{\mathrm{NH}} 3282$, 1532, $v_{\text {CO }} 1677 \mathrm{~cm}^{-1}$. Anal. Calc. for $\mathrm{C}_{42} \mathrm{H}_{39} \mathrm{~N}_{3} \mathrm{OP}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 74.99 ; \mathrm{H}$, 5.99; N, 6.25. Found C, 75.37; H, 6.00; N, 6.34\%.
$\left(\mathbf{C}_{10} \mathbf{H}_{7} \mathbf{O}_{2}\right) \mathbf{N H C O C H} \mathbf{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}} 4.28 \mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.200 \mathrm{~g}, 0.926 \mathrm{mmol})$, $\mathbf{4 . 2 0}$ ( $0.096 \mathrm{~g}, 0.42 \mathrm{mmol}$ ), stirred for 3 h . Yield: $0.149 \mathrm{~g}, 57 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta$ $-26.2 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.32-6.44(\mathrm{~m}, 23 \mathrm{H}$, arom. H$), 6.18(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{COCH}), 4.10(\mathrm{bs}, 1 \mathrm{H}, \mathrm{NH}), 3.71\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right), 3.67\left(\mathrm{~d}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 5.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{P}\right)$, 2.39 (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3314,1577, v_{\mathrm{CO}} 1717,1685 \mathrm{~cm}^{-1}$.
$\mathbf{F c N H C O C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{4 . 2 9}$ Compound $4.21(0.100 \mathrm{~g}, \quad 0.367 \mathrm{mmol})$, $\mathrm{Ph}_{2} \mathrm{PCH}_{2} \mathrm{OH}(0.178 \mathrm{~g}, 0.741 \mathrm{mmol})$, stirred at reflux for 10 d and solvent evaporated under reduced pressure. Attempts to obtain an analytically pure sample of 4.29 were hampered by incomplete reaction. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ : $\delta-27.0 \mathrm{ppm}$. MS $\left(\mathrm{FAB}^{+}\right)$: $\mathrm{m} / \mathrm{z} 667[\mathrm{M}]^{+}, 199\left[\mathrm{CH}_{2} \mathrm{Fc}\right]^{+}$.

### 5.8.5 Coordination chemistry of $4.22-4.28$.

Complexes 4.30 - $\mathbf{4 . 3 7}$ were prepared in a similar manner to 3.42.
cis- $\mathbf{P t C l}_{2}\left\{\mathbf{P h N H C O C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{4 . 3 0}$ Phosphine 4.22 ( $0.091 \mathrm{~g}, 0.17 \mathrm{mmol}$ ) and $\mathrm{PtCl}_{2}$ (cod) $(0.062 \mathrm{~g}, 0.17 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(20 \mathrm{~cm}^{3}\right)$. Yield: $0.132 \mathrm{~g}, 97 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-6.4 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3411 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.85-6.86$ (m, 25 H , arom. H), $7.64(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 3.76$ (dd, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 2.0 \mathrm{~Hz},{ }^{3} J_{\mathrm{PtH}} 15.2 \mathrm{~Hz}$, $\mathrm{CH}_{2} \mathrm{PPt}$ ), 3.41 (s, $2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3301,1525$, $v_{\mathrm{CO}} 1684$, $v_{\mathrm{PtCl}} 314$, $290 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 777 \quad[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{PtCl}_{2} \cdot 1.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires $\mathrm{C}, 45.36 ; \mathrm{H}, 3.75$; $\mathrm{N}, 2.99$. Found $\mathrm{C}, 45.74$; H, 3.91; N, 2.55\%.
cis- $\mathbf{P t C l}_{2}\left\{\left(\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{7}\right) \mathbf{N H C O C H} \mathbf{2}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{2}\right\}$ 4.31 Phosphine 4.23 (0.103 g, 0.173 $\mathrm{mmol})$ and $\mathrm{PtCl}_{2}(\operatorname{cod})(0.065 \mathrm{~g}, 0.17 \mathrm{mmol})$. Yield: 0.149 g , Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\mathrm{CDCl}_{3}$ ): $\delta-5.0 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3416 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.06(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$, $7.88-6.98\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $3.75\left(\mathrm{dd}, 4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 2.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{PtH}} 16.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{PPt}\right)$, 3.55 (s, 2H, $\mathrm{COCH}_{2} \mathrm{~N}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3280,1528, v_{\mathrm{CO}} 1684, v_{\mathrm{PtCl}} 314,291 \mathrm{~cm}^{-1}$. MS ( $\mathrm{FAB}^{+}$): m/z $827[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{38} \mathrm{H}_{34} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{PtCl}_{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, 49.43; H, 3.83; N, 2.96. Found C, 49.17; H, 4.08; N, 2.68\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\left(\mathbf{C}_{\mathbf{1}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\}$ 4.32 Phosphine 4.25 ( $0.107 \mathrm{~g}, 0.169$ $\mathrm{mmol})$ and $\mathrm{PtCl}_{2}($ cod $)(0.061 \mathrm{~g}, 0.162 \mathrm{mmol})$. Yield: $0.145 \mathrm{~g}, 95 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-8.0 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3406 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.74(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.86-$ $6.99\left(\mathrm{~m}, 29 \mathrm{H}\right.$, arom. H), 3.88 (dd, $4 \mathrm{H},{ }^{2} J_{\mathrm{PH}} 1.2 \mathrm{~Hz},{ }^{3} J_{\mathrm{PtH}} 16.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{PPt}$ ), $3.80(\mathrm{~s}$, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $3.49\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3305,1529, v_{\mathrm{CO}} 1675, v_{\mathrm{PtCl}} 313,291$ $\mathrm{cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 865 \quad[\mathrm{M}-\mathrm{Cl}]^{+}, 829 \quad[\mathrm{M}-2 \mathrm{Cl}]^{+}$. Anal. Calc. for
$\mathrm{C}_{41} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{PtCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ requires C, 53.60; H, 4.17; N, 3.05. Found C, 53.72; H, 4.13; N, 2.96\%.
cis- $\mathbf{P t C l}_{2}\left\{\left(\mathbf{C}_{\mathbf{1 2}} \mathbf{H}_{\mathbf{9}}\right) \mathbf{N H C O C H} \mathbf{2}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right)_{2}\right\} \mathbf{4 . 3 3}$ Phosphine 4.26 (0.051 g, 0.058 $\mathrm{mmol})$ and $\mathrm{PtCl}_{2}($ cod $)(0.022 \mathrm{~g}, 0.059 \mathrm{mmol})$. Yield: $0.037 \mathrm{~g}, 72 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-11.1 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3393 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.43$ (s, $\left.1 \mathrm{H}, \mathrm{NH}\right), 7.73-$ $7.07\left(\mathrm{~m}, 29 \mathrm{H}\right.$, arom. H), $3.64\left(\mathrm{bm}, 4 \mathrm{H},{ }^{3} J_{\mathrm{PtH}} 18.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{PPt}\right), 3.23(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{COCH}_{2} \mathrm{~N}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3285,1512, v_{\mathrm{CO}} 1680, v_{\mathrm{PtCl}} 310,283 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right):$ $\mathrm{m} / \mathrm{z} 853[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{40} \mathrm{H}_{36} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{PtCl}_{2} \cdot 0.5 \mathrm{H}_{2} \mathrm{O}$ requires C, $53.39 ; \mathrm{H}$, 4.18; N, 3.11. Found C, 52.95; H, 4.18; N, 2.89\%.
cis- $\left.\mathbf{P t C l}_{\mathbf{2}}\left\{\mathbf{( C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{1 2}} \mathbf{N}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{\mathbf{2}}\right)_{\mathbf{2}}\right\} \mathbf{4 . 3 4}$ Phosphine 4.27 ( $0.102 \mathrm{~g}, 0.153$ $\mathrm{mmol})$ and $\mathrm{PtCl}_{2}(\operatorname{cod})(0.570 \mathrm{~g}, 0.152 \mathrm{mmol})$. Yield: $0.124 \mathrm{~g}, 87 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta-9.3 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3405 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.24(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.04-$ $7.16\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $4.32\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 3.73\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.72$ (s, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), $3.71\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 1.40\left(\mathrm{~s}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$. FT-IR ( KBr ): $v_{\mathrm{NH}} 3345,1531, v_{\mathrm{CO}} 1677, v_{\mathrm{PtCl}} 316,296 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 929[\mathrm{M}]^{+}, 894[\mathrm{M}-$ $\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{42} \mathrm{H}_{39} \mathrm{~N}_{3} \mathrm{OP}_{2} \mathrm{PtCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ requires $\mathrm{C}, 53.23 ; \mathrm{H}, 4.36 ; \mathrm{N}, 4.43$. Found C, 53.50; H, 4.26; N, 4.42\%.
cis- $\mathbf{P t C l}_{\mathbf{2}}\left\{\left(\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{7}} \mathbf{O}_{\mathbf{2}}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \quad 4.35 \mathrm{PtCl}_{2}(\mathrm{cod}) \quad\left(\begin{array}{llll}0.044 & \mathrm{~g}, & 0.12\end{array}\right.$ $\mathrm{mmol})$ and $4.28(0.103 \mathrm{~g}, 0.103 \mathrm{mmol})$. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta-9.7 \mathrm{ppm},{ }^{1} J_{\mathrm{PtP}} 3419 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR ((CD $\left.)_{2} \mathrm{SO}\right): \delta 10.18(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$, $7.95-7.36\left(\mathrm{~m}, 23 \mathrm{H}\right.$, arom. H), $6.34(\mathrm{~s}, 1 \mathrm{H}, \mathrm{COCH}), 4.28$ (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.59(\mathrm{~s}$, $2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}$ ), $2.45\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3324,1577$, $v_{\mathrm{CO}} 1718,1701$, $1618, v_{\mathrm{PtCl}} 314,293 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 859[\mathrm{M}-\mathrm{Cl}]^{+}$. Attempts to obtain an ideal elemental analysis result were unsuccessful: Anal. Calc. for $\mathrm{C}_{38} \mathrm{H}_{34} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{PtCl}_{2} \cdot 0.1 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $50.67 ; \mathrm{H}, 3.82 ; \mathrm{N}, 3.10$. Found C, 50.80 ; H, 4.11; N, 3.70\%.
cis- $\mathbf{P d C l}_{\mathbf{2}}\left\{\left(\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{\mathbf{7}} \mathbf{O}_{\mathbf{2}}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \quad \mathbf{4 . 3 6} \mathrm{PdCl}_{2}(\operatorname{cod})(0.034 \mathrm{~g}, 0.12$ mmol) and 4.28 ( $0.075 \mathrm{~g}, 0.12 \mathrm{mmol})$. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 6.0 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 10.15(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.88-7.29(\mathrm{~m}$, 23 H , arom. H), 6.25 (s, $1 \mathrm{H}, \mathrm{COCH}$ ), 4.16 (bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.54\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right)$,
2.38 (s, 3H, CH3 ). FT-IR (KBr): $v_{\mathrm{NH}} 3316,3263,1579$, $v_{\mathrm{CO}} 1719,1702,1617, v_{\mathrm{PdCl}}$ 304 and $298 \mathrm{~cm}^{-1}$. MS $\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 771 \quad[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{38} \mathrm{H}_{34} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{PdCl}_{2} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $54.50 ; \mathrm{H}, 4.16$; N, 3.30. Found C, 54.58 ; H, 4.17; N, 3.64\%.
cis-Pd(Me)Cl$\left\{\left(\mathbf{C}_{\mathbf{1 0}} \mathbf{H}_{7} \mathbf{O}_{\mathbf{2}}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{4 . 3 7} \mathrm{Pd}(\mathrm{Me}) \mathrm{Cl}(\mathrm{cod})(0.032 \mathrm{~g}$, $0.12 \mathrm{mmol})$ and $4.28(0.075 \mathrm{~g}, 0.12 \mathrm{mmol})$. Yield: Quantitative. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 22.4,-10.8 \mathrm{ppm},{ }^{2} J_{\mathrm{PP}} 48 \mathrm{~Hz} .{ }^{1} \mathrm{H}$ NMR $\left(\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right): \delta 9.73(\mathrm{~s}, 1 \mathrm{H}$, NH), $7.58-7.00\left(\mathrm{~m}, 23 \mathrm{H}\right.$, arom. H), 6.04 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{COCH}$ ), 3.94 (bs, $2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), 3.80 (bs, $2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.24\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right), 2.17\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 0.12\left(\mathrm{bs}, 3 \mathrm{H}, \mathrm{PdCH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3317,1579, v_{\mathrm{CO}} 1724,1702,1617 \mathrm{~cm}^{-1}$. MS (FAB ${ }^{+}$): m/z $771[\mathrm{M}-$ $\left.\mathrm{CH}_{3}\right]^{+}$. Anal. Calc. for $\mathrm{C}_{39} \mathrm{H}_{37} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{PdCl} \cdot 0.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ requires C, $57.30 ; \mathrm{H}, 4.63 ; \mathrm{N}$, 3.38. Found C, 57.48; H, 4.65; N, 3.62\%.
$\left\{\mathbf{R u C l}_{2}(\boldsymbol{p}-\mathbf{c y m})\right\}_{2}\left\{\mathbf{P h N H C O C H}_{2} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{2}\right\} \mathbf{4 . 3 8}$ A solution of $4.22(0.067 \mathrm{~g}$, $0.12 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$ was added to a stirred solution of $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-$ cym) $]_{2}(0.108 \mathrm{~g}, 0.176 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}\left(10 \mathrm{~cm}^{3}\right)$. The resulting solution was stirred for 0.5 h and concentrated to $c a .2 \mathrm{~cm}^{3}$ under reduced pressure. Diethyl ether ( 25 $\mathrm{cm}^{3}$ ) was added and the resulting orange precipitate filtered and dried under reduced pressure. Yield: $0.096 \mathrm{~g}, 67 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 16.5 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 8.00(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.86-7.01\left(\mathrm{~m}, 25 \mathrm{H}\right.$, arom. H), $5.18\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}\right.$, CH ), $5.04\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6 \mathrm{~Hz}, \mathrm{CH}\right), 3.94\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}\right), 2.53\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right), 2.37$ (sept, $\left.{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}\right), 1.74\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 0.85\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{CH}_{3}\right)$. FTIR (KBr): $v_{\mathrm{NH}} 3283,1522, v_{\mathrm{CO}} 1684, v_{\mathrm{RuCl}} 291 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1123[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{54} \mathrm{H}_{6} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{Cl}_{4} \mathrm{Ru}_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O}$ requires: C, $53.47 ; \mathrm{H}, 5.48 ; \mathrm{N}, 2.31$. Found: C, 53.72; H, 5.13; N, 2.23\%.

Complexes 4.39 - 4.41 were made in a similar manner to $\mathbf{4 . 3 8}$.
$\left\{\mathrm{RuCl}_{2}(\boldsymbol{p}-\mathbf{c y m})\right\}_{2}\left\{\left(\mathbf{C}_{10} \mathbf{H}_{7}\right) \mathbf{N H C O C H}_{\mathbf{2}} \mathbf{N}\left(\mathbf{C H}_{2} \mathbf{P P h}_{2}\right)_{\mathbf{2}} \mathbf{4 . 3 9}\right.$ Phosphine 4.23 ( 0.081 g , $0.14 \mathrm{mmol})$ and $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.100 \mathrm{~g}, 0.163 \mathrm{mmol})$. Yield: $0.122 \mathrm{~g}, 59 \%$. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 18.3 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.92(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.88-$ $7.35\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $5.13\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{CH}\right), 4.97\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 5.6 \mathrm{~Hz}\right.$, CH ), 3.95 ( $\mathrm{s}, 4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $2.92\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right.$ ), 2.37 (sept, $\left.{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}\right)$,
$1.72\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 0.79\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 6.8 \mathrm{~Hz}, \mathrm{CH}_{3}\right)$. FT-IR (KBr): $v_{\mathrm{NH}} 3314,1509$, $v_{\mathrm{CO}} 1692, \mathrm{v}_{\mathrm{RuCl}} 290 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1173[\mathrm{M}-\mathrm{Cl}]^{+}$.
$\left\{\operatorname{RuCl}_{2}(\boldsymbol{p} \text {-cym })\right\}_{2}\left\{\left(\mathbf{C}_{13} \mathbf{H}_{9}\right) \mathbf{N H C O C H}_{2} \mathbf{N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{2}\right\} \mathbf{4 . 4 0}$ Phosphine $\mathbf{4 . 2 5}$ ( 0.104 g , $0.163 \mathrm{mmol})$ and $[\mathrm{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.100 \mathrm{~g}, 0.163 \mathrm{mmol})$. Yield: 0.181 g , $89 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 16.9 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.97(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$, $7.80-7.06\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $5.11\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{CH}\right), 4.96\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6 \mathrm{~Hz}\right.$, CH ), 3.90 ( bs, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), $3.79\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.55\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{COCH}_{2} \mathrm{~N}\right.$ ), $2.30\left(\mathrm{sept},{ }^{3} J_{\mathrm{HH}}\right.$ $6.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}$ ), $1.67\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 0.77\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{CH}_{3}\right)$. FT-IR ( KBr ): $v_{\mathrm{NH}} 3281,1520, v_{\mathrm{CO}} 1686, v_{\mathrm{RuCl}} 290 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1213[\mathrm{M}-\mathrm{Cl}]^{+}$. Anal. Calc. for $\mathrm{C}_{61} \mathrm{H}_{64} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{Cl}_{4} \mathrm{Ru}_{2}$ requires: C, 58.65; H, 5.16; N, 2.24. Found: C, 58.23; H, 4.85; N, 2.26\%.
$\left\{\operatorname{RuCl}_{2}(\boldsymbol{p}-\mathbf{c y m})\right\}_{2}\left\{\left(\mathbf{C}_{\mathbf{1 4}} \mathbf{H}_{\mathbf{1 2}} \mathbf{N}\right) \mathbf{N H C O C H N}\left(\mathbf{C H}_{\mathbf{2}} \mathbf{P P h}_{2}\right)_{\mathbf{2}}\right\} \mathbf{4 . 4 1}$ Phosphine 4.27 (0.121 $\mathrm{g}, 0.182 \mathrm{mmol})$ and $[\operatorname{RuCl}(\mu-\mathrm{Cl})(p-\mathrm{cym})]_{2}(0.114 \mathrm{~g}, 0.186 \mathrm{mmol})$. Yield: 0.144 g , $62 \% .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 17.2 \mathrm{ppm} .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 7.96(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$, $7.90-7.21\left(\mathrm{~m}, 27 \mathrm{H}\right.$, arom. H), $5.17\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0 \mathrm{~Hz}, \mathrm{CH}\right), 5.02\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 6.0\right.$ $\mathrm{Hz}, \mathrm{CH}), 4.35\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ), 3.97 (s, $4 \mathrm{H}, \mathrm{CH}_{2} \mathrm{P}$ ), 2.63 (s, 2 H , $\mathrm{COCH}_{2} \mathrm{~N}$ ), 2.38 (sept, ${ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}$ ), $1.75\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 1.43\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}} 7.2\right.$ $\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 0.83 (d, ${ }^{3} J_{\mathrm{HH}} 6.8 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{CH}_{3}$ ). FT-IR (KBr): $v_{\mathrm{NH}} 3272,1528, v_{\mathrm{CO}}$ 1676, $v_{\mathrm{RuCl}} 290 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{FAB}^{+}\right): \mathrm{m} / \mathrm{z} 1277[\mathrm{M}]^{+}, 1242[\mathrm{M}-\mathrm{Cl}]^{+}$.

Chapter 7

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Chapter 8
Appendix

### 8.1 List of Publications:

Publications directly related to this research (copies of papers overleaf and on enclosed CD);
M. R. J. Elsegood, A. J. Lake, R. J. Mortimer, M. B. Smith, G. W. Weaver, J. Organomet. Chem., 2008, 693, 2317-2326.
M. R. J. Elsegood, A. J. Lake, C. L. Elliott, M. B. Smith and G. W. Weaver, Phosphorus, Sulfur Silicon Relat. Elem.,2008, 183, 435-439.

Collaborative publications not directly related to the research discussed therein (copies of papers on enclosed CD);
M. R. J. Elsegood, A. J. Lake, M. B. Smith, Eur. J. Inorg. Chem., 2009, 1068-1078.
A. T. Ekubo, S. E. Dann, M. R. J. Elsegood, P. F. Kelly, A. J. Lake and M. B. Smith, Inorg. Chem., 2009, 48, 2633-2638.
M. R. J. Elsegood, A. J. Lake, M. B. Smith, Dalton Trans., 2009, 30-32.
G. M. Brown, M. R. J. Elsegood, A. J. Lake, N. M. Sanchez Ballester, M. B. Smith, T. S. Varley and K. Blann, Eur. J. Inorg. Chem., 2007, 1405-1414.

### 8.2 Presentations / Conferences attended:

Poster at the RSC Dalton Division Meeting, Warwick, March 2008.

Poster at the joint meeting of the RSC UK Macrocycles and Supramolecular Chemistry Group and The Coordination Chemistry Discussion Group, Belfast, December 2006.

Poster at the RSC Dalton Division Meeting, Birmingham, September 2006.

### 8.3 Details of Refinements for Molecular Structures.

Table 8.1 Crystal data and structure refinement for the solid solution of $\mathbf{2 . 4}$ and 2.6.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$ F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection Index ranges
Completeness to $\theta=26.00^{\circ}$
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final R indices $\left[F^{2}>2 \sigma\right.$ ]
R indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{63} \mathrm{H}_{54} \mathrm{~N}_{2} \mathrm{O}_{1.40} \mathrm{P}_{2}$
923.42

150(2) K
MoKa, $0.71073 \AA$
triclinic, $\mathrm{P} \overline{1}$
$a=9.4580(13) \AA \quad \alpha=68.121(2)^{\circ}$
$b=10.2273(14) \AA \quad \beta=76.863(3)^{\circ}$
$\mathrm{c}=13.712(2) \AA \quad \gamma=73.803(2)^{\circ}$
$1170.6(3) \AA^{3}$
1
$0.142 \mathrm{~mm}^{-1}$
487
colourless, $0.32 \times 0.09 \times 0.07 \mathrm{~mm}^{3}$
11831 ( $\theta$ range 2.25 to $28.22^{\circ}$ )
Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames
1.62 to $28.39^{\circ}$
h -12 to $12, \mathrm{k}-13$ to $13,1-18$ to 18
99.5 \%

11831
$5778\left(\mathrm{R}_{\mathrm{int}}=0.0289\right)$
4400
semi-empirical from equivalents
0.9560 and 0.9901
direct methods
Full-matrix least-squares on $\mathrm{F}^{2}$
$0.0784,0.2893$
5778 / 7 / 328
$\mathrm{R} 1=0.0515, \mathrm{wR} 2=0.1313$
$\mathrm{R} 1=0.0723, \mathrm{wR} 2=0.1449$
1.040
0.001 and 0.000
0.470 and $-0.354 \mathrm{e} \AA^{-3}$
2.4 / 2.6: The asymmetric unit was found to contain half a molecule of $\mathbf{2 . 4}$ and a solvating MeOH molecule of crystallisation. The ligand was positioned on a crystallographic inversion centre, located at the mid-point of the ethylenediaminyl backbone [symmetry operator for equivalent atoms, ' $=-\mathrm{x}+2,-\mathrm{y}+1,-\mathrm{z}$ ]. The phosphorus atom $\mathrm{P}(1)$ was found to be partially oxidised, to give a solid solution containing 2.4 and its component oxide (2.6) [occupancy freely refined to 19.77(3)\%]. Anisotropic displacement parameters of C(32) and O(2) (of the solvating molecule of MeOH ) were restrained to be similar.

Table 8.2 Crystal data and structure refinement for 2.5.

| Chemical formula | $\mathrm{C}_{63} \mathrm{H}_{59} \mathrm{D}_{6} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{P}_{2} \mathrm{~S}_{3}$ |
| :---: | :---: |
| Formula weight | 1094.33 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ Å |
| Crystal system, space group | monoclinic, $\mathrm{C} 2 / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=20.6510(8) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=17.1299(6) \AA \quad \beta=107.234(2)^{\circ}$ |
|  | $\mathrm{c}=16.9338(6) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 5721.4(4) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.236 \mathrm{~mm}^{-1}$ |
| F(000) | 2300 |
| Crystal colour and size | colourless, $1.06 \times 0.62 \times 0.54 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 9947 ( $\theta$ range 2.20 to $28.32^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.57 to $28.32^{\circ}$ |
| Index ranges | $\mathrm{h}-27$ to $27, \mathrm{k}-22$ to $22,1-22$ to 22 |
| Completeness to $\theta=26.00^{\circ}$ | 99.9 \% |
| Reflections collected | 29134 |
| Independent reflections | $7110\left(\mathrm{R}_{\mathrm{int}}=0.0216\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 6135 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.788 and 0.883 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0909, 6.1408 |
| Data / restraints / parameters | 7110 / 15 / 350 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0477, \mathrm{wR} 2=0.1430$ |
| R indices (all data) | $\mathrm{R} 1=0.0548, \mathrm{wR} 2=0.1509$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.049 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.071 and $-0.660 \mathrm{e}^{\text {A }}{ }^{-3}$ |

2.5: The asymmetric unit was found to contain half a molecule of $\mathbf{2 . 5}$ and one and a half molecules of solvating $\operatorname{SO}\left(\mathrm{CD}_{3}\right)_{2}$. Compound $\mathbf{2 . 5}$ was found to be located on a crystallographic inversion centre located at the mid-point of the ethylenediaminyl backbone [symmetry operation for equivalent atoms , $='-x,-y+2,-z+1$ ]. The half $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}$ molecule was found to be disordered over a second symmetry operator (" $=-x, y,-z+3 / 2)$. The anisotropic displacement parameters were restrained to be similar for this disordered solvent molecule.

Table 8.3 Crystal data and structure refinement for 2.7.

| Chemical formula | $\mathrm{C}_{43} \mathrm{H}_{44} \mathrm{Cl}_{4} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 987.63 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073$ A |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=10.4196(10) \AA \quad \alpha=81.036(10)^{\circ}$ |
|  | $\mathrm{b}=11.6938(11) \AA \quad \beta=82.278(2)^{\circ}$ |
|  | $\mathrm{c}=18.0832(17) \AA \quad \gamma=68.640(10)^{\circ}$ |
| Cell volume | 2019.7(3) $\AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $3.851 \mathrm{~mm}^{-1}$ |
| F(000) | 984 |
| Crystal colour and size | colourless, $0.59 \times 0.49 \times 0.13 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 8981 ( $\theta$ range 2.28 to $30.38^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.88 to $30.55^{\circ}$ |
| Index ranges | $\mathrm{h}-14$ to $14, \mathrm{k}-16$ to $16,1-25$ to 25 |
| Completeness to $\theta=26.00^{\circ}$ | 99.7 \% |
| Reflections collected | 23941 |
| Independent reflections | $12068\left(\mathrm{R}_{\text {int }}=0.0461\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 10504 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.2097 and 0.6344 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0636, 0.4231 |
| Data / restraints / parameters | 12068 / 3 / 459 |
| Final $R$ indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0448, \mathrm{wR} 2=0.1104$ |
| R indices (all data) | $\mathrm{R} 1=0.0527, \mathrm{wR} 2=0.1150$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.025 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 4.251 and $-1.700 \mathrm{e} \AA^{-3}$ |

2.7: The asymmetric unit was found to contain one molecule of $\mathbf{2 . 7}$ and one solvating molecule of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The geometry of the phenyl ring containing $\mathrm{C}(37)$ to $\mathrm{C}(42)$ was restrained to be more planar. The anisotropic displacement parameters of the chlorine atoms within the solvating $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were restrained to be similar.

Table 8.4. Crystal data and structure refinement for 2.8.

| Chemical formula | $\mathrm{C}_{50} \mathrm{H}_{46} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 1002.82 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoKa, 0.71073 A |
| Crystal system, space group | orthorhombic, $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
| Unit cell parameters | $a=11.3131(7) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=18.3971(11) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=19.9341(12) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 4148.8(4) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $3.627 \mathrm{~mm}^{-1}$ |
| F(000) | 2008 |
| Crystal colour and size | colourless, $0.66 \times 0.17 \times 0.12 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 8461 ( $\theta$ range 2.21 to $29.40^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.51 to $29.63^{\circ}$ |
| Index ranges | $\mathrm{h}-15$ to $15, \mathrm{k}-25$ to $24,1-27$ to 27 |
| Completeness to $\theta=26.00^{\circ}$ | 100.0 \% |
| Reflections collected | 45385 |
| Independent reflections | $11673\left(\mathrm{R}_{\text {int }}=0.0398\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 10390 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.1981 and 0.6701 |
| Structure solution | Patterson synthesis |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0322, 3.9366 |
| Data / restraints / parameters | 11673 / 0 / 515 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0319, \mathrm{wR} 2=0.0686$ |
| R indices (all data) | $\mathrm{R} 1=0.0421, \mathrm{wR} 2=0.0730$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.060 |
| Absolute structure parameter | 0.354(5) |
| Largest and mean shift/su | 0.008 and 0.000 |
| Largest diff. peak and hole | 1.416 and $-1.184 \mathrm{e} \AA^{-3}$ |

2.8: The asymmetric unit was found to contain one molecule of complex 2.8. The non-centrosymmetric structure was found to be twinned by inversion [major twin domain 64.5(5)\%].

Table 8.5. Crystal data and structure refinement for 2.9.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$
F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection
Index ranges
Completeness to $\theta=31.57^{\circ}$
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ]
R indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Extinction coefficient
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{60.50} \mathrm{H}_{56} \mathrm{Cl}_{3} \mathrm{~N}_{2} \mathrm{O}_{0.50} \mathrm{P}_{2} \mathrm{Pt}$
1182.45

150(2) K
synchrotron, $0.8462 \AA$
monoclinic, $\mathrm{P} 2_{1} / \mathrm{n}$
$a=26.658(3) \AA \quad \alpha=90^{\circ}$
$\mathrm{b}=14.9329(16) \AA \quad \beta=102.741(2)^{\circ}$
$\mathrm{c}=27.408(3) \AA \quad \gamma=90^{\circ}$
10642(2) $\AA^{3}$
8
$2.890 \mathrm{~mm}^{-1}$
4768
pale yellow, $0.12 \times 0.07 \times 0.04 \mathrm{~mm}^{3}$
2545 ( $\theta$ range 3.70 to $21.67^{\circ}$ )
Bruker APEX II CCD diffractometer
$\omega$ rotation with narrow frames
3.70 to $31.57^{\circ}$
h -32 to $32, \mathrm{k}-18$ to $18,1-33$ to 32
98.6 \%

74210
$20842\left(\mathrm{R}_{\text {int }}=0.1310\right)$
12315
semi-empirical from equivalents
0.723 and 0.893
direct methods
Full-matrix least-squares on $\mathrm{F}^{2}$
0.0865, 18.9717

20842 / 14 / 1254
$\mathrm{R} 1=0.0780, \mathrm{wR} 2=0.1803$
$R 1=0.1367, w R 2=0.2085$
1.022
$0.00035(4)$
0.002 and 0.000
2.266 and -1.885 e $\AA^{-3}$
2.9: The asymmetric unit was found to contain two molecules of 2.9 and two solvating molecules of crystallisation (one $\mathrm{Et}_{2} \mathrm{O}$ and one $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). The methylene group, $\mathrm{C}(117)$, of the solvating $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was found to be disordered over two sets of positions [major occupancy $71(4) \%$ ]. The minor and major disorder components of the solvating $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were restrained to have similar anisotropic displacement parameters and geometry. The methylene group, $\mathrm{C}(11 \mathrm{X})$, of the minor disorder component was also restrained to be more isotropic.

Table 8.6 Crystal data and structure refinement for 2.10.

| Chemical formula | $\mathrm{C}_{68} \mathrm{H}_{65} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{1.50} \mathrm{P}_{2} \mathrm{Pt}$ |
| :--- | :--- |
| Formula weight | 1262.15 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P}_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=16.3600(6) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=23.2479(8) \AA \quad \beta=117.030(2)^{\circ}$ |
|  | $\mathrm{c}=17.7823(6) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $6024.5(4) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $2.516 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 2564 |
| Crystal colour and size | colourless, $0.36 \times 0.23 \times 0.17 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | $7607\left(\theta\right.$ range 2.24 to $\left.25.42^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.56 to $25.42^{\circ}$ |
| Index ranges | $\mathrm{h}-19$ to $19, \mathrm{k}-28$ to $28,1-21$ to 21 |
| Completeness to $\theta=25.42^{\circ}$ | $99.9 \%$ |
| Reflections collected | 49139 |
| Independent reflections | $11111\left(\mathrm{R}_{\text {int }}=0.0256\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 9716 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.465 and 0.674 |
| Structure solution | Patterson synthesis |
| Refinement method | Full-matrix least-squares on $F^{2}$ |
| Weighting parameters a, b | $0.0310,0.4271$ |
| Data $/$ restraints $/$ parameters | $11111 / 0 / 622$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0192$, wR2 $=0.0489$ |
| R indices (all data) | $\mathrm{R} 1=0.0235$, wR2 $=0.0502$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.039 |
| Largest and mean shift/su | 0.009 and 0.000 |
| Largest diff. peak and hole | 0.849 and -0.485 e $\AA \AA^{-3}$ |
|  |  |

2.10: The asymmetric unit was found to contain one molecule of $\mathbf{2 . 1 0}$ and one and a half molecules of $\mathrm{Et}_{2} \mathrm{O}$. Platon was used to model the highly disordered $\mathrm{Et}_{2} \mathrm{O}$ solvate molecules as a diffuse region of electron density within the unit cell ("squeeze" procedure). ${ }^{229}$

Table 8.7 Crystal data and structure refinement for 2.17.

| Chemical formula | $\mathrm{C}_{59} \mathrm{H}_{53} \mathrm{ClN}_{2} \mathrm{P}_{2} \mathrm{Pd}$ |
| :---: | :---: |
| Formula weight | 993.82 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoKa, 0.71073 Å |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=24.1237(9) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=11.1156(4) \AA \quad \beta=109.427(2)^{\circ}$ |
|  | $\mathrm{c}=18.7303(7) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 4736.6 (3) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.558 \mathrm{~mm}^{-1}$ |
| F(000) | 2056 |
| Crystal colour and size | colourless, $0.49 \times 0.10 \times 0.04 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 49443 ( $\theta$ range 2.40 to $24.48^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer <br> $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.79 to $28.34^{\circ}$ |
| Index ranges | $\mathrm{h}-32$ to $32, \mathrm{k}-14$ to $14,1-24$ to 24 |
| Completeness to $\theta=26.00^{\circ}$ | 99.9 \% |
| Reflections collected | 48077 |
| Independent reflections | $11786\left(\mathrm{R}_{\text {int }}=0.0631\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 8726 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.7716 and 0.9780 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0464, 1.1363 |
| Data / restraints / parameters | 11786 / 0 / 587 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0419, w R 2=0.0908$ |
| R indices (all data) | $\mathrm{R} 1=0.0664, \mathrm{wR} 2=0.1009$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.016 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.659 and $-0.601 \mathrm{e} \AA^{-3}$ |

2.17: The asymmetric unit was found to contain one molecule of 2.17.

Table 8.8. Crystal data and structure refinement for 2.22.

| Chemical formula | $\mathrm{C}_{64} \mathrm{H}_{54} \mathrm{Cl}_{4} \mathrm{MoN}_{2} \mathrm{O}_{4} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 1214.77 |
| Temperature | 120(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | orthorhombic, Pna $2_{1}$ |
| Unit cell parameters | $a=19.6207(3) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=14.2242(2) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=20.2724(4) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 5657.80(16) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.528 \mathrm{~mm}^{-1}$ |
| F(000) | 2496 |
| Crystal colour and size | Colourless, $0.26 \times 0.22 \times 0.10 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 43360 ( $\theta$ range 2.91 to $27.48^{\circ}$ ) |
| Data collection method | Bruker-Nonius 95 mm CCD camera on $\kappa$-goniostat |
|  | $\phi \& \omega$ scans |
| $\theta$ range for data collection | 3.21 to $27.56^{\circ}$ |
| Index ranges | $\mathrm{h}-25$ to $24, \mathrm{k}-18$ to $18,1-26$ to 26 |
| Completeness to $\theta=26.00^{\circ}$ | 99.6 \% |
| Reflections collected | 43355 |
| Independent reflections | $12805\left(\mathrm{R}_{\text {int }}=0.0340\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 12166 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.875 and 0.949 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0212, 2.6430 |
| Data / restraints / parameters | 12805 / $1 / 694$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0278, \mathrm{wR} 2=0.0619$ |
| R indices (all data) | $\mathrm{R} 1=0.0305, \mathrm{wR} 2=0.0633$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.014 |
| Absolute structure parameter | -0.008(16) |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.672 and -0.645 e $\AA^{-3}$ |

2.22: The asymmetric unit was found to contain one molecule of $\mathbf{2 . 2 2}$ and two solvating molecules of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.

Table 8.9 Crystal data and structure refinement for 3.1.

| Chemical formula | $\mathrm{C}_{50} \mathrm{H}_{50} \mathrm{Fe}_{2} \mathrm{~N}_{2} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 852.56 |
| Temperature | 150(2) K |
| Radiation, wavelength | synchrotron, $0.6710 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=7.6347(4) \AA \quad \alpha=95.6966(5)^{\circ}$ |
|  | $b=11.3939(5) \AA \quad \beta=103.7690(5)^{\circ}$ |
|  | $\mathrm{c}=12.7421(6) \AA \quad \gamma=102.5657(5)^{\circ}$ |
| Cell volume | 1037.36(9) $\AA^{3}$ |
| Z | 1 |
| Absorption coefficient $\mu$ | $0.814 \mathrm{~mm}^{-1}$ |
| F(000) | 446 |
| Crystal colour and size | orange, $0.19 \times 0.04 \times 0.03 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 6520 ( $\theta$ range 3.00 to $30.81^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.75 to $31.02^{\circ}$ |
| Index ranges | $\mathrm{h}-11$ to $11, \mathrm{k}-17$ to $17,1-18$ to 19 |
| Completeness to $\theta=25.00^{\circ}$ | 97.4 \% |
| Intensity decay | 3\% |
| Reflections collected | 13143 |
| Independent reflections | $6964\left(\mathrm{R}_{\text {int }}=0.0326\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 5999 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.861 and 0.976 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0483, 0.1963 |
| Data / restraints / parameters | 6964 / 0 / 253 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0360, \mathrm{wR} 2=0.0944$ |
| R indices (all data) | $\mathrm{R} 1=0.0429, \mathrm{wR} 2=0.0988$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.038 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.673 and -0.368 e $\AA^{-3}$ |

3.1: The asymmetric unit was found to contain half a unique molecule of 3.1, as the phosphine was found to lie on a crystallographic inversion centre located at the midpoint of the ethylenediamine backbone. The molecular structure was determined using synchrotron radiation, with data collected at Daresbury Laboratory Station 9.8, due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature.

Table 8.10 Crystal data and structure refinement for 3.3.

| Chemical formula | $\mathrm{C}_{46} \mathrm{H}_{62} \mathrm{Fe}_{2} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 912.62 |
| Temperature | 150(2) K |
| Radiation, wavelength | Synchrotron, 0.6710 A |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=12.8278(7) \AA \quad \alpha=81.7595(7)^{\circ}$ |
|  | $b=13.4835(8) \AA \quad \beta=65.1133(7)^{\circ}$ |
|  | $\mathrm{c}=14.4471(8) \AA \quad \gamma=79.1612(7)^{\circ}$ |
| Cell volume | 2220.6(2) $\AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $0.775 \mathrm{~mm}^{-1}$ |
| F(000) | 964 |
| Crystal colour and size | orange, $0.13 \times 0.09 \times 0.04 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 8295 ( $\theta$ range 2.47 to $30.18^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.47 to $30.83^{\circ}$ |
| Index ranges | $\mathrm{h}-18$ to $18, \mathrm{k}-19$ to $19,1-21$ to 21 |
| Completeness to $\theta=25.00^{\circ}$ | 99.1 \% |
| Intensity decay | 3\% |
| Reflections collected | 28081 |
| Independent reflections | $14806\left(\mathrm{R}_{\text {int }}=0.0252\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 10184 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.906 and 0.970 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0637, 1.0595 |
| Data / restraints / parameters | 14806 / 0 / 531 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0485, \mathrm{wR} 2=0.1211$ |
| R indices (all data) | $\mathrm{R} 1=0.0795, \mathrm{wR} 2=0.1388$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.037 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.858 and -0.645 e $\AA^{-3}$ |

3.3: The asymmetric unit was found to contain one unique molecule of 3.3. The molecular structure was determined using synchrotron radiation, with data collected at Daresbury Laboratory Station 9.8, due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature.

Table 8.11 Crystal data and structure refinement for 3.4.

| Chemical formula | $\mathrm{C}_{51} \mathrm{H}_{52} \mathrm{Cl}_{4} \mathrm{Fe}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 1203.48 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073$ Å |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{n}$ |
| Unit cell parameters | $\mathrm{a}=17.6469(17) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=12.6761(12) \AA \quad \beta=104.448(2)^{\circ}$ |
|  | $\mathrm{c}=21.866(2) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $4736.6(8) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $3.882 \mathrm{~mm}^{-1}$ |
| F(000) | 2400 |
| Crystal colour and size | yellow, $0.29 \times 0.18 \times 0.11 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 48941 ( $\theta$ range 1.18 to $12.95^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer <br> $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.71 to $28.34^{\circ}$ |
| Index ranges | $\mathrm{h}-23$ to $23, \mathrm{k}-16$ to $16,1-29$ to 29 |
| Completeness to $\theta=26.00^{\circ}$ | 99.9 \% |
| Reflections collected | 47747 |
| Independent reflections | $11782\left(\mathrm{R}_{\text {int }}=0.0867\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 8537 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.387 and 0.655 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0533, 4.5153 |
| Data / restraints / parameters | 11782 / 37 / 578 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0485, \mathrm{wR} 2=0.1056$ |
| R indices (all data) | $\mathrm{R} 1=0.0788, \mathrm{wR} 2=0.1187$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.025 |
| Largest and mean shift/su | 0.002 and 0.000 |
| Largest diff. peak and hole | 3.286 and -1.260 e $\AA^{-3}$ |

3.4: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 4}$ and a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule of crystallisation. The $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule was found to be disordered over two sets of positions, with $\mathrm{Cl}(3)$ common to both disorder components [major occupancy $59.2(9) \%$ ]. The minor and major disorder components were restrained to have similar anisotropic displacement parameters and geometry.

Table 8.12 Crystal data and structure refinement for 3.10.

| Chemical formula | $\mathrm{C}_{102} \mathrm{H}_{100} \mathrm{Cl}_{2} \mathrm{Fe}_{4} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{P}_{4} \mathrm{Rh}_{2}$ |
| :---: | :---: |
| Formula weight | 2037.86 |
| Temperature | 150(2) K |
| Radiation, wavelength | Synchrotron, $0.6884 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{n}$ |
| Unit cell parameters | $\mathrm{a}=13.0780(10) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=20.4797(16) \AA \quad \beta=105.1038(11)^{\circ}$ |
|  | $\mathrm{c}=17.3102(13) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 4476.1(6) $\AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $1.176 \mathrm{~mm}^{-1}$ |
| F(000) | 2088 |
| Crystal colour and size | Yellow, $0.07 \times 0.04 \times 0.02 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 4694 ( $\theta$ range 2.26 to $23.30^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.52 to $29.50^{\circ}$ |
| Index ranges | $\mathrm{h}-18$ to $18, \mathrm{k}-28$ to $29,1-24$ to 24 |
| Completeness to $\theta=29.00^{\circ}$ | 99.9 \% |
| Intensity decay | 8\% |
| Reflections collected | 51962 |
| Independent reflections | $13698\left(\mathrm{R}_{\text {int }}=0.0895\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 8236 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.922 and 0.977 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0480, 0.0000 |
| Data / restraints / parameters | 13698 / 0 / 541 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0488$, wR2 $=0.0975$ |
| R indices (all data) | $\mathrm{R} 1=0.1034, \mathrm{wR} 2=0.1169$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.957 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.079 and $-0.457 \mathrm{e} \AA^{-3}$ |

3.10 : The molecular structure was determined using synchrotron radiation, with data collected at Daresbury Laboratory Station 9.8, due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature. The dimer was found to lie on a crystallographic inversion centre located at the centroid of the 18membered ring. As a consequence, the asymmetric unit was found to contain half a unique molecule of $\mathbf{3 . 1 0}$.

Table 8.13 Crystal data and structure refinement for 3.11.

| Chemical formula | $\mathrm{C}_{54.50} \mathrm{H}_{50.50} \mathrm{Cl}_{1.50} \mathrm{Fe}_{2} \mathrm{MoN}_{2} \mathrm{O}_{4} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 1120.22 |
| Temperature | 120(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P} 21 / \mathrm{n}$ |
| Unit cell parameters | $\mathrm{a}=18.1242(3) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=12.7301(2) \AA \quad \beta=109.4910(8)^{\circ}$ |
|  | $\mathrm{c}=22.9350(3) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 4988.39(13) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $1.014 \mathrm{~mm}^{-1}$ |
| F(000) | 2292 |
| Crystal colour and size | Orange, $0.26 \times 0.09 \times 0.05 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 34662 ( $\theta$ range 2.91 to $27.48^{\circ}$ ) |
| Data collection method | Bruker-Nonius Roper CCD camera on $\kappa$-goniostat $\phi$ \& $\omega$ scans |
| $\theta$ range for data collection | 2.97 to $27.89^{\circ}$ |
| Index ranges | $\mathrm{h}-23$ to $23, \mathrm{k}-16$ to $16,1-29$ to 29 |
| Completeness to $\theta=27.00^{\circ}$ | 99.8 \% |
| Reflections collected | 53164 |
| Independent reflections | $11463\left(\mathrm{R}_{\text {int }}=0.0500\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 9498 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.779 and 0.951 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0572, 5.8741 |
| Data / restraints / parameters | 11463 / 0 / 587 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0433, \mathrm{wR} 2=0.1148$ |
| R indices (all data) | $\mathrm{R} 1=0.0555, \mathrm{wR} 2=0.1212$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.050 |
| Extinction coefficient | 0.0024(3) |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.508 and -0.558 e $\AA^{-3}$ |

3.11: The molecular structure of $\mathbf{3 . 1 1}$ was determined from reflection data files collected by the EPSRC National Crystallography Service. The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 1 1}$ and half a molecule of disordered $\mathrm{CHCl}_{3}$ of crystallisation. Platon was used to model the disordered $\mathrm{CHCl}_{3}$ molecule as a diffuse region of electron density (Platon "squeeze" procedure). ${ }^{229}$

Table 8.14 Crystal data and structure refinement for 3.12.

| Chemical formula | $\mathrm{C}_{72} \mathrm{H}_{82} \mathrm{Cl}_{8} \mathrm{Fe}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Ru}_{2}$ |
| :---: | :---: |
| Formula weight | 1634.78 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $a=10.4845(4) \AA \quad \alpha=96.720(2)^{\circ}$ |
|  | $\mathrm{b}=12.6125(5) \AA \quad \beta=105.962(2)^{\circ}$ |
|  | $\mathrm{c}=15.1788(7) \AA \quad \gamma=106.968(2)^{\circ}$ |
| Cell volume | 1802.81(13) $\AA^{3}$ |
| Z | 1 |
| Absorption coefficient $\mu$ | $1.188 \mathrm{~mm}^{-1}$ |
| F(000) | 834 |
| Crystal colour and size | orange, $0.40 \times 0.28 \times 0.11 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 9792 ( $\theta$ range 2.16 to $30.52^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.99 to $30.56^{\circ}$ |
| Index ranges | $\mathrm{h}-14$ to $14, \mathrm{k}-18$ to $18,1-21$ to 21 |
| Completeness to $\theta=27.50^{\circ}$ | 99.4 \% |
| Reflections collected | 21443 |
| Independent reflections | $10789\left(\mathrm{R}_{\text {int }}=0.0187\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 9248 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.648 and 0.880 |
| Structure solution | Patterson synthesis |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0381, 0.1006 |
| Data / restraints / parameters | 10789 / 0 / 373 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0280, \mathrm{wR} 2=0.0691$ |
| R indices (all data) | $\mathrm{R} 1=0.0338, \mathrm{wR} 2=0.0715$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.040 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.712 and $-0.469 \mathrm{e} \AA^{-3}$ |

3.12: The asymmetric unit was found to contain half a unique molecule of $\mathbf{3 . 1 2}$ and one molecule of badly disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallisation. Platon was used to model the disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule as a diffuse region of electron density (Platon "squeeze" procedure). ${ }^{229}$

Table 8.15 Crystal data and structure refinement for 3.13.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$ F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection
Index ranges
Completeness to $\theta=27.54^{\circ}$
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final $R$ indices $\left[F^{2}>2 \sigma\right.$ ]
R indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Extinction coefficient
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{51} \mathrm{H}_{52} \mathrm{Au}_{2} \mathrm{Cl}_{4} \mathrm{Fe}_{2} \mathrm{~N}_{2} \mathrm{P}_{2}$
1402.32
$120(2) \mathrm{K}$
$\mathrm{MoK} \alpha, 0.71073 \AA$
triclinic, $\mathrm{P} \overline{1}$
$\mathrm{a}=11.9161(2) \AA \quad \alpha=72.111(2)^{\circ}$
$\mathrm{b}=12.7979(2) \AA \quad \beta=81.279(2)^{\circ}$
$\mathrm{c}=17.2109(3) \AA \quad \gamma=80.243(2)^{\circ}$
$2447.75(7) \AA^{3}$
2
$6.877 \mathrm{~mm}^{-1}$
1360
Yellow, $0.18 \times 0.08 \times 0.04 \mathrm{~mm}^{3}$
$11130\left(\theta\right.$ range 2.91 to $\left.27.48^{\circ}\right)$
Bruker-Nonius 95 mm CCD camera on
K -goniostat $\phi \& \omega$ scans
3.00 to $27.54^{\circ}$
$\mathrm{h}-15$ to $15, \mathrm{k}-16$ to $16,1-22$ to 22
$99.3 \%$
52848
$11242\left(\mathrm{R}_{\text {int }}=0.0406\right)$
9950
semi-empirical from equivalents
0.367 and 0.763
Patterson synthesis
Full-matrix least-squares on $\mathrm{F}^{2}$
$0.0168,8.7042$
$11242 / 31 / 588$
$\mathrm{R} 1=0.0278$, wR2 $=0.0609$
$\mathrm{R} 1=0.0343$, wR2 $=0.0637$
1.042
$0.00056(6)$
0.002 and 0.000
1.597 and -2.065 e $\AA \AA^{-3}$
3.13: The molecular structure of $\mathbf{3 . 1 3}$ was determined from reflection data files collected by the EPSRC National Crystallography Service. The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 1 3}$ and a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule of crystallisation. The $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule was found to be disordered over two sets of positions, with $\mathrm{Cl}(3)$ common to both disorder components [major occupancy $70.907(5) \%]$. The minor and major disorder components were restrained to have similar anisotropic displacement parameters and geometry.

Table 8.16 Crystal data and structure refinement for 3.14.

| Chemical formula | $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{FeNP}$ |
| :---: | :---: |
| Formula weight | 441.31 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ £ |
| Crystal system, space group | triclinic, P1 |
| Unit cell parameters | $\mathrm{a}=8.0463(6) \AA \quad \alpha=104.4063(10)^{\circ}$ |
|  | $\mathrm{b}=8.3660(6) \AA \quad \beta=94.8944(9)^{\circ}$ |
|  | $\mathrm{c}=9.0178(7) \AA \quad \gamma=106.7138(9)^{\circ}$ |
| Cell volume | 555.00(7) $\AA^{3}$ |
| Z | 1 |
| Absorption coefficient $\mu$ | $0.763 \mathrm{~mm}^{-1}$ |
| F(000) | 232 |
| Crystal colour and size | orange, $0.53 \times 0.32 \times 0.20 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 5501 ( $\theta$ range 2.37 to $30.48^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer <br> $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 2.37 to $30.55^{\circ}$ |
| Index ranges | $\mathrm{h}-11$ to $11, \mathrm{k}-11$ to $11,1-12$ to 12 |
| Completeness to $\theta=26.00^{\circ}$ | 99.6 \% |
| Reflections collected | 6457 |
| Independent reflections | $5764\left(\mathrm{R}_{\text {int }}=0.0111\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 5722 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.688 and 0.862 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0409, 0.0338 |
| Data / restraints / parameters | 5764 / 3 / 264 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0231, \mathrm{wR} 2=0.0602$ |
| R indices (all data) | $\mathrm{R} 1=0.0233, \mathrm{wR} 2=0.0603$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.053 |
| Absolute structure parameter | 0.560(6) |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.482 and $-0.244 \mathrm{e} \AA^{-3}$ |

3.14: The asymmetric unit contained one unique molecule of 3.14. The molecular structure also showed the phosphine to have crystallised in the non-centrosymmetric space group P1 [major enantiomer 56.0(6)\%].

Table 8.17 Crystal data and structure refinement for 3.15.

| Chemical formula | $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{AuClFeNP}$ |
| :--- | :--- |
| Formula weight | 673.73 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | MoK $\alpha, 0.7107 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=10.6779(5) \AA \quad \alpha=73.8740(7)^{\circ}$ |
|  | $\mathrm{b}=10.9810(6) \AA \quad \beta=86.1150(7)^{\circ}$ |
|  | $\mathrm{c}=11.6654(6) \AA \quad \gamma=65.4743(7)^{\circ}$ |
| Cell volume | $1193.67(11) \AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $6.939 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 656 |
| Crystal colour and size | yellow, $0.25 \times 0.24 \times 0.08 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | $7585\left(\theta\right.$ range 2.61 to $\left.30.52^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.82 to $30.55^{\circ}$ |
| Index ranges | $\mathrm{h}-15$ to $14, \mathrm{k}-15$ to $15,1-16$ to 16 |
| Completeness to $\theta=28.00^{\circ}$ | $99.3 \%$ |
| Reflections collected | 13968 |
| Independent reflections | $7118\left(\mathrm{R}_{\text {int }}=0.0238\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 6637 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.194 and 0.316 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.0332,5.4921$ |
| Data / restraints $/$ parameters | $7118 / 0 / 281$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0341, \mathrm{wR} 2=0.0897$ |
| R indices (all data $)$ | $\mathrm{R} 1=0.0372, \mathrm{wR} 2=0.0909$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.102 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.735 and $-1.229 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

3.15: The asymmetric unit contained one unique molecule of the bimetallic complex.

Table 8.18 Crystal data and structure refinement for 3.19.

| Chemical formula | $\mathrm{C}_{84} \mathrm{H}_{94} \mathrm{Cl}_{12} \mathrm{Fe}_{3} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Ru}_{2}$ |
| :--- | :--- |
| Formula weight | 1988.64 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | MoKa, $0.7107 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=11.6191(7) \AA \quad \alpha=101.5303(11)^{\circ}$ |
|  | $\mathrm{b}=19.8758(12) \AA \quad \mathrm{A}=104.1117(11)^{\circ}$ |
| Cell volume | $\mathrm{c}=20.5317(13) \AA \quad \gamma=105.8676(11)^{\circ}$ |
| Z | $4238.8(5) \AA^{3}$ |
| Absorption coefficient $\mu$ | 2 |
| $\mathrm{~F}(000)$ | $1.310 \mathrm{~mm}^{-1}$ |
| Crystal colour and size | 2024 |
| Reflections for cell refinement | orange, $0.25 \times 0.21 \times 0.07 \mathrm{~mm}^{3}$ |
| Data collection method | $4390\left(\theta\right.$ range 2.22 to $\left.22.62^{\circ}\right)$ |
|  | Bruker APEX 2 CCD diffractometer |
| $\theta$ range for data collection | $\omega$ rotation with narrow frames |
| Index ranges | 1.11 to $26.00^{\circ}$ |
| Completeness to $\theta=26.00^{\circ}$ | $\mathrm{h}-14$ to $14, \mathrm{k}-24$ to $24,1-25$ to 25 |
| Reflections collected | $99.8 \%$ |
| Independent reflections | 37260 |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | $16638\left(\mathrm{R}_{\text {int }}=0.0518\right)$ |
| Absorption correction | 10858 |
| Min. and max. transmission | semi-empirical from equivalents |
| Structure solution | 0.735 and 0.914 |
| Refinement method | direct methods |
| Weighting parameters a, b | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints $/$ parameters | $0.1100,0.0000$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $16638 / 206 / 971$ |
| R indices (all data | $\mathrm{R} 1=0.0671$, wR2 $=0.1875$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | $\mathrm{R} 1=0.0975$, wR2 $=0.2080$ |
| Largest and mean shift/su | 1.088 |
| Largest diff. peak and hole | 0.001 and 0.000 |
|  | 2.000 and -1.648 e $\AA \AA^{-3}$ |
|  |  |

3.19: The asymmetric unit was found to contain a unique molecule of $\mathbf{3 . 1 9}$ and five molecules of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallisation, two of which were badly disordered. Platon was used to model the disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules as diffuse regions of electron density (Platon "squeeze" procedure). ${ }^{229}$ The cyclopentadienyl ring containing $\mathrm{C}(43)$ to $\mathrm{C}(47)$ was found to be disordered over two sets of positions, [major occupancy $54.29(2) \%$ ], for which the geometry and anisotropic displacement parameters of both disorder components were restrained to be similar.

Table 8.19 Crystal data and structure refinement for 3.26.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$ F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection
Index ranges
Completeness to $\theta=25.00^{\circ}$
Intensity decay
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final $R$ indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ]
$R$ indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{73} \mathrm{H}_{71} \mathrm{Cl}_{11} \mathrm{Fe}_{4} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{Pt}$
1846.70

150(2) K
synchrotron, $0.6942 \AA$
triclinic, $\mathrm{P} \overline{1}$
$\mathrm{a}=12.6556(4) \AA \quad \alpha=76.6416(3)^{\circ}$
$b=17.9459(5) \AA \quad \beta=79.9146(3)^{\circ}$
$\mathrm{c}=18.5019(5) \AA \quad \gamma=71.5298(3)^{\circ}$
3854.07(19) $\AA^{3}$

2
$3.008 \mathrm{~mm}^{-1}$
1844
yellow, $0.10 \times 0.05 \times 0.02 \mathrm{~mm}^{3}$
44738 ( $\theta$ range 2.31 to $27.64^{\circ}$ )
Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames
1.47 to $29.72^{\circ}$
h -18 to $18, \mathrm{k}-25$ to $25,1-26$ to 26
99.5 \%

3\%
44729
$22963\left(\mathrm{R}_{\text {int }}=0.0388\right)$
18880
semi-empirical from equivalents
0.753 and 0.942
direct methods
Full-matrix least-squares on $\mathrm{F}^{2}$
$0.0645,0.0000$
22963/0/766
$\mathrm{R} 1=0.0466, \mathrm{wR} 2=0.1242$
$\mathrm{R} 1=0.0570, \mathrm{wR} 2=0.1312$
1.092
0.002 and 0.000
3.005 and -1.174 e $\AA^{-3}$
3.26: The molecular structure was determined using synchrotron radiation, with data collected at Daresbury Laboratory Station 9.8, due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ). The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 2 6}$ and three molecules of $\mathrm{CHCl}_{3}$ of crystallisation, two of which were badly disordered. Platon was used to model the disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules as diffuse regions of electron density (Platon "squeeze" procedure). ${ }^{229}$

Table 8.20 Crystal data and structure refinement for 3.28.

| Chemical formula | $\mathrm{C}_{37} \mathrm{H}_{59} \mathrm{FeNP}_{2}$ |
| :--- | :--- |
| Formula weight | 635.64 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.7107 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=10.0903(8) \AA \quad \alpha=79.4391(13)^{\circ}$ |
|  | $\mathrm{b}=10.9029(9) \AA \quad \beta=89.9822(13)^{\circ}$ |
|  | $\mathrm{c}=16.7823(14) \AA \quad \gamma=75.1802(12)^{\circ}$ |
| Cell volume | $1752.5(2) \AA^{3}$ |
| Z | 2 |
| Calculated density | $1.205 \mathrm{~g} / \mathrm{cm}^{3}$ |
| Absorption coefficient $\mu$ | $0.547 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 688 |
| Crystal colour and size | orange, $0.16 \times 0.16 \times 0.10 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | $5213\left(\theta\right.$ range 2.38 to $\left.28.01^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.97 to $30.57^{\circ}$ |
| Index ranges | $\mathrm{h}-14$ to $14, \mathrm{k}-15$ to $15,1-23$ to 23 |
| Completeness to $\theta=28.00^{\circ}$ | $99.4 \%$ |
| Reflections collected | 20803 |
| Independent reflections | $10466\left(\mathrm{R}_{\text {int }}=0.0275\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 7799 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.918 and 0.947 |
| Structure solution | direct methods |
| Refinement method | $\mathrm{Full-matrix} \mathrm{least-squares} \mathrm{on} \mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.0684,0.1837$ |
| Data / restraints $/$ parameters | $10466 / 0 / 370$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0471, \mathrm{wR} 2=0.1197$ |
| R indices (all data | $\mathrm{R} 1=0.0679, \mathrm{wR} 2=0.1313$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.045 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.180 and $-0.274 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

3.28: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 2 8}$.

Table 8.21 Crystal data and structure refinement for 3.29.

| Chemical formula | $\mathrm{C}_{33} \mathrm{H}_{47} \mathrm{FeNO}_{6} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 671.51 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $a=7.4827(7) \AA \quad \alpha=106.684(2)^{\circ}$ |
|  | $\mathrm{b}=12.6557(12) \AA \quad \beta=91.252(2)^{\circ}$ |
|  | $\mathrm{c}=17.9902(17) \AA \quad \gamma=96.106(2)^{\circ}$ |
| Cell volume | $1620.2(3) \AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $0.609 \mathrm{~mm}^{-1}$ |
| F(000) | 712 |
| Crystal colour and size | colourless, $0.22 \times 0.12 \times 0.05 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 2166 ( $\theta$ range 2.33 to $23.26^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.69 to $26.43^{\circ}$ |
| Index ranges | $\mathrm{h}-9$ to $9, \mathrm{k}-15$ to $15,1-22$ to 22 |
| Completeness to $\theta=26.00^{\circ}$ | 99.8 \% |
| Reflections collected | 14755 |
| Independent reflections | $6658\left(\mathrm{R}_{\mathrm{int}}=0.0462\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 4697 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.878 and 0.970 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0414, 0.3315 |
| Data / restraints / parameters | 6658 / 0 / 396 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0461, \mathrm{wR} 2=0.0939$ |
| R indices (all data) | $\mathrm{R} 1=0.0755, \mathrm{wR} 2=0.1063$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.017 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.414 and -0.310 e $\AA^{-3}$ |

3.29: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 2 9}$.

Table 8.22 Crystal data and structure refinement for 3.30.

| Chemical formula | $\mathrm{C}_{38} \mathrm{H}_{35} \mathrm{Cl}_{5} \mathrm{DFeNP}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 997.81 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ Å |
| Crystal system, space group | orthorhombic, Pnma |
| Unit cell parameters | $\mathrm{a}=17.8032(7) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=17.0967(7) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=12.2692(5) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 3734.4(3) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $4.604 \mathrm{~mm}^{-1}$ |
| F(000) | 1960 |
| Crystal colour and size | yellow, $0.21 \times 0.17 \times 0.11 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 6858 ( $\theta$ range 2.29 to $28.09^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 2.02 to $30.58^{\circ}$ |
| Index ranges | $\mathrm{h}-25$ to $22, \mathrm{k}-24$ to $24,1-17$ to 17 |
| Completeness to $\theta=27.00^{\circ}$ | 100.0 \% |
| Reflections collected | 33826 |
| Independent reflections | $5885\left(\mathrm{R}_{\mathrm{int}}=0.0516\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 4808 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.445 and 0.631 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0320, 0.8163 |
| Data / restraints / parameters | 5885 / 11/238 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0288, \mathrm{wR} 2=0.0617$ |
| R indices (all data) | $\mathrm{R} 1=0.0415, \mathrm{wR} 2=0.0669$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.032 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.291 and $-0.935 \mathrm{e}^{\text {A }}{ }^{-3}$ |

3.30: The molecular structure of $\mathbf{3 . 3 0}$ showed the complex to lie on a crystallographic mirror plane which bisects the $\mathrm{FcCH}_{2} \mathrm{~N}$ moiety and the platinum(II) centre. As a result the asymmetric unit was found to contain half a unique molecule of complex and half a molecule of $\mathrm{CDCl}_{3}$ of crystallisation. The geometry and anisotropic displacement parameters of the $\mathrm{CDCl}_{3}$ molecule were restrained.

Table 8.23 Crystal data and structure refinement for 3.31.

| Chemical formula | $\mathrm{C}_{38} \mathrm{H}_{61} \mathrm{Cl}_{4} \mathrm{FeNP}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 986.56 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=12.3528(3) \AA \quad \alpha=90^{\circ}$ |
|  | $b=20.5818(5) \AA \quad \beta=99.7668(3)^{\circ}$ |
|  | $\mathrm{c}=15.8585(4) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 3973.47(17) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $4.260 \mathrm{~mm}^{-1}$ |
| F(000) | 1992 |
| Crystal colour and size | yellow, $0.44 \times 0.28 \times 0.21 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 48474 ( $\theta$ range 2.18 to $31.79^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.64 to $31.92^{\circ}$ |
| Index ranges | $\mathrm{h}-17$ to $17, \mathrm{k}-29$ to $29,1-22$ to 22 |
| Completeness to $\theta=27.00^{\circ}$ | 100.0 \% |
| Reflections collected | 47764 |
| Independent reflections | $12692\left(\mathrm{R}_{\text {int }}=0.0266\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 11583 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.256 and 0.468 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0296, 3.2887 |
| Data / restraints / parameters | 12692 / 0 / 424 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0231, \mathrm{wR} 2=0.0562$ |
| R indices (all data) | $\mathrm{R} 1=0.0267, w R 2=0.0576$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.025 |
| Largest and mean shift/su | 0.004 and 0.000 |
| Largest diff. peak and hole | 2.546 and -1.185 e $\AA^{-3}$ |

3.31: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 3 1}$ and one $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallisation.

Table 8.24 Crystal data and structure refinement for 3.32.

| Chemical formula | $\mathrm{C}_{34.50} \mathrm{H}_{48.50} \mathrm{Cl}_{6.50} \mathrm{FeNO}_{6} \mathrm{P}_{2} \mathrm{Pt}$ |
| :--- | :--- |
| Formula weight | 1116.55 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P}_{1} / \mathrm{c} \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=20.7242(10) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=15.1367(7) \AA \quad \beta=109.7375(7)^{\circ}$ |
|  | $\mathrm{c}=14.4952(7) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $4279.9(4) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $4.127 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 2220 |
| Crystal colour and size | orange, $0.40 \times 0.26 \times 0.17 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | $9908\left(\theta\right.$ range 2.48 to $\left.30.64^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.04 to $31.32^{\circ}$ |
| Index ranges | $\mathrm{h}-30$ to $30, \mathrm{k}-22$ to $21,1-21$ to 21 |
| Completeness to $\theta=29.00^{\circ}$ | $99.9 \%$ |
| Reflections collected | 50484 |
| Independent reflections | $13553\left(\mathrm{R}_{\text {int }}=0.0346\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 10015 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.289 and 0.541 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.0480,0.3116$ |
| Data / restraints / parameters | $13553 / 0 / 459$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0367$, wR2 $=0.0923$ |
| R indices (all data | $\mathrm{R} 1=0.0554$, wR2 $=0.0974$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.120 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 1.887 and $-1.428 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

3.32: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 3 2}$ and one and half molecules of $\mathrm{CHCl}_{3}$ of crystallisation. Platon was used to model the half a molecule of $\mathrm{CHCl}_{3}$ as a diffuse region of electron density (Platon "squeeze" procedure). ${ }^{229}$

Table 8.25 Crystal data and structure refinement for 3.36.

| Chemical formula | $\mathrm{C}_{41} \mathrm{H}_{35} \mathrm{CrFeNO}_{4} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 775.49 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073$ Å |
| Crystal system, space group | monoclinic, $\mathrm{P} 21 / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=19.4883(14) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=17.9200(13) \AA \quad \beta=102.7413(16)^{\circ}$ |
|  | $\mathrm{c}=21.0204(16) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $7160.2(9) \AA^{3}$ |
| Z | 8 |
| Absorption coefficient $\mu$ | $0.842 \mathrm{~mm}^{-1}$ |
| F(000) | 3200 |
| Crystal colour and size | orange, $0.42 \times 0.23 \times 0.07 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 13143 ( $\theta$ range 2.27 to $26.70^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.07 to $28.36^{\circ}$ |
| Index ranges | $\mathrm{h}-26$ to $25, \mathrm{k} 0$ to 23, 10 to 28 |
| Completeness to $\theta=27.00^{\circ}$ | 99.9 \% |
| Reflections collected | 104580 |
| Independent reflections | $17901\left(\mathrm{R}_{\text {int }}=0.0553\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 14364 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.719 and 0.943 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0412, 3.0823 |
| Data / restraints / parameters | 18003 / 0 / 902 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0404, \mathrm{wR} 2=0.0869$ |
| R indices (all data) | $\mathrm{R} 1=0.0594, \mathrm{wR} 2=0.0961$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.014 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.556 and -0.345 e $\AA^{-3}$ |

3.36: The crystal structure of $\mathbf{3 . 3 6}$ was determined using multiple diffraction data files (SHELXL-97 hklf5 format), after the crystal lattice was found to be pseudomerohedrally twinned [major component $57.33(6) \%$, twin law; $179.9^{\circ}$ rotation about the real axis 101$]$. The asymmetric unit was found to contain two unique molecules of $\mathbf{3 . 3 6}$.

Table 8.26 Crystal data and structure refinement for $\mathbf{3 . 3 8}$.

| Chemical formula | $\mathrm{C}_{37.50} \mathrm{H}_{48} \mathrm{ClCrFeNO}_{10} \mathrm{P}_{2}$ |
| :---: | :---: |
| Formula weight | 878.033 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ Å |
| Crystal system, space group | orthorhombic, Pbca |
| Unit cell parameters | $\mathrm{a}=20.3076(10) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=16.2377(8) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=24.6999(12) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 8144.8(7) $\AA^{3}$ |
| Z | 8 |
| Absorption coefficient $\mu$ | $0.822 \mathrm{~mm}^{-1}$ |
| F(000) | 3656 |
| Crystal colour and size | orange, $1.13 \times 0.21 \times 0.21 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 84255 ( $\theta$ range 2.30 to $28.32^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.65 to $28.32^{\circ}$ |
| Index ranges | $\mathrm{h}-27$ to 27, $\mathrm{k}-21$ to 21, 1-32 to 31 |
| Completeness to $\theta=28.00^{\circ}$ | 100.0 \% |
| Reflections collected | 80379 |
| Independent reflections | $10146\left(\mathrm{R}_{\text {int }}=0.0335\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 8522 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.457 and 0.846 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0595, 2.0664 |
| Data / restraints / parameters | 10146 / 416 / 565 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0368, \mathrm{wR} 2=0.1001$ |
| R indices (all data) | $\mathrm{R} 1=0.0444, \mathrm{wR} 2=0.1039$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.061 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.654 and -0.530 e $\AA^{-3}$ |

3.38: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 3 8}$ and half a molecule of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallisation. Platon was used to model the solvating $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ as a diffuse region of electron density (Platon "squeeze" procedure). ${ }^{229}$ The cyclopentadienyl rings of the ferrocenyl group were found to be two-fold disordered over two sets of positions, with $\mathrm{C}(4)$ being common between both disorder components [occupancy refined to $60.4(6) \%$ for the major component]. The geometry and anisotropic displacement parameters of the major and minor disorder components were restrained to be similar.

Table 8.27 Crystal data and structure refinement for 3.40.

| Chemical formula | $\mathrm{C}_{16} \mathrm{H}_{21} \mathrm{FeNO}_{2}$ |
| :---: | :---: |
| Formula weight | 315.19 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ Å |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=17.6334(14) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=9.3924(7) \AA \quad \beta=96.7281(12)^{\circ}$ |
|  | $\mathrm{c}=9.3443(7) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 1536.9(2) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.982 \mathrm{~mm}^{-1}$ |
| F(000) | 664 |
| Crystal colour and size | orange, $0.36 \times 0.14 \times 0.08 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 3987 ( $\theta$ range 2.33 to $26.13^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 2.33 to $30.55^{\circ}$ |
| Index ranges | h -25 to $25, \mathrm{k}-13$ to $13,1-13$ to 13 |
| Completeness to $\theta=29.00^{\circ}$ | 99.9 \% |
| Reflections collected | 17353 |
| Independent reflections | $4662\left(\mathrm{R}_{\text {int }}=0.0359\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 3414 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.719 and 0.926 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0405, 0.1568 |
| Data / restraints / parameters | 4662 / 0 / 187 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0342, \mathrm{wR} 2=0.0777$ |
| R indices (all data) | $\mathrm{R} 1=0.0556, \mathrm{wR} 2=0.0860$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.025 |
| Largest and mean shift/su | 0.000 and 0.000 |
| Largest diff. peak and hole | 0.399 and $-0.404 \mathrm{e} \AA^{-3}$ |

3.40: The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 4 0}$.

Table 8.28 Crystal data and structure refinement for 3.42.

| Chemical formula | $\mathrm{C}_{35} \mathrm{H}_{31} \mathrm{FeNP}_{2}$ |
| :---: | :---: |
| Formula weight | 583.40 |
| Temperature | 120(2) K |
| Radiation, wavelength | Synchrotron, 0.6943 A |
| Crystal system, space group | orthorhombic, $\mathrm{Pca}_{2}$ |
| Unit cell parameters | $\mathrm{a}=17.022(6) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=13.583(5) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=12.377(4) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 2861.7(17) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.664 \mathrm{~mm}^{-1}$ |
| F(000) | 1216 |
| Crystal colour and size | yellow, $0.20 \times 0.05 \times 0.04 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 3455 ( $\theta$ range 2.34 to $25.44^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.46 to $27.65^{\circ}$ |
| Index ranges | h - 22 to $16, \mathrm{k}-18$ to $18,1-16$ to 16 |
| Completeness to $\theta=27.00^{\circ}$ | 99.8 \% |
| Intensity decay | 5.3\% |
| Reflections collected | 18835 |
| Independent reflections | 6973 ( $\left.\mathrm{R}_{\text {int }}=0.0710\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 4899 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.879 and 0.974 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0757, 0.0000 |
| Data / restraints / parameters | 6973 / 1 / 353 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0570, \mathrm{wR} 2=0.1299$ |
| R indices (all data) | $\mathrm{R} 1=0.0926, \mathrm{wR} 2=0.1458$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.005 |
| Absolute structure parameter | 0.03(2) |
| Extinction coefficient | $0.0117(14)$ |
| Largest and mean shift/su | 0.000 and 0.000 |
| Largest diff. peak and hole | 1.001 and $-0.581 \mathrm{e} \AA^{-3}$ |

3.42: The molecular structure was determined using synchrotron radiation, with data collected at Daresbury Laboratory Station 9.8, due to the size of the crystals (at least one dimension $<0.05 \mathrm{~mm}$ ) and their poorly diffracting nature. The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 4 2}$.

Table 8.29 Crystal data and structure refinement for 3.43.

| Chemical formula | $\mathrm{C}_{35} \mathrm{H}_{31} \mathrm{Cl}_{2} \mathrm{FeNP}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 849.39 |
| Temperature | 150(2) K |
| Radiation, wavelength | $\mathrm{MoK} \alpha, 0.71073$ £ |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{n}$ |
| Unit cell parameters | $\mathrm{a}=8.7986(6) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=20.4581(15) \AA \quad \beta=92.4870(11)^{\circ}$ |
|  | $\mathrm{c}=17.6152(13) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 3167.8(4) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $5.165 \mathrm{~mm}^{-1}$ |
| F(000) | 1664 |
| Crystal colour and size | orange, $0.46 \times 0.32 \times 0.05 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 9995 ( $\theta$ range 2.30 to $31.85^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.53 to $29.00^{\circ}$ |
| Index ranges | $\mathrm{h}-12$ to $11, \mathrm{k} 0$ to 27,10 to 24 |
| Completeness to $\theta=29.00^{\circ}$ | 99.8 \% |
| Reflections collected | 21635 |
| Independent reflections | 17856 ( $\mathrm{R}_{\text {int }}=0.0518$ ) |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.200 and 0.782 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0474, 10.6713 |
| Data / restraints / parameters | 17856 / 0 / 380 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0417, \mathrm{wR} 2=0.1025$ |
| R indices (all data) | $\mathrm{R} 1=0.0528, \mathrm{wR} 2=0.1093$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.058 |
| Largest and mean shift/su | 0.003 and 0.000 |
| Largest diff. peak and hole | 1.643 and $-1.496 \mathrm{e}^{\text {- }}{ }^{-3}$ |

3.43: The molecular structure of $\mathbf{3 . 4 3}$ was determined using multiple diffraction data files (SHELXL-97 hklf5 format) collected by the EPSRC National Crystallography Service, after the crystal lattice was found to be merohedrally twinned [major component $86.05(3) \%$, twin law; $180^{\circ}$ about the reciprocal axis $10.001-0.83$ ]. The asymmetric unit was found to contain one unique molecule of $\mathbf{3 . 4 3}$.

Table 8.30 Crystal data and structure refinement for 4.2a.

| Chemical formula | $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{NO}_{2} \mathrm{P}$ |
| :---: | :---: |
| Formula weight | 373.37 |
| Temperature | 150(2) K |
| Radiation, wavelength | synchrotron, 0.6710 A |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=17.555(4) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=8.207(2) \AA \quad \beta=97.774(3)^{\circ}$ |
|  | $\mathrm{c}=13.106(3) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 1870.9(8) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.165 \mathrm{~mm}^{-1}$ |
| F(000) | 784 |
| Crystal colour and size | colourless, $0.16 \times 0.06 \times 0.03 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 1140 ( $\theta$ range 2.91 to $21.29^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 2.21 to $24.99^{\circ}$ |
| Index ranges | $\mathrm{h}-22$ to $22, \mathrm{k}-10$ to $10,1-15$ to 16 |
| Completeness to $\theta=24.99^{\circ}$ | 97.1 \% |
| Reflections collected | 10293 |
| Independent reflections | 3813 ( $\left.\mathrm{R}_{\text {int }}=0.0827\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 2175 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.9741 and 0.9951 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0692, 0.0000 |
| Data / restraints / parameters | 3813 / 0 / 249 |
| Final $R$ indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0541, \mathrm{wR} 2=0.1195$ |
| R indices (all data) | $\mathrm{R} 1=0.1140, \mathrm{wR} 2=0.1477$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.987 |
| Extinction coefficient | 0.033(3) |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 0.262 and -0.320 e $\AA^{-3}$ |

4.2a: The asymmetric unit was found to contain one unique molecule of 4.2a. All hydrogen atoms except $\mathrm{H}(1)$ were modelled using a riding model.

Table 8.31 Crystal data and structure refinement for 4.3.

| Chemical formula | $\mathrm{C}_{43} \mathrm{H}_{37} \mathrm{Cl}_{8} \mathrm{NP}_{2} \mathrm{Pt}$ |
| :--- | :--- |
| Formula weight | 1108.37 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | Synchrotron, $0.6939 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P} 2_{1} / \mathrm{n} \quad$ |
| Unit cell parameters | $\mathrm{a}=9.222(3) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=13.443(5) \AA \quad \beta=90.889(9)^{\circ}$ |
|  | $\mathrm{c}=35.150(13) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $4357(3) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $3.817 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 2184 |
| Crystal colour and size | colourless, $0.13 \times 0.06 \times 0.03 \mathrm{~mm}{ }^{3}$ |
| Reflections for cell refinement | $1362\left(\theta\right.$ range 2.68 to $\left.24.08^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.58 to $27.72^{\circ}$ |
| Index ranges | $\mathrm{h}-12$ to $12, \mathrm{k} 0$ to 17,10 to 46 |
| Completeness to $\theta=23.00^{\circ}$ | $95.7 \%$ |
| Reflections collected | 29989 |
| Independent reflections | $12033\left(\mathrm{R}_{\text {int }}=0.0856\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 9318 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.637 and 0.894 |
| Structure solution | Patterson synthesis |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.0000,222.9707$ |
| Data $/$ restraints $/$ parameters | $12033 / 107 / 497$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.1080, \mathrm{wR} 2=0.2376$ |
| R indices (all data $)$ | $\mathrm{R} 1=0.1382, \mathrm{wR} 2=0.2527$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.153 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 3.325 and $-5.361 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

4.3: The molecular structure of $\mathbf{4 . 3}$ was determined using multiple diffraction data files (SHELXL - 97 .hklf5 format), after the crystal lattice was found to be nonmerohedrally twinned [major component $76.19(18) \%$ ]. The atom $\mathrm{C}(1)$ was initially found to be non-positive-definite and was restrained to be more isotropic, in addition to being restrained to have a similar anisotropic displacement parameters to neighbouring atoms within the phenyl ring $\mathrm{C}(1)-\mathrm{C}(6)$. The atoms within the solvating chloroform molecules and the atoms $\mathrm{N}(1), \mathrm{C}(13), \mathrm{C}(14)$ and $\mathrm{C}(29)$ were also restrained to have similar anisotropic displacement parameters.

Table 8.32 Crystal data and structure refinement for 4.14a.

| Chemical formula | $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{O}_{5}$ |
| :---: | :---: |
| Formula weight | 362.39 |
| Temperature | 120(2) K |
| Radiation, wavelength | MoK $\alpha, 0.71073 \AA$ |
| Crystal system, space group | triclinic, $\mathrm{P} \overline{1}$ |
| Unit cell parameters | $\mathrm{a}=4.8441(6) \AA \quad \alpha=84.727(7)^{\circ}$ |
|  | $\mathrm{b}=10.4738(10) \AA \beta=87.267(5)^{\circ}$ |
|  | $\mathrm{c}=17.6121(18) \AA \quad \gamma=83.198(7)^{\circ}$ |
| Cell volume | 882.91(16) $\AA^{3}$ |
| Z | 2 |
| Absorption coefficient $\mu$ | $0.102 \mathrm{~mm}^{-1}$ |
| F(000) | 384 |
| Crystal colour and size | colourless, $0.26 \times 0.06 \times 0.03 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 3073 ( $\theta$ range 2.91 to $27.48^{\circ}$ ) |
| Data collection method | Bruker-Nonius 95 mm CCD camera on $\kappa$-goniostat, $\phi \& \omega$ scans |
| $\theta$ range for data collection | 2.91 to $25.00^{\circ}$ |
| Index ranges | $\mathrm{h}-5$ to $5, \mathrm{k}-12$ to $12,1-20$ to 20 |
| Completeness to $\theta=25.00^{\circ}$ | 97.1 \% |
| Reflections collected | 12773 |
| Independent reflections | 3026 ( $\left.\mathrm{R}_{\text {int }}=0.0693\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 2339 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.974 and 0.997 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0561, 2.6375 |
| Data / restraints / parameters | 3026 / 152 / 296 |
| Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ] | $\mathrm{R} 1=0.0862, \mathrm{wR} 2=0.1924$ |
| R indices (all data) | $\mathrm{R} 1=0.1127, \mathrm{wR} 2=0.2089$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.067 |
| Largest and mean shift/su | 0.000 and 0.000 |
| Largest diff. peak and hole | 0.428 and -0.345 e $\AA^{-3}$ |

4.14a: The asymmetric unit contained an ammonium cation of 4.14, a carbamic derivative of 4.14 and a solvating water molecule. The phenyl ring $\mathrm{C}(12)-\mathrm{C}(17)$ was two-fold disordered over two sets of equivalent positions, with $\mathrm{C}(12)$ and $\mathrm{C}(15)$ common between the two disorder components (occupancy refined to $51.0(6) \%$ for the major component). The anisotropic displacement parameters and geometry of the phenyl ring $\mathrm{C}(12)-\mathrm{C}(17)$ and its disorder component were restrained to be similar.

Table 8.33 Crystal data and structure refinement for 4.15a.

| Chemical formula | $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{2}$ |
| :--- | :--- |
| Formula weight | 247.31 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | $\mathrm{MoKa}, 0.8457 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P}_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=19.233(4) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=6.4959(13) \AA \quad \beta=92.110(3)^{\circ}$ |
|  | $\mathrm{c}=9.5553(18) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $1193.0(4) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $0.093 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 532 |
| Crystal colour and size | colourless, $0.16 \times 0.12 \times 0.01 \mathrm{~mm}{ }^{3}$ |
| Reflections for cell refinement | $1556\left(\theta\right.$ range 3.94 to $\left.30.66^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 3.94 to $27.49^{\circ}$ |
| Index ranges | $\mathrm{h}-20$ to $20, \mathrm{k}-7$ to $7,1-10$ to 10 |
| Completeness to $\theta=27.49^{\circ}$ | $99.6 \%$ |
| Reflections collected | 6010 |
| Independent reflections | $1617\left(\mathrm{R}_{\text {int }}=0.0527\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 1309 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.985 and 0.999 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.1306,1.3449$ |
| Data / restraints $/$ parameters | $1617 / 356 / 264$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0681, \mathrm{wR} 2=0.1903$ |
| R indices (all data) | $\mathrm{R} 1=0.0805, \mathrm{wR} 2=0.2023$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.051 |
| Largest and mean shift/su | 0.000 and 0.000 |
| Largest diff. peak and hole | 0.725 and $-0.281 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

4.15a: The asymmetric unit contains one unique molecule of an ammonium cation of 4.15 and an $[\mathrm{EtO}]^{-}$counterion. The ethanoate anion and the naphthyl group, including nitrogen atom $\mathrm{N}(2)$, were both found to be two-fold disordered over two sets of equivalent positions (occupancies refined to $55.7(12) \%$ and $93.2(3) \%$ respectively for the major components). The anisotropic displacement parameters and geometry of the major and minor disorder components were restrained to be similar. The naphylene moietie's disorder components were also restrained to be more planar.

Table 8.34 Crystal data and structure refinement for 4.30.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$ F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection
Index ranges
Completeness to $\theta=25.00^{\circ}$
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ]
$R$ indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{36.33} \mathrm{H}_{38.33} \mathrm{Cl}_{3} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{P}_{2} \mathrm{PtS}$
930.46

150(2) K
MoKa, $0.71073 \AA$
monoclinic, $\mathrm{P}_{2} / \mathrm{n}$
$a=10.3997(5) \AA \quad \alpha=90^{\circ}$
$\mathrm{b}=46.949(2) \AA \quad \beta=93.394(2)^{\circ}$
$\mathrm{c}=22.9518(11) \AA \gamma=90^{\circ}$
$11186.7(9) \AA^{3}$
12
$4.155 \mathrm{~mm}^{-1}$
5536
colourless, $0.16 \times 0.12 \times 0.01 \mathrm{~mm}^{3}$
81371 ( $\theta$ range 1.73 to $25.00^{\circ}$ )
Bruker SMART 1000 CCD
diffractometer
$\omega$ rotation with narrow frames
1.73 to $25.00^{\circ}$
$\mathrm{h}-12$ to $12, \mathrm{k}-55$ to $55,1-27$ to 27
100.0 \%

81371
$19718\left(\mathrm{R}_{\text {int }}=0.1078\right)$
12922
semi-empirical from equivalents
0.556 and 0.960
direct methods
Full-matrix least-squares on $\mathrm{F}^{2}$
$0.0000,305.3245$
19718/383/1288
$\mathrm{R} 1=0.0765, \mathrm{wR} 2=0.1446$
$R 1=0.1274, w R 2=0.1657$
1.113
0.702 and 0.004
2.265 and -2.376 e $\AA^{-3}$
4.30: The asymmetric unit was found to contain three unique molecules of $\mathbf{4 . 3 0}$ and four solvent molecules [one $\mathrm{CHCl}_{3}$ and three $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SO}$ ]. The solvating $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{SO}$ molecule containing $\mathrm{O}(5)$ was found to be disordered over two equivalent sets of positions (occupancies refined to $81.1(1) \%$ for the major component), the anisotropic displacement parameters and geometry of the major and minor disorder components of the solvate were restrained to be similar. The anisotropic displacement parameters of the atoms within phenyl rings $\mathrm{C}(35)-\mathrm{C}(40), \mathrm{C}(41)-\mathrm{C}(46), \mathrm{C}(69)-\mathrm{C}(74)$ and $C(75)-C(80)$ were restrained to be similar. The sulfur atom, $S(1)$, was originally found to be non-positive-definite and was restrained to be more isotropic. The anisotropic displacement parameters of all four solvent molecules were restrained.

Table 8.35 Crystal data and structure refinement for 4.31.

| Chemical formula | $\mathrm{C}_{40} \mathrm{H}_{36} \mathrm{Cl}_{8} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 1101.34 |
| Temperature | 150(2) K |
| Radiation, wavelength | synchrotron, $0.6719 \AA$ |
| Crystal system, space group | orthorhombic, $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
| Unit cell parameters | $a=10.0491(6) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=15.0403(9) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=27.6518(16) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 4179.3(4) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $3.981 \mathrm{~mm}^{-1}$ |
| F(000) | 2168 |
| Crystal colour and size | colourless, $0.14 \times 0.08 \times 0.06 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 35755 ( $\theta$ range 2.45 to $31.17^{\circ}$ ) |
| Data collection method | Bruker APEX 2 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 2.69 to $31.17^{\circ}$ |
| Index ranges | $\mathrm{h}-15$ to $14, \mathrm{k}-22$ to $23,1-23$ to 40 |
| Completeness to $\theta=24.00^{\circ}$ | 92.8 \% |
| Reflections collected | 35754 |
| Independent reflections | $14124\left(\mathrm{R}_{\text {int }}=0.0434\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 13927 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.606 and 0.796 |
| Structure solution | Patterson synthesis |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0311, 4.3240 |
| Data / restraints / parameters | 14124 / 0 / 488 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0290, \mathrm{wR} 2=0.0788$ |
| R indices (all data) | $\mathrm{R} 1=0.0293, \mathrm{wR} 2=0.0791$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.027 |
| Absolute structure parameter | 0.433(4) |
| Largest and mean shift/su | 0.004 and 0.000 |
| Largest diff. peak and hole | 0.633 and -1.095 e $\AA^{-3}$ |

4.31: The asymmetric unit was found to contain one unique molecule of $\mathbf{4 . 3 1}$ and two solvating chloroform molecules.

Table 8.36 Crystal data and structure refinement for $\mathbf{4 . 3 2}$.

| Chemical formula | $\mathrm{C}_{41} \mathrm{H}_{36} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{OP}_{2} \mathrm{Pt}$ |
| :--- | :--- |
| Formula weight | 900.65 |
| Temperature | $150(2) \mathrm{K}$ |
| Radiation, wavelength | Synchrotron, $0.8462 \AA$ |
| Crystal system, space group | monoclinic, $\mathrm{P}_{1} / \mathrm{c}$ |
| Unit cell parameters | $\mathrm{a}=16.690(4) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=14.837(3) \AA \quad \beta=117.831(3)^{\circ}$ |
|  | $\mathrm{c}=16.087(3) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | $3522.9(13) \AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $4.263 \mathrm{~mm}^{-1}$ |
| $\mathrm{~F}(000)$ | 1784 |
| Crystal colour and size | colourless, $0.15 \times 0.05 \times 0.02$ mm ${ }^{3}$ |
| Reflections for cell refinement | $24946\left(\theta\right.$ range 3.66 to $\left.26.85^{\circ}\right)$ |
| Data collection method | Bruker APEX 2 CCD diffractometer |
|  | $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 3.66 to $33.00^{\circ}$ |
| Index ranges | $\mathrm{h}-21$ to $21, \mathrm{k}-19$ to $19,1-20$ to 20 |
| Completeness to $\theta=26.00^{\circ}$ | $99.0 \%$ |
| Reflections collected | 24946 |
| Independent reflections | $7435\left(\mathrm{R}_{\text {int }}=0.0765\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 5972 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.567 and 0.920 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters a, b | $0.0327,222.3130$ |
| Data / restraints $/$ parameters | $7435 / 399 / 442$ |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right]$ | $\mathrm{R} 1=0.0800, \mathrm{wR} 2=0.2133$ |
| R indices (all data $)$ | $\mathrm{R} 1=0.0950, \mathrm{wR} 2=0.2199$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.117 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 5.222 and $-4.702 \mathrm{e} \AA \AA^{-3}$ |
|  |  |

4.32: The asymmetric unit was found to contain one unique molecule of 4.32. There was evidence of twinning ( $F_{\text {obs }}^{2}>F_{\text {calc }}^{2}$ ), but this could not be resolved. The anisotropic displacement parameters for all carbon, nitrogen, phosphorus and oxygen atoms were restrained.

Table 8.37 Crystal data and structure refinement for $\mathbf{4 . 3 4}$.

| Chemical formula | $\mathrm{C}_{46} \mathrm{H}_{49} \mathrm{Cl}_{2} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}_{2} \mathrm{Pt}$ |
| :---: | :---: |
| Formula weight | 1003.81 |
| Temperature | 150(2) K |
| Radiation, wavelength | MoKa, $0.7107 \AA$ |
| Crystal system, space group | orthorhombic, Pnma |
| Unit cell parameters | $\mathrm{a}=28.768(2) \AA \quad \alpha=90^{\circ}$ |
|  | $\mathrm{b}=17.1489(15) \AA \quad \beta=90^{\circ}$ |
|  | $\mathrm{c}=8.0686(7) \AA \quad \gamma=90^{\circ}$ |
| Cell volume | 3980.6(6) $\AA^{3}$ |
| Z | 4 |
| Absorption coefficient $\mu$ | $3.784 \mathrm{~mm}^{-1}$ |
| F(000) | 2016 |
| Crystal colour and size | colourless, $0.27 \times 0.20 \times 0.04 \mathrm{~mm}^{3}$ |
| Reflections for cell refinement | 22753 ( $\theta$ range 1.85 to $29.24^{\circ}$ ) |
| Data collection method | Bruker SMART 1000 CCD diffractometer $\omega$ rotation with narrow frames |
| $\theta$ range for data collection | 1.85 to $29.24^{\circ}$ |
| Index ranges | $\mathrm{h}-38$ to $37, \mathrm{k}-22$ to $22,1-9$ to 11 |
| Completeness to $\theta=26.00^{\circ}$ | 99.3 \% |
| Reflections collected | 22753 |
| Independent reflections | $5058\left(\mathrm{R}_{\text {int }}=0.0356\right)$ |
| Reflections with $\mathrm{F}^{2}>2 \sigma$ | 4091 |
| Absorption correction | semi-empirical from equivalents |
| Min. and max. transmission | 0.428 and 0.863 |
| Structure solution | direct methods |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Weighting parameters $\mathrm{a}, \mathrm{b}$ | 0.0797, 6.4112 |
| Data / restraints / parameters | 5058 / 185 / 269 |
| Final R indices $\left[\mathrm{F}^{2}>2 \sigma\right.$ ] | $\mathrm{R} 1=0.0426, \mathrm{wR} 2=0.1180$ |
| R indices (all data) | $\mathrm{R} 1=0.0536, \mathrm{wR} 2=0.1251$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.056 |
| Largest and mean shift/su | 0.001 and 0.000 |
| Largest diff. peak and hole | 2.699 and -1.042 e $\AA^{-3}$ |

4.34: The asymmetric unit was found to contain half a molecule of 4.34. The complex was positioned on a crystallographic mirror plane which bisected the platinum centre, peptide group and carbazole moiety [symmetry operations for equivalent atoms ' $=x,-y+1 / 2, z]$. The anisotropic displacement parameters of the carbazole moiety were restrained to be similar. The distance between $\mathrm{N}(3)-\mathrm{C}(24)$ and $\mathrm{N}(3)-\mathrm{C}(24)$ were restrained to be similar. Platon was used to model molecules of highly disordered solvate as a diffuse regions of electron density (Platon "squeeze" procedure). ${ }^{229}$

Table 8.38 Crystal data and structure refinement for 4.37.

Chemical formula
Formula weight
Temperature
Radiation, wavelength
Crystal system, space group
Unit cell parameters

Cell volume
Z
Absorption coefficient $\mu$ F(000)
Crystal colour and size
Reflections for cell refinement
Data collection method
$\theta$ range for data collection
Index ranges
Completeness to $\theta=26.00^{\circ}$
Reflections collected
Independent reflections
Reflections with $\mathrm{F}^{2}>2 \sigma$
Absorption correction
Min. and max. transmission
Structure solution
Refinement method
Weighting parameters $\mathrm{a}, \mathrm{b}$
Data / restraints / parameters
Final R indices [ $\mathrm{F}^{2}>2 \sigma$ ]
$R$ indices (all data)
Goodness-of-fit on $\mathrm{F}^{2}$
Largest and mean shift/su
Largest diff. peak and hole
$\mathrm{C}_{40} \mathrm{H}_{36} \mathrm{Cl}_{3} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{P}_{2} \mathrm{Pd}$
867.40
$150(2) \mathrm{K}$
$\mathrm{MoK}, 0.71073 \AA$
orthorhombic, Pnma
$\mathrm{a}=28.571(3) \AA$
$\mathrm{b}=17.5634(18) \AA \quad \alpha=90^{\circ}$
$\mathrm{c}=8.2536(8) \AA$
$4141.6(7) \AA^{3} \AA^{\circ}$
4
$0.757 \mathrm{~mm}^{-1}$
1764
colourless, $0.27 \times 0.21 \times 0.07 \mathrm{~mm}^{3}$
$32496\left(\theta\right.$ range 1.16 to $\left.13.98^{\circ}\right)$
Bruker SMART 1000 CCD
diffractometer
$\omega$ rotation with narrow frames
1.84 to $27.50^{\circ}$
$\mathrm{h}-35$ to $36, \mathrm{k}-22$ to $22,1-10$ to 10
$100.0 \%$
32496
$4871\left(\mathrm{R}_{\text {int }}=0.0611\right)$
3720
semi-empirical from equivalents
0.822 and 0.949
Patterson synthesis
Full-matrix least-squares on $\mathrm{F}^{2}$
$0.0587,20.4425$
$4871 / 143 / 245$
$\mathrm{R} 1=0.0628$, wR2 $=0.1534$
$\mathrm{R} 1=0.0838$, wR2 $=0.1612$
1.045
0.001 and 0.000
1.298 and -1.149 e $\AA \AA^{-3}$
4.37: The asymmetric unit was found to contain half of a molecule of 4.37 , with the complex lying across crystallographic mirror plane which bisects the palladium(II) centre and the $\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{O}_{2}\right) \mathrm{NHCOCH}_{2} \mathrm{~N}$ moiety. The auxiliary ligand site was therefore found to be two fold disordered $[\mathrm{C}(26)$ and $\mathrm{Cl}(1)$ occupancy symmetry imposed to 50:50]. The anisotropic displacement parameters for $\mathrm{Cl}(1)$ and $\mathrm{C}(26)$ were constrained to be identical. The anisotropic displacement parameters for the phenyl rings, $C(1)-C(6), C(7)-C(12)$ and the atoms $N(1), C(14)$ and $C(15)$ were restrained to be similar. The geometry of the phenyl rings $\mathrm{C}(1)-\mathrm{C}(6), \mathrm{C}(7)-\mathrm{C}(12)$ was also restrained to be similar. Platon was used to model molecules of highly disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solvate as diffuse regions of electron density ("squeeze" procedure). ${ }^{229}$


[^0]:    ${ }^{a} \mathrm{~N}(2)-\mathrm{C}(\mathrm{X}), \mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X})$ and $\mathrm{C}(28)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X}) \mathrm{X}=36$ (2.7), 40 (2.8), 44 (2.9), 46 (2.10).

[^1]:    ${ }^{\mathrm{a}} \mathrm{N}(2)-\mathrm{C}(\mathrm{X}), \mathrm{C}(27)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X})$ and $\mathrm{C}(28)-\mathrm{N}(2)-\mathrm{C}(\mathrm{X}) \mathrm{X}=36$ (2.7), 40 (2.8), 44 (2.9), 46 (2.10).

[^2]:    Symmetry operator for equivalent atoms ' $=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+1$.
    $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24)$.

[^3]:    $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(13)$ to $\mathrm{C}(17), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(18)$ to $\mathrm{C}(22), \mathrm{CpC}_{\text {cent }}=\mathrm{C}(26)$ to $\mathrm{C}(30), \mathrm{CpD}_{\text {cent }}=\mathrm{C}(31)$ to $\mathrm{C}(35)$.

[^4]:    $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(15)$ to $\mathrm{C}(19), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(20)$ to $\mathrm{C}(24)$.

[^5]:    ${ }^{\mathrm{a}} \mathrm{A}=9$ (3.30), 14 (3.31), 17 (3.32); $\mathrm{B}=15$ ( $\left.\mathbf{3 . 3 0}\right), 20(\mathbf{3 . 3 1}), 22(\mathbf{3 . 3 2}) ; \mathrm{C}=9^{\prime}(\mathbf{3 . 3 0}), 26(\mathbf{3 . 3 1}), 25(\mathbf{3 . 3 2}), \mathrm{D}=15^{\prime}(\mathbf{3} .30), 32(\mathbf{3 . 3 1}), 30(\mathbf{3 . 3 2})$. $\mathrm{E}=3$ (3.30), 4 (3.31 and 3.32); $\mathrm{F}=6$ (3.30), 10 (3.31 and 3.32); $\mathrm{P}(2)=\mathrm{P}\left(1^{\prime}\right), \mathrm{Cl}(2)=\mathrm{Cl}\left(1^{\prime}\right), \mathrm{C}(2)=\mathrm{C}\left(1^{\prime}\right), \mathrm{C}(3)=\mathrm{C}(2)$ (3.30). ${ }^{\mathrm{b}}$ Symmetry operator for equivalent atoms ' $\mathrm{x},-\mathrm{y}+1 / 2, \mathrm{z}$.
    $\mathrm{CpA}_{\text {cent }}=\mathrm{C}(3)$ to $\mathrm{C}\left(5^{\prime}\right), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(6)$ to $\mathrm{C}\left(8^{\prime}\right)(\mathbf{3 . 3 0}) ; \mathrm{CpA}_{\text {cent }}=\mathrm{C}(4)$ to $\mathrm{C}(8), \mathrm{CpB}_{\text {cent }}=\mathrm{C}(9)$ to $\mathrm{C}(13)$ (3.31 and 3.32).

[^6]:    ${ }^{\mathrm{a}} \mathrm{D}=$ donor atom, $\mathrm{A}=$ Acceptor atom.
    Symmetry operations for equivalent atoms; ' $=\mathrm{x}, \mathrm{y}-1, \mathrm{z} .{ }^{\prime \prime}=-\mathrm{x},-\mathrm{y}+1,-\mathrm{z}+2 . *=-\mathrm{x}+1,-\mathrm{y}+1,-\mathrm{z}+2$.
    $+=\mathrm{x}+1, \mathrm{y}, \mathrm{z} . \#=\mathrm{x}+1, \mathrm{y}+1, \mathrm{z}$.

[^7]:    ${ }^{\mathrm{a}} \mathrm{X}=$ relates to the minor disorder component.

[^8]:    ${ }^{a} \mathrm{P}(2)=\mathrm{P}\left(1^{\prime}\right)$ and $\mathrm{Cl}(2)=\mathrm{Cl}\left(1^{\prime}\right)$. Symmetry operations for equivalent atoms ${ }^{\prime}=\mathrm{x},-\mathrm{y}+1 / 2$, z .
    ${ }^{\mathrm{b}} \mathrm{X}=22$ (4.30), 26 (4.31), 29 (4.32), $13^{\prime}$ (4.34).

