Synthesis and Coordination of Bicyclic Phosphorus-Nitrogen Ligands

by

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Abstract

This thesis describes the synthesis and coordination chemistry of bicyclic phosphorus-nitrogen (PN) ligands containing the rigid and preorganised bicyclo[3.3.1]nonan-9-one framework.

The PN ligands were prepared *via* the Mannich condensation reaction of four different phosphorinanone classes with amines and aldehydes. The phosphorinanone compounds, 2,6-dimethyl-3,5-diphenyl-4-phenyl-4-phosphacyclohexanone (isomers **50** and **51**), 3,5-diphenyl-4-phenyl-4-phosphacyclohexanone (**44**, **45**) and 4-phenyl-4-phosphacyclohexanone (**42**) were prepared by literature methods, whereas the isomers of 4-*t*-butyl-2,6-di(carbomethoxy)-3,5-bis(*p*-dimethylaminophenyl)-4-phosphacyclohexanone (**53**, **54**) were synthesised by the reaction of Bu^tPH₂ with 2,4-di(carbomethoxy)-1,5-bis(*p*-dimethylaminophenyl)penta-1,4-dien-3-one (**38**). The Mannich reactions of phosphorinanones **50** and **51** were not successful, whereas the reactions of **44**, **45** and **42** produced unidentifiable products. The reaction of phosphorinanone **53** with methylamine and formaldehyde produced the bicyclic PN compound 7-*t*-butyl-1,5-di(carbomethoxy)-6,8-bis(*p*-dimethylaminophenyl)-3-methyl-3-aza-7-phosphabicyclo[3.3.1]nonan-9-one (**65**). The identical Mannich reaction of phosphorinanone **54** also yielded **65**, as well as the PN compound 4-*t*-butyl-6-carbomethoxy-5-(*p*-dimethylaminophenyl)-2-methyl-2-aza-4-phosphacyclohexanone (**66**) and the *E/Z* isomers of 3-(*p*-dimethylaminophenyl)methyl-2-propenoate (**67**).

The bicyclic PN ligand **65** adopts a chair-chair conformation in solution and the solid state as confirmed by *X*-ray crystallography. The coordination chemistry of this ligand was comprehensively explored with rhodium, palladium and platinum, and a wide range of complexes were synthesised including $[\text{ML}_2(\mathbf{65})]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L} = \text{Cl}, \text{Me}$), $[\text{ML}(\mathbf{65})]$ ($\text{M} = \text{Rh}, \text{Pd}, \text{Pt}$; $\text{L} = \text{C}_2\text{H}_4, \text{cod}, \text{dba}, \text{norb}$) ($\text{cod} = \text{cycloocta-1,5-diene}$, $\text{dba} = \text{trans,trans-dibenzylideneacetone}$, $\text{norb} = \text{norborn-2-ene}$), $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mathbf{65})]\text{X}$ ($\text{X} = \text{Cl}, \text{SbF}_6$) and $[\text{PtL}(\mathbf{65})]\text{CH}(\text{SO}_2\text{CF}_3)_2$ ($\text{L} = 1\text{-}\sigma,4\text{-5-}\eta\text{-C}_8\text{H}_{13}, 1\text{-3-}\eta\text{-C}_8\text{H}_{13}$).

Cycloplatinatation at the *ortho*-position of the 6,8-dimethylaminophenyl substituents was an interesting feature of the coordination chemistry of PN ligand **65**. *Ortho*-metallation at both dimethylaminophenyl groups led to the formation of complex $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65}\text{-2H})]$ (**76**), whereas metallation of only one aryl group produced the complex $[\text{Pt}(\text{C}_8\text{H}_{13})(\mathbf{65}\text{-H})]$ (**87**). Further reaction of complex **76** yielded the *trans*- and *cis*-hydroxo-bridged dimers $[\text{Pt}_2(\mu\text{-OH})_2(\mathbf{65}\text{-H})_2]$ (**98**, **101**). The nitrogen donor atom is not coordinated to the platinum metal centres in the cyclometallated PN complexes.

Protonation of $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65})]$ (**75**) with $\text{CH}_2(\text{SO}_2\text{CF}_3)_2$ produced the hydride complex $[\text{PtH}\{\text{CH}(\text{SO}_2\text{CF}_3)_2\}(\mathbf{65})]$ (**92**) and the agostic ethyl complex $[\text{Pt}(\text{C}_2\text{H}_5)(\mathbf{65})]\text{CH}(\text{SO}_2\text{CF}_3)_2$ (**93**). Similarly, protonation of $[\text{Pt}(\text{norb})(\mathbf{65})]$ (**74**) with $\text{CHPh}(\text{SO}_2\text{CF}_3)_2$ gave the norbornyl agostic complex $[\text{Pt}(\text{C}_7\text{H}_{11})(\mathbf{65})]\text{CPh}(\text{SO}_2\text{CF}_3)_2$ (**94**) as confirmed by *X*-ray crystallography.

In addition, hydrated analogues of some of the coordination complexes of PN ligand **65** mentioned previously were also observed. In such complexes, the central carbonyl group at position 9 was hydrated to form a geminal diol. The hydrated complexes exhibited similar chemical characteristics to their ketone counterparts.

The ^{15}N NMR chemical shifts of the nitrogen donor atom in PN ligand **65** and its various metal complexes were obtained from inversely-detected $^1\text{H}-^{15}\text{N}$ HMBC experiments. The NMR data showed no explicit relationship between the coordination mode of the nitrogen group and the ^{15}N chemical shift.

To my parents:

*In loving memory of my father,
Ismaeil Zayya Helo,
who instilled in me the love of learning
and taught me to aim high.*

*And to my mother, Khazo Keryakos Bahram,
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Glossary

Ar	<i>p</i> -dimethylaminophenyl (<i>p</i> -(Me ₂ N)C ₆ H ₄)
COD	cycloocta-1,5-diene
dba	<i>trans,trans</i> -dibenzylideneacetone
E	electrophile
ESI	electrospray ionisation
HMBC	heteronuclear multiple-bond correlation (¹ H to ¹³ C or ¹⁵ N correlations depicted by)
HRESIMS	high resolution electrospray ionisation mass spectrometry
HSQC	gradient heteronuclear single-quantum correlation
<i>I</i>	spin quantum number (NMR spectroscopy)
<i>m/z</i>	mass to charge ratio
norb	norborn-2-ene
PN	phosphorus-nitrogen (ligand)

Chapter 1

Introduction

This thesis gives an account of my research into the synthesis and coordination of a new class of bicyclic phosphorus-nitrogen (PN) ligands based on the rigid framework of bicyclo[3.3.1]nonan-9-one. The coordination mode of the PN ligands towards rhodium, palladium and platinum metals was specifically explored. NMR spectroscopy was a vital tool in the characterisation of ligands and the resultant metal complexes.

1.1 Coordination complexes

The chemistry of coordination complexes is very rich and diverse. It is determined by the nature of the metal and the type of ligands present in the complex. The metal atom may have a number of roles based on its oxidation state, coordination geometry and magnetic and electronic properties. Ligands also have a strong influence on a metal complex. The binding mode of individual ligands, the number of donor atoms and donated electrons, and the electronic and steric properties of ligands are important factors in determining the chemical characteristics of metal complexes. Consequently, understanding the properties of metals and ligands allows the design of metal complexes that are tailored for specific purposes.

Coordination complexes have a wide range of technological and industrial applications ranging from catalysis^{1,2} to anti-cancer drugs.³ Coordination compounds are able to catalyse chemical transformations because of the dramatic change in reactivity of substrate molecules upon coordination to a metal. Highly reactive species can be stabilised to react further in a controlled and productive manner, and the ligands present may exert control on the occurring reactions to achieve selective transformations.

Bidentate ligands are very important in transition metal coordination chemistry. They can act as chelating ligands when both donor atoms are able to bind to the same metal. The distance between and orientation of the donor atoms influence the nature of the interactions between the metal and the ligand. An important parameter of bidentate ligands is the bite angle,⁴ which is defined as the ligand-metal-ligand angle formed when a bidentate ligand coordinates to a metal centre. The magnitude of the bite angle can have a pronounced effect on the rate and selectivity of metal-catalysed reactions.

Complexes with chelating bidentate ligands are thermodynamically more stable than those with an equivalent number of comparable monodentate ligands due to the chelate effect. This is one of the oldest concepts in coordination chemistry and has been successfully explained largely in terms of the entropy change involved in the chelation process.⁵ Once one end of a bidentate ligand is attached to a metal, the second end is in the vicinity of the metal and can bind without all the translational and rotational entropy cost of the first binding interaction. Thus, chelate binding by a bidentate ligand can have a Gibbs energy more than twice that of the monodentate analogue. This results in a considerably stronger chelate binding than in monodentate binding. Another advantage of chelate binding by bidentate ligands is the well-defined geometry of the resulting complex compared with the variable and often unpredictable geometry available in monodentate binding. The well-defined geometry of the metal complex can

be used to direct chemical reactions and enhance their rates and selectivities.

Bidentate ligands may contain the same type of donor atom such as in bis-phosphine⁶ and bis-nitrogen^{7,8} ligands. These ligands are ubiquitous in coordination chemistry as their metal complexes are reactive in homogeneous catalysis. Bidentate ligands can also have two different donor atoms to produce heterobidentate or hybrid ligands.⁹ A distinguished and highly studied family of hybrid ligands are the phosphorus-nitrogen (PN) chelates.¹⁰⁻¹²

1.2 Phosphorus-nitrogen ligands

Phosphorus-nitrogen ligands are excellent chelates for transition metals because they possess many unique characteristics. They are endowed with soft phosphorus and hard nitrogen donor atoms, which results in clearly differentiated coordination sites in the respective *trans*-positions on the metal. They combine the individual characteristics of bis-phosphine and bis-nitrogen chelating ligands to display a new mode of complexation to transition metals. The π -acceptor character of the phosphorus donor atom can stabilise metal centres in low oxidation states, while the σ -donor ability of the nitrogen donor atom can stabilise electron-poor metals. Many different phosphorus and nitrogen donor moieties have been used for the synthesis of PN ligands. Nitrogen donors include amines, imines, pyridines, amides and nitriles, while the great majority of phosphorus donors are diaryl and dialkylphosphino groups or heteroatom bound phosphorus donors.

Many PN ligands have been reported, making it impossible to comprehensively mention all the different types, therefore only a few examples will be briefly noted here. PN ligands containing the oxazoline unit constitute a very successful ligand class in asymmetric synthesis.^{11,13} The modular structure of these ligands allows extensive variation of the oxazoline ring. They are stable

towards oxidation and hydrolysis, and are applicable to a wide range of reactions in which high enantioselectivities are obtained. For example, the palladium-catalysed allylic substitution reaction^{13–16} of 1,3-diphenyl-2-propenylacetate (**1**) with different nucleophiles affords **2** in more than 90% yield and high enantiomeric excess (Scheme 1.1).

Scheme 1.1

Phosphorus-nitrogen ligands also have the potential to be hemilabile. The concept of ligand hemilability was first introduced by Jeffrey and Rauchfuss¹⁷ in 1979. It is based on small energy differences, of the order of 50 kJ/mol, that are involved in the dynamic processes of dissociation and recoordination of the weakly bonding group. The labile group stabilises the reactive transition metal centre in the absence of substrates and provides an additional vacant coordination site as it can be easily displaced by coordinating substrate or solvent molecules. Meanwhile, the inert group anchors the hemilabile ligand to the metal centre. In the case of PN ligands, the substitutionally inert phosphorus moiety maintains the strong coordination to the metal while the nitrogen group binds weakly and therefore is easily displaced by other coordinating ligands or solvent molecules, but remains available for recoordination to the metal centre (Scheme 1.2).

The hemilabile behaviour of PN ligands is the result of either fluxional ligand

P = substitutionally inert group
 N = substitutionally labile group
 S = substrate or solvent molecule

Scheme 1.2

exchange processes or ligand displacement reactions involving small molecules. For example, complex **3** was observed to undergo a fluxional ligand exchange reaction¹⁸ of bound and unbound amino groups at room temperature in CD_2Cl_2 (Scheme 1.3). On the other hand, upon the reaction of complex **4** with CO,¹⁹ the pyridine moiety rather than the ether group is displaced due to the strong *trans*-effect of the triphenylphosphine ligand (Scheme 1.3).

Scheme 1.3

In addition, the hemilability of the nitrogen group in PN ligands could

potentially lead to the formation of unexpected new complexes. For instance, upon the dissociation of the nitrogen arm of PN ligand **5** in complex **6**, the chloro-bridged dimer **7** is formed.²⁰ The recoordination of the nitrogen arms in **7** in turn results in the formation of two more dinuclear derivatives **8** and **9** (Scheme 1.4).

Scheme 1.4

An interesting bicyclic PN ligand is the open cage aminophosphine 7-phospha-1,3,5-triazabicyclo[3.3.1]nonane (**10**), which is known as PTN.²¹ It is derived from the water-soluble phosphine ligand 1,3,5-triaza-7-phosphaadamantane (**11**), which is usually abbreviated as PTA.²² PTN has the potential to be used in green aqueous catalytic systems as it is a bidentate hemilabile PN ligand featuring similar stereoelectronic properties and water solubility as PTA.

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The coordination chemistry of the PTN ligand has been explored with a few transition metals including Mo, Ru, Rh, Os, Pd and Au.^{23–25} The PTN ligand can adopt either a mono- or bidentate coordination mode depending on the metal precursor and the reaction conditions. It is also possible to form 2:1 ligand to metal PTN complexes in which either one or both coordination modes are present. For example, complex **12** features two monodentate units of PTN (Scheme 1.5).²⁴ Upon chloride abstraction, complex **13** is formed in which mono- and bidentate PTN units are observed. Addition of water to **13** results in the formation of complex **14**, which suggests hemilabile behaviour of the bidentate PTN unit.

Furthermore, rhodium-PTN complexes such as **15** have been employed in homogeneous catalysis in biphasic organic/water solvent systems.²³ The complexes had comparable results to analogous rhodium-PTA compounds in olefin hydroformylation reactions, and similar activities as other aminophosphine rhodium catalysts in transfer hydrogenation tests. Moreover, the anti-cancer

Scheme 1.5

activity of ruthenium (**16**) and osmium (**17**) PTN compounds was evaluated and contrasted with PTA complexes in order to study the effect of forming a PN chelate complex without significantly altering the water solubility and acid-base properties of the resulting complexes.²⁵ Metal-based drugs can either react with proteins, such as ubiquitin, or bind to DNA bases. Osmium complexes showed no or very low reactivity toward both proteins and DNA. The ruthenium-PTN compounds showed comparable reactivity toward ubiquitin as their PTA analogues, but a much lower reactivity toward DNA.

In addition to all the advantageous properties of phosphorus-nitrogen ligands, their study is assisted by NMR spectroscopy. As the ^{31}P nuclide is NMR active, its effect on the proton and carbon nuclei present in a molecule are reflected in the ^1H and ^{13}C NMR spectra respectively. Detailed structural and bonding information can also be obtained from the $^{31}\text{P}-^1\text{H}$ and $^{31}\text{P}-^{13}\text{C}$ coupling constants. Moreover, the ^{31}P NMR spectrum is very important and useful as any chemical changes around the phosphorus atom will be reflected in the ^{31}P NMR chemical shift. On the other hand, valuable information about the nitrogen chemical environment can be acquired from ^{15}N NMR spectroscopy. This is an insensitive technique and samples generally need to be enriched with the NMR active ^{15}N nuclide. Inversely-detected $^1\text{H}-^{15}\text{N}$ 2D NMR experiments present an opportunity to analyse normal NMR samples to obtain the ^{15}N chemical shifts of different compounds containing the same PN ligand. Analogous to the $^1\text{H}-^{13}\text{C}$ correlations, the $^1\text{H}-^{15}\text{N}$ correlations can provide further insight into the nitrogen bonding environment.

1.3 Bispidinone chemistry

A prominent group of compounds containing the bicyclo[3.3.1]nonan-9-one framework are the bispidinones. These are bis-nitrogen chelating ligands upon which the target phosphorus-nitrogen ligands discussed in this thesis are modelled.

Synthesis and conformation

Bispidinone compounds were first reported by Mannich and Mohs in 1930.²⁶ They contain the rigid diazaadamantane-based framework found in the natural product sparteine (**18**), but with a carbonyl group at the bridge head position (**19**).

In general, bispidinone compounds can be easily prepared by the Mannich condensation reaction (Scheme 1.6).^{27,28} The reaction of a ketone with acidic C–H protons, an aldehyde and a primary amine in the ratio of 1:2:1 in a protic solvent leads to a piperidinone (**20**).²⁹ This intermediate can either be isolated or condensed further with two equivalents of an aldehyde and one equivalent of a primary amine to produce diazabicyclo[3.3.1]nonan-9-one (**21**). In total, four Mannich condensations are required to yield the final bispidinone.

Scheme 1.6

The mechanism^{28,30} of the Mannich reaction consists of a complex series of equilibria controlled by the nature of the reactants and the reaction conditions. A simplified mechanism is given in Scheme 1.7. The accepted mechanism proceeds *via* the formation of an iminium ion (**22**) formed in small amounts *in situ* by the attack of the amine on the aldehyde. This then reacts with the enol tautomer of the ketone **23**, also present in small concentrations, to give the hydrochloride salt of the α -aminocarbonyl compound **24**. To produce cyclic products, primary amines are used which can undergo two Mannich reactions

to first yield a secondary amine then a tertiary amine and form the cyclic end product. The substitution pattern around the bicyclic bispidinone framework is variable to a large extent. Different amines, aldehydes and ketones have been employed to synthesise a wide range of bispidinone compounds.^{27,31–34}

Scheme 1.7

Bispidinone compounds can theoretically exist in any of the three conformations depicted in Figure 1.1. The chair-chair (cc), chair-boat (cb) and boat-boat (bb) conformations are stable and free from angular strain. The most stable geometry is the chair-chair conformation, however depending on the size and nature of the substituents, the chair-boat conformation has also been observed in solution. The boat-boat conformation has not been observed, probably due to steric hindrance.

Figure 1.1. Possible conformations of bispidinone compounds.

Medical and chemical applications

Some bispidinone derivatives were found to possess useful biological activities.²⁷ A series of 3,7-diazabicyclo[3.3.1]nonan-9-ones were reported to have analgesic properties as they displayed selective affinity for the μ -opioid receptors.^{35–38} One of the most studied compounds is **HZ2** (Figure 1.2), which exhibited strong antinociceptive characteristics with a potency comparable to morphine.³⁶ Other sulfur³⁹ and selenium⁴⁰ derivatives containing the bispidinone bicyclic backbone possessed good antiarrhythmic potencies but were also found to be quite toxic (Figure 1.2).

Figure 1.2. Biologically active bispidinone derivatives.

The coordination chemistry of bispidinone compounds has been extensively explored.³³ The rigid and highly preorganised bispidinone ligands form very stable metal complexes in which they adopt the chair-chair conformation (**25**).

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The rigidity of the bispidinone ligands in the metal complexes is measured by the distance between the two nitrogen donor atoms. The distance range is 2.7-3.0 Å, but on average it is 2.9 Å. It is very similar for free and coordinated bispidinone ligands and is practically constant in most metal complexes. This shows that the ligand structure does not change significantly upon metal coordination, hence the degree of ligand preorganisation is transferred onto the resultant metal complexes. Furthermore, the size of the ligand cavity can be finely tuned by the nitrogen substituents, such that sterically demanding groups result in slightly longer N–N distances.

A large variation in the bond distances from the metal centres to the two nitrogen donor atoms is observed, but the individual bond lengths are generally in the expected ranges for the respective metal ions. This results in considerable elasticity in the coordination sphere of the rigid bispidinone ligands, thus metal ions of quite different sizes can fit into the ligand cavity without inducing much steric strain.³³ In addition, due to their fairly easy synthesis and the wide range of reactants that could be employed, bispidinone compounds can be designed and synthesised with substituents that occupy the space above and below the metal coordination plane to provide further metal protection and lead to stable metal complexes. Also, a series of related metal complexes can be readily prepared to investigate substituent effects on the stability of the metal complexes and to tune their chemical and physical properties.

Numerous bispidinone metal complexes have been reported with first row transition metals and palladium and platinum. Complexes of alkali and heavier transition metal ions as well as lanthanides have also been described but not structurally characterised.³³ Iron and copper bispidinone coordination chemistry has been of particular interest in catalysis and biomimetics. Tetradentate bispidinone derivatives such as **26** provide a rigid backbone and enforce *cis*-octahedral or square pyramidal coordination geometries.^{41,42} Copper complexes

of the type $[\text{CuCl}(\mathbf{26})]$ are active in the synthesis of aziridines (Scheme 1.8), the nitrogen analogues of epoxides.⁴³ Furthermore, bispidinone-copper complexes have been used as models to study electron transfer and dioxygen activation in copper proteins,^{44,45} while iron complexes containing similar tetradentate bispidinone ligands have been investigated as catalysts for the oxidation of hydrocarbons by hydrogen peroxide as high-valent iron oxidants are known to be catalytically active species in heme enzymes.^{46,47}

Scheme 1.8

Few reports concerning bispidinone complexes of palladium and platinum metals have been published. The complexes were prepared easily through general ligand displacement reactions using appropriate metal precursors. These include dihalide complexes^{31,48} of general structure **27**, as well as palladium allyl complexes, which were synthesised to study the dynamic behaviour of the allyl system.^{32,48–50}

In addition, Shen⁵¹ reported the synthesis of some bispidinone complexes for the purpose of C–H activation of small molecules. For example, the palladium dichloro complex **28** promoted C–H activation of CH_2Cl_2 (Scheme 1.9). In

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contrast, the platinum analogues showed no potential in small molecule C–H activation.

Scheme 1.9

Bispidinone derivatives

Replacement of one of the nitrogen atoms in bispidinone compounds with a heteroatom leads to 3-aza-7-heterobicyclo[3.3.1]nonan-9-ones.^{27,52} Oxygen,⁵³ sulfur^{39,54} and selenium⁴⁰ analogues have been prepared by the Mannich reaction starting from the respective 4-heterocyclohexanones. These bispidinone analogues were used for conformational studies and were tested for potential biological activity. Furthermore, modifications of the central ketone group in bispidinones can result in additional analogues.³³ Wolff-Kishner reduction of the carbonyl group leads to the corresponding bispidines (**29**), while reduction of bispidinones with LiAlH_4 or NaBH_4 yields bispidoles (**30**). The reduction procedures are also applicable to the bispidinone analogues.

1.4 Bicyclic PN compounds

Phosphorinanones

Phosphorus-nitrogen compounds containing the bicyclic bispidinone framework are the synthetic targets for this research project. The bispidinone synthetic method is not chemically viable to prepare the analogous PN compounds because there is no equivalent for the iminium ion in phosphorus chemistry due to the weakness of P=C bonds. Thus, a different route must be developed to obtain the 3-aza-7-phoshabicyclo[3.3.1]nonan-9-ones (**31**).

The Mannich reaction used to construct the bispidinone compounds yields a piperidinone as an intermediate which can undergo two further Mannich condensations to produce the bicyclic end product. The phosphorus analogues of the piperidinones (**32** and **33**), known as 4-phosphorinanones, could potentially be used to synthesise the target bicyclic PN compounds.

Phosphorinanones were first reported by Welcher, Johnson and Wystrach⁵⁵ in 1960. They were prepared by the Thorpe-type cyclisation

of bis(2-cyanoethyl)phosphine **34** (Scheme 1.10) to give the simple phosphorinanone **32**. An improved synthetic methodology was later reported by Welcher and Day⁵⁶ in 1962 in which a primary phosphine was added to a conjugated dienone (**35**) to produce the substituted phosphorinanone **33** (Scheme 1.10). As can be seen from the reaction scheme, changing the phosphorus substituent as well as using more elaborate dienone derivatives would result in different phosphorinanone compounds.

Scheme 1.10

Most of the published work on phosphorinanone compounds has primarily been concerned with ring conformational analysis.^{57–61} Specifically, the studies investigated the configurational preferences of the phosphorus substituents and those located around the heterocyclic ring. It was found that a phenyl group on phosphorus would normally occupy an axial position, but upon oxidation and sulfurisation, the P–Ph bond became equatorial. This was attributed to the presence of a minor equatorial conformer in solution. Phosphorinanone conformations also ranged from a perfect chair to a twist-boat depending on the nature and number of substituents.

The palladium and platinum coordination chemistry of phosphorinanones

was explored by Pringle and co-workers.⁶¹ They reported diastereoselective complexation of the *rac*-form of ligand **36** over the *meso*-form (Scheme 1.11). This was explained by the accessibility of the phosphorus electron lone pair being hindered in the *meso*-form because of the *cis*-phenyl substituents.

Scheme 1.11

Synthetic methodology of PN compounds

Until recently, bispidinone derivatives containing phosphorus and nitrogen as the donor atoms were not known. The first example of a 3-aza-7-phosphabicyclo[3.3.1]nonan-9-one compound (**37**) was prepared by Vagana⁴⁸ in 2005 as shown in Scheme 1.12. The first step required a Michael addition reaction between dienone derivative **38** and phenylphosphine to produce phosphorinanone **39**. This intermediate was then subjected to two Mannich condensation reactions in the second step with two equivalents of formaldehyde and one equivalent of a primary amine to yield the bicyclic PN compound. Different primary amines were used in the synthesis and it was found that steric bulk at the nitrogen donor atom had no influence on the rate and yield of the Mannich reaction. The new PN compounds favoured the twin-chair conformation both in solution and the solid state, and there was no evidence for the presence of other conformers.

The coordination chemistry of the new 3-aza-7-phosphabicyclo[3.3.1]nonan-

Scheme 1.12

9-ones was very briefly explored by Vagana.⁴⁸ Dimethylplatinum and dichloropalladium complexes (**40**) were prepared in moderate yields in which the PN ligands were bound *via* both donor atoms.

In addition, a gold(I) complex (**41**) was synthesised by Lim and co-workers,⁶² where the PN ligand was monodentate as it was bound through the phosphorus atom only. This was not surprising as Au(I) is a soft Lewis acid, hence preferring to bind to soft donor atoms such as phosphorus.

M = Pd, Pt
 X = Me, Cl
 R = Me, Et, Buⁱ
 Ar = *p*-(Me₂N)C₆H₄

3-Aza-7-phosphabicyclo[3.3.1]nonan-9-ones

Phosphorus-nitrogen compounds based on the bispidinone backbone are attractive synthetic targets as heterobidentate ligands for transition metals. The presence of both phosphorus and nitrogen donor atoms ensures great complex stability for various metal oxidation states. The different characteristics of the donor atoms, nitrogen being a hard centre while phosphorus is soft, and their contrasting *trans*-influences will induce electronic differentiation on the metal centre and the respective *trans*-positions. Moreover, it is feasible for the nitrogen group to be hemilabile as the hard ends are weakly coordinated to soft metal centres and can be easily dissociated in solution. This provides a vacant coordination site on the metal whenever demanded, but the reversible binding of the nitrogen group confers stability to the metal centre in the absence of substrate.

In addition, the rigid bicyclo[3.3.1]nonan-9-one framework is expected to provide extra stability to resultant metal complexes due to its high degree of preorganisation and complementarity. Metal ions of different sizes can fit into the ligand cavity without inducing much steric strain in the ligand. This is attributed to the elasticity of the ligand coordination sphere where the structure of the ligand backbone remains constant while the metal donor bonds vary in the expected ranges. Furthermore, the potential for substitution around the heterobicyclic ring presents the opportunity to design PN ligands with bulky substituents that could provide out-of-plane protection to the metal centre. The rigid framework can also enforce certain coordination geometries that can stabilise unusual electronic structures of transition metal complexes. Therefore, incorporation of phosphorus and nitrogen donor atoms in the bicyclic bispidinone framework should lead to stable metal complexes with interesting properties.

1.5 Research objectives

The aims of this project are to design and synthesise a new class of bicyclic phosphorus-nitrogen ligands based on the bicyclo[3.3.1]nonan-9-one framework, and to explore extensively their coordination chemistry with rhodium, palladium and platinum. PN compounds with different substitution patterns around the bicyclic backbone will be prepared to compile a ligand library from which general conclusions will be drawn about this novel class of PN ligands. Finally, the binding mode and the hemilability potential of the nitrogen group will be studied by ^{15}N NMR spectroscopy.

1.6 Concluding remarks

Phosphorus-nitrogen ligands are very important in coordination chemistry. Their aptitude to display hemilabile behaviour in the coordination sphere of a metal complex and the electronic differentiation imposed by the different donor atoms renders their metal complexes potentially useful in a wide range of chemical applications. PN compounds containing the bicyclo[3.3.1]nonan-9-one backbone are expected to be rigid and highly preorganised. The combination of this advantageous framework with the different properties of phosphorus and nitrogen donor atoms is anticipated to produce excellent chelating ligands for rhodium, palladium and platinum metals.

Chapter 2

Synthesis of Bidentate

Phosphorus-Nitrogen Ligands

Phosphorus-nitrogen (PN) compounds containing the bicyclo[3.3.1]nonan-9-one organic framework are attractive synthetic targets as ligands for transition metal complexes. The combination of the rigid bicyclic backbone and the different features associated with each donor atom is expected to provide unique reactivity to the resultant metal complexes. The synthetic methodology of such PN ligands consists of two steps: first a Michael addition reaction between an α,β -unsaturated carbonyl compound and an aryl- or alkylphosphine (or a derivative) to produce a phosphorinanone intermediate, which is then combined with an aldehyde and a primary amine in the Mannich condensation reaction to give the bicyclic PN compound.

Four different phosphorinanone classes (Figure 2.1) were employed in the synthesis of the phosphorus-nitrogen ligands. The six-membered phosphorinanone rings varied in the substituents at the 2,6- and 3,5-positions with respect to the carbonyl moiety as well as different groups on the phosphorus atom. The Mannich reaction was attempted with each phosphorinanone class to produce PN compounds with different substitution patterns around the bicyclic framework.

Figure 2.1. Different phosphorinanone compounds.

2.1 Phosphorinanone synthesis

The Michael addition reaction was used to prepare most of the phosphorinanone compounds employed in the synthesis of the bicyclic PN ligands. This reaction involves the addition of a nucleophile to the α -position of a double bond of an α, β -unsaturated carbonyl group.⁶³ The phospho-Michael (*P*-Michael) reaction, i.e. the addition of a phosphorus nucleophile to the α, β -unsaturated carbonyl compound, represents one of the most important tools for the formation of P–C bonds.⁶⁴ In this section, aryl- and alkylphosphine nucleophiles or their derivatives were used in the *P*-Michael additions. In such reactions, the phosphorus nucleophile undergoes two sequential Michael additions - first inter- and then intramolecularly - to form the six-membered phosphorinanone compounds.

2.1.1 4-Phenylphosphorinanone compound

At the outset, the simple unsubstituted 4-phenylphosphorinanone (**42**) was prepared by a known literature route⁶⁵ as shown in Scheme 2.1. The *P*-Michael reaction was not used in this case because of the synthetic and handling problems

Scheme 2.1

associated with preparing the required α,β -unsaturated carbonyl compound, 1,4-pentadien-3-one (also known as divinyl ketone).^{66,67} Furthermore, there is no precedence for the use of divinyl ketone to prepare phosphorinanone **42** in the literature.

2.1.2 3,5-Diphenyl phosphorinanone system

To gradually introduce substituents in the six-membered phosphacycles, phosphorinanone compounds with phenyl groups at the 3,5-positions were prepared. The reaction of dibenzylideneacetone (**43**), usually abbreviated as dba, with either phenylphosphine or bis(hydroxymethyl)phenylphosphine* produced the phosphorinanone isomers **44** and **45** (Scheme 2.2).^{58,60,61} Although the asymmetric isomer of 3,4,5-triphenylphosphorinanone (**44**) was the major product from the *P*-Michael reaction, pure samples of each isomer could not be obtained. Thus, all Mannich reactions were performed with phosphorinanone samples containing both **44** and **45**.

*Bis(hydroxymethyl)phenylphosphine is frequently used as a proxy for PhPH_2 .

Scheme 2.2

2.1.3 2,6-Dimethyl phosphorinanone system

To further increase the substitution pattern around the phosphacycles, phosphorinanone compounds with methyl groups at the 2,6-positions as well as 3,5-phenyl substituents were prepared using 2,4-dimethyl-1,5-diphenyl-1,4-pentadien-3-one (**46**). The general procedure of Japp and Maitland⁶⁸ was used to prepare compound **46** and is outlined in Scheme 2.3. In our hands, three different products were obtained *via* this route, the structures of which were elucidated by NMR spectroscopy. They included the desired dba derivative **46**, which was produced in very low yields (17%), and compounds **47** and **48**. All products were white crystalline solids, but had very different morphologies: dba derivative **46** formed as glistening flat plates, compound **47** had the appearance of a ‘fluffy’ solid made up of very small needles, and finally compound **48** was produced as long fine needles.

Compound **47** was first reported by Otto and Ebner⁶⁹ in 1976 and was produced by the identical reaction of -pyrone derivative **49** with KOH in ethanol. The formation of compound **48** as a by-product was mentioned by

Scheme 2.3

Japp and Maitland in 1904 but the quantity obtained was too small for further examination. Compound **48** was also noted later by Yates and co-workers⁷⁰ in 1958 but no structural information was given.

The *P*-Michael addition reaction of dba derivative **46** with *t*-butylphosphine in pyridine was not successful (Scheme 2.4). This was not surprising as the same result was observed previously with phenylphosphine.⁵⁹ However, if phenylphosphine is converted to bis(hydroxymethyl)phenylphosphine, then reacted with compound **46**, the desired 4-phenylphosphorinanones can be formed.⁵⁹ Thus, *t*-butylphosphine was converted to Bu^tP(CH₂OH)₂, which then was reacted with **46**. Many products were formed, as shown by a plethora of peaks in the ¹H and ³¹P NMR spectra, which could not be separated nor identified. For this reason, the previously reported 4-phenylphosphorinanones **50** and **51** were used instead.⁵⁹ However, 100% pure samples of each phosphorinanone isomer could not be obtained despite many cycles of crystallisations from ethanol. Subsequently, samples containing

Scheme 2.4

different ratios of isomers **50** and **51** were used in the Mannich reactions.

2.1.4 2,6-Diester phosphorinanone system

Finally, considerable success had been achieved with the use of 2,4-di(carbomethoxy)-1,5-bis(*p*-dimethylaminophenyl)penta-1,4-dien-3-one (**38**) as the acidic C–H component in the *P*-Michael reaction to prepare phosphorinanone compound **39** (Scheme 1.12).⁴⁸ Thus, a similar synthetic procedure was adopted using *t*-butylphosphine instead of phenylphosphine as the phosphorus source.

Compound **38** was synthesised *via* the condensation of dimethyl 1,3-acetonedicarboxylate (**52**) with *p*-dimethylaminobenzaldehyde (Scheme 2.5). The *P*-Michael addition reaction of **38** and *t*-butylphosphine in pyridine at room temperature produced phosphorinanones **53** and **54** in a 2:1 ratio based on isolated yields. The keto tautomer of **54** is a diastereoisomer of phosphorinanone **53**. Most of compound **53** precipitated from the reaction mixture as a white solid, while isomer **54** remained in solution. Removal of solvent and several cycles

Scheme 2.5

of crystallisation from hot methanol yielded **54** as air stable fine white needles. The filtrate still contained small amounts of **53** and **54** plus potentially other diastereoisomers as evident from the signals in the ^1H and ^{31}P NMR spectra. The isolation of the other isomers was not practical as they were present in very small amounts.

Phosphorinane isomer **53** exists in the ketone form with normal IR carbonyl stretches for a ketone at 1707 cm^{-1} and an ester at 1755 cm^{-1} . The ^1H NMR spectrum of **53** in benzene- d_6 was simple owing to the presence of a plane of symmetry, while the ^{31}P NMR spectrum showed one resonance at 13.0 ppm. The methyl substituents in the dimethylaminophenyl and carbomethoxy groups resonated at 2.91 and 3.51 ppm respectively. The pairs of equivalent protons

H₃/H₅ and H₂/H₆ appeared as doublets of doublets at 3.59 and 3.97 ppm respectively, each with J_{HH} coupling of 12.7 Hz. This large diaxial coupling constant indicates that the bulky carbomethoxy and dimethylaminophenyl groups are in equatorial positions. Two doublets (J_{HH} 8.5 Hz) were observed at 6.62 and 7.21 ppm for the eight aromatic protons in a ratio of 1:1, implying that both of the aryl rings are rotating freely. A summary of the NMR data for phosphorinanone isomer **53** is given in Tables 2.1 and 2.2 on page 34.

From previous conformational analysis work on six-membered phosphacycles,^{61,71} the bulky Bu^t group on phosphorus is expected to occupy an equatorial position. Quin *et al.*⁷¹ showed that 1-R-phosphorinanes (R = CH₃, C₂H₅, *i*-C₃H₇, C₆H₅) gave a single ³¹P NMR signal at 300 K, but on lowering the temperature, separate sharp signals for the axial-R and equatorial-R conformers were observed. However, in the case of 1-*t*-butylphosphorinane (**55**) only one signal was observed over the entire temperature range (129-300 K) corresponding to the equatorial conformer. Moreover, Pringle and co-authors found that the Bu^t group in 4-*t*-butyl-3,5-diphenyl-4-phosphorinanone (**56**) also occupied an equatorial position.⁶¹ The strong preference of the Bu^t group for the equatorial position may be attributed to its large size.

As a result of keto-enol tautomerism, phosphorinanone isomer **54** was isolated in the enol form. The IR spectrum showed a broad enolic OH stretch at 3453 cm⁻¹ and a group of bands at 1644, 1610 and 1519 cm⁻¹ associated with the carbonyl groups. In the ³¹P NMR spectrum, compound **54** had a signal at 6.0 ppm. Two non-equivalent methoxy (3.62 and 3.66 ppm) and

dimethylamino (2.91 and 2.95 ppm) signals were observed in the ^1H NMR spectrum indicating asymmetry in isomer **54**. The enolic proton resonated at 12.84 ppm and H_3 was observed as a doublet at 4.28 ppm with J_{PH} coupling of 5.9 Hz. Unfortunately, the signals for H_5 and H_6 overlapped to give a multiplet centred at approximately 3.90 ppm (Figure 2.2). Thus, useful stereochemical information from the magnitude of vicinal and phosphorus couplings for H_5 and H_6 were instead obtained from a coupled HSQC spectrum.^{72–75}

Figure 2.2. ^1H NMR spectrum of phosphorinanone isomer **54** shown as an expanded-scale display of the overlapping signal for H_5 and H_6 , CDCl_3 , 600 MHz.

A coupled HSQC experiment is performed in the absence of broadband ^{13}C decoupling and with an extended acquisition time as compared with a regular HSQC. Extraction of 1D traces from the coupled HSQC spectrum at the carbon frequency allows the observation of proton multiplets with high resolution nearly equal to that of a conventional proton spectrum. The resolution is further enhanced by the increased acquisition time. The primary doublet splitting is due to the large $^1J_{\text{CH}}$ coupling constant as a result of coupling to ^{13}C nuclei. Residual coupling constants can also be measured from the 1D traces as second-order effects caused by strong proton–proton coupling is eliminated. In ^1H NMR spectra, complex coupling patterns result from strongly coupled $^1\text{H}-^{12}\text{C}-^{12}\text{C}-^1\text{H}$ spin systems. In the coupled HSQC experiment these strong couplings are removed and only coupling from $^1\text{H}-^{13}\text{C}-^{12}\text{C}-^1\text{H}$

units are observed. Consequently, undistorted first-order multiplets are restored from which proton–proton and proton–phosphorus coupling constants can be extracted.

The 1D traces (Figure 2.3) from a coupled HSQC spectrum of phosphorinanone isomer **54** showed H₅ as a doublet of doublets (J_{HH} 11.4 Hz, J_{PH} 6.3 Hz) and H₆ as a doublet with J_{HH} of 12.4 Hz, indicating a diaxial arrangement. Nothing can be said about the configuration at C₃ because of the isolated position of H₃, and also as NOE experiments proved inconclusive. The signals for the eight aromatic protons overlapped to give four resonances in a ratio of 3:3:1:1. This suggests that one of the dimethylaminophenyl rings is rotating freely to give rise to two signals each integrating for two protons, while the other group is experiencing restricted rotation resulting in four resonances integrating for one proton each. Since the configuration at C₅/C₆ is diaxial, the dimethylaminophenyl ring at position 5 is in an equatorial position and would be free to rotate according to a stereomodel of **54**. By contrast, the other ring on the enol side of the molecule at position 3 would be restricted in rotation if it is in an axial position and would give rise to four signals in the ¹H NMR spectrum. As this was the case, the H₃ proton must therefore be in an equatorial position while the dimethylaminophenyl group is axial. Such configuration at C₃ is consistent with the observation of two methyl signals for the dimethylaminophenyl groups in phosphorinanone isomer **54**. All attempts to grow suitable crystals of compound **54** for single crystal X-ray crystallography failed. A boron adduct was therefore made by reacting **54** with borane–dimethyl sulfide in THF. More than one site on **54** was boronated but the exact structure could not be determined by NMR and all crystallisation attempts were unsuccessful. The NMR data for phosphorinanone isomer **54** are compiled in Tables 2.1 and 2.2 on page 34.

NMR analysis of a sample containing phosphorinanone isomers **53** and

Figure 2.3. Expanded-scale displays of 1D traces from a coupled HSQC spectrum of phosphorinanone isomer **54** at the frequency of the corresponding carbon atoms for (a) H₅ and (b) H₆, CDCl₃, 600 MHz.

54 also showed a complete set of signals corresponding to a second enolic isomer (**57**) which resonated at 17.5 ppm in the ³¹P NMR spectrum. The dimethylaminophenyl and the carbomethoxy groups at positions 5 and 6 are both equatorial because a large diaxial coupling constant of 12.7 Hz was observed between H₅ and H₆. The H₃ proton displayed no phosphorus coupling as it resonated as a singlet at 4.13 ppm. Meanwhile, four signals in a ratio of 2:2:2:2 were observed for the aromatic protons, suggesting free rotation for both of the dimethylaminophenyl rings. To assign a molecular structure to the minor enolic isomer **57**, the configuration at C₃ is very important. Since no restricted rotation was observed for the aryl groups, the dimethylaminophenyl group at position 3

must be equatorial. So far the substituent arrangement in isomer **57** is the same as isomer **53**. Considering that the enol tautomer of **53** was never observed, for the enolic isomer **57** to be different from **53**, the Bu^t group on phosphorus atom has to be in an axial position even though such arrangement has not been observed before. The ¹H and ¹³C NMR parameters for phosphorinanone isomer **57** are summarised in Tables 2.1 and 2.2 respectively.

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Keto-enol tautomerism has also been observed in nitrogen⁷⁶ and sulfur⁷⁷ analogues of the phosphorinanones (Figure 2.4). Galvez *et al.*⁷⁶ reported a tautomer (**58**) and a configurational isomer (**59**) for piperidinone **60**, a key intermediate in the synthesis of bispidinones as new GABA_B receptor antagonists. However, the authors offer no evidence for the equilibrium between piperidinones **58** and **59**. Additionally, Chen and co-workers⁷⁷ observed the formation of **61** from the reaction of the dibenzylideneacetone derivative **38** with H₂S in connection with the synthesis of 4H-thiopyrans. The nitrogen and sulfur enol isomers were isolated and characterised but were not used in any further reactions.

Table 2.1. ^1H NMR data of phosphorinanone isomers **53**, **54** and **57**.

Group	53	54	57
H ₂	3.97 (dd, 12.7 Hz, 5.4 Hz)	—	—
H ₃	3.59 (dd, 12.7 Hz, 5.9 Hz)	3.90 (m)	4.13 (s)
H ₅	3.59 (dd, 12.7 Hz, 5.9 Hz)	3.90 (m)	3.78 (dd, 12.6 Hz, 3.2 Hz)
H ₆	3.97 (dd, 12.7 Hz, 5.4 Hz)	4.28 (d, 5.9 Hz)	4.42 (dd, 12.6 Hz, 1.0 Hz)
OMe	3.51 (s)	3.62 (s)	3.58 (s)
		3.66 (s)	3.61 (s)
NMe ₂	2.91 (s)	2.91 (br s)	2.90 (s)
		2.95 (br s)	2.90 (s)
Bu ^t	0.63 (d, 10.7 Hz)	0.52 (d, 11.6 Hz)	0.96 (d, 11.3 Hz)
OH	—	12.84 (s)	13.13 (s)

Spectra obtained in CDCl₃. Chemical shifts in ppm. Multiplicity and coupling constants given in parentheses.

Table 2.2. ^{13}C NMR data of phosphorinanone isomers **53**, **54** and **57**.

Group	53	54	57
C ₁	199.4 (d, 3.4 Hz)	168.3 (d, 6.2 Hz)	169.9 (s)
C ₂	65.4 (d, 15.8 Hz)	103.8 (d, 9.0 Hz)	99.9 (d, 2.8 Hz)
C ₃	42.3 (d, 19.7 Hz)	35.2 (d, 24.1 Hz)	34.5 (d, 13.5 Hz)
C ₅	42.3 (d, 19.7 Hz)	36.5 (d, 19.1 Hz)	34.3 (d, 21.3 Hz)
C ₆	65.4 (d, 15.8 Hz)	57.3 (d, 17.4 Hz)	48.1 (d, 2.0 Hz)
COO	168.2 (d, 10.6 Hz)	172.6 (d, 13.2 Hz)	172.6 (d, 6.7 Hz)
		172.8 (d, 6.7 Hz)	173.1 (s)
OMe	52.1 (s)	52.6 (s)	52.0 (s)
		52.4 (s)	52.0 (s)
NMe ₂	40.6 (s)	40.7 (br s)	40.0 (s)
		40.8 (br s)	40.0 (s)
C(CH ₃) ₃	28.7 (d, 10.1 Hz)	27.6 (d, 12.3 Hz)	29.8 (d, 13.7 Hz)
C(CH ₃) ₃	30.9 (d, 20.6 Hz)	30.2 (d, 21.3 Hz)	31.7 (d, 30.9 Hz)

Spectra obtained in CDCl₃. Chemical shifts in ppm. Multiplicity and coupling constants given in parentheses.

Figure 2.4. Keto-enol tautomers of piperidinones and thiopyrans.

2.2 PN ligand synthesis

The four classes of phosphorinanone compounds were reacted with different amines and aldehydes in the Mannich reaction to synthesise bicyclic phosphorus-nitrogen ligands. To construct the nitrogen-containing ring, two consecutive Mannich reactions (first inter- and then intramolecularly) are required at the α -positions to the central carbonyl group in the phosphorinanone compounds.

2.2.1 4-Phenylphosphorinanone

The Mannich reaction of 4-phenylphosphorinanone (**42**) with formaldehyde in ethanol was attempted with three different amines, namely methylamine, cyclohexylamine and benzylamine (Scheme 2.6). Numerous products were formed as indicated by the number of signals in the ^{31}P NMR spectrum.

Extensive NMR analyses yielded no useful information on whether PN bicyclic compounds were produced in these reactions.

Scheme 2.6

2.2.2 3,5-Diphenyl phosphorinanones

Samples containing predominantly the asymmetric phosphorinanone isomer **44** were subjected to typical Mannich reaction conditions using methylamine and formaldehyde in boiling ethanol (Table 2.3). Many products were obtained from the reactions as shown by the plethora of signals in the ^{31}P NMR spectrum. Changing the reactants gave similar results, except for *t*-butylamine which did not react at all, probably due to steric reasons. All efforts were made to purify the products, including the use of column chromatography, and extensive NMR analyses were performed on the mixture of products but no reasonable conclusions could be drawn about the synthesis of bicyclic PN ligands.

2.2.3 2,6-Dimethyl phosphorinanones

The synthesis of PN compounds from phosphorinanone isomers **50** and **51** was attempted. A summary of all Mannich reaction conditions used are compiled in Table 2.4. No reaction was observed between the phosphorinanones and methylamine and formaldehyde in ethanol for different reaction times. Addition of either acid or base (as the Mannich reaction can be done under acidic or basic conditions) resulted in the isomerisation of the asymmetric isomer **50** into **51**. The use of different amines, aldehydes and solvents was also unsuccessful, as was

Table 2.3. Summary of Mannich reaction conditions of 3,5-diphenyl phosphorinanone isomers **44** and **45**.

Amine	Aldehyde	Solvent	Temp	Time	Result
MeNH ₂	CH ₂ O	EtOH	reflux	24 hr	Unidentifiable products
Bu ^t NH ₂	CH ₂ O	EtOH	reflux	43 hr	No reaction
PhCH ₂ NH ₂	CH ₂ O	EtOH	reflux	43 hr	Unidentifiable products
CyNH ₂	CH ₂ O	EtOH	reflux	24 hr	Unidentifiable products
CH ₃ CO ₂ NH ₄	anisaldehyde	EtOH	reflux	24 hr	Unidentifiable products
MeNH ₂	CH ₂ O	MeCN	reflux	24 hr	Unidentifiable products
MeNH ₂	CH ₂ O	MeOH	reflux	24 hr	Unidentifiable products

the attempted reaction under microwave conditions. In view of these results, a double Mannich reaction was perhaps not feasible with this phosphorinanone system. Thus, a single Mannich reaction was attempted with Me₂NH and its hydrochloride salt but neither produced the desired products.

The outcome from the Mannich reactions of the dimethyl phosphorinanones was surprising as analogous bispidinone compounds with methyl substituents at the α -positions to the central carbonyl group have been reported.^{31,32} Such bispidinones were prepared by the Mannich condensation reaction with the aldehyde, ketone and amine components present in the reaction mixture in a 4:1:2 ratio. However the yields were very low, never exceeding 18%. This suggests that diethyl ketone is not effective as the ketonic substrate in these syntheses. The methyl groups could be deactivating the α -positions to the carbonyl group, hence disfavours a double Mannich reaction. Further support for such a hypothesis came from work published by Omarov and co-workers.⁷⁸ They report the successful condensation of 3,5-diphenylpiperidinone (**62**) and 2-methyl-3,5-diphenylpiperidinone (**63**) to the corresponding bispidinone compounds,

Table 2.4. Summary of Mannich reaction conditions of 2,6-dimethyl phosphorinanone isomers **50** and **51**.

Amine	Aldehyde	Solvent	Temp	Time	Other reactants	Result
MeNH ₂	CH ₂ O	EtOH	reflux	12 hr	—	No reaction
MeNH ₂	CH ₂ O	EtOH	reflux	24 hr	—	No reaction
MeNH ₂	CH ₂ O	EtOH	reflux	4 days	—	No reaction
MeNH ₂	CH ₂ O	EtOH	reflux	5 hr	acetic acid	Isomerisation of SM*
MeNH ₂	CH ₂ O	EtOH	reflux	24 hr	acetic acid	Isomerisation of SM
MeNH ₂	CH ₂ O	EtOH	reflux	24 hr	NaOEt	Isomerisation of SM
MeNH ₂	CH ₂ O	MeCN	reflux	18 hr	TsOH	No reaction
MeNH ₂	CH ₂ O	MeCN	reflux	18 hr	piperidine	Isomerisation of SM
PhCH ₂ NH ₂	PhCHO	EtOH	reflux	24 hr	—	No reaction
PhCH ₂ NH ₂	PhCHO	EtOH	microwave, 80 °C	10 min	—	No reaction
PhCH ₂ NH ₂	CH ₂ O	THF	RT	20 hr	—	No reaction
CH ₃ CH ₂ NH ₂	CH ₂ O	THF	RT	18 hr	NaOEt	Isomerisation of SM
CH ₃ CO ₂ NH ₄	anisaldehyde	EtOH	reflux	24 hr	—	No reaction
Me ₂ NH	CH ₂ O	EtOH	reflux	24 hr	—	No reaction
Me ₂ NH HCl	CH ₂ O	EtOH	reflux	24 hr	HCl	Isomerisation of SM

*Starting Material.

p-Toluenesulfonic acid.

although the rate of condensation of **63** was much slower than **62**, but 2,6-dimethyl-3,5-diphenylpiperidinone (**64**) did not react at all (Scheme 2.7). These observations suggest that a double Mannich reaction using diethyl ketone can be performed if the synthesis is carried out in one pot. However, the Mannich reaction is unsuccessful when 2,6-dimethyl piperidinones are used as the starting materials. As the results from this project have shown, the same is true for phosphorinanone isomers **50** and **51**.

Scheme 2.7

To investigate the degree of reactivity of the α -positions to the central carbonyl group in the dimethyl phosphorinanone isomers, a series of small scale exchange experiments were performed using samples containing mainly the symmetrical isomer **51** to obtain simpler NMR spectra (Table 2.5). Since basic amines are used in Mannich reactions, a H/D exchange experiment was carried out in MeOH-d₄ in the presence of diisopropylamine as it has a much

higher boiling point than methylamine. No deuterium exchange was observed at the α -positions. In light of this result, it is not so surprising that a complex double Mannich reaction was never observed with isomers **50** and **51**.

The H/D exchange was successful when performed in the presence of a strong base such as NaOMe. In the ^1H NMR spectrum, the two methyl substituents in phosphorinanone isomer **51** normally resonate as doublets due to coupling to the α -protons, but after the exchange only a singlet at 0.88 ppm was observed. The α -protons, which usually appear as a doublet of doublets due to coupling to the β -protons as well as phosphorus, now resonated as only a doublet at 2.99 ppm.

Following the success of the H/D exchange in the presence of NaOMe, a larger electrophile was used. The H/Me exchange reactions resulted in the formation of several unidentified products. However, performing a similar experiment in CDCl_3 at room temperature without any base produced a phosphonium ion as methylation had occurred on the phosphorus atom. The ^1H NMR spectrum of the phosphonium ion showed an extra doublet at 2.62 ppm (J_{PH} 12.5 Hz), while the ^{31}P NMR spectrum showed that the phosphorus atom in **51** was very deshielded as its signal shifted from 0.70 to 26.0 ppm. Formation of the phosphonium ion indicates that the phosphorus atom is nucleophilic and is competing with the enol form of **51** for the methyl electrophile. Finally, some exchange experiments were done under acidic conditions. The presence of sulfuric acid also resulted in the formation of many products that were not identified.

2.2.4 2,6-Diester phosphorinanones

Mannich reaction of phosphorinanone isomer **53**

The Mannich reaction of phosphorinanone isomer **53** with methylamine and two equivalents of formaldehyde in ethanol produced a bicyclic phosphorus-nitrogen compound (**65**) in good yields (Scheme 2.8). The PN compound crystallised out

Table 2.5. Summary of exchange experiments at the α -positions of 2,6-dimethyl phosphorinanone isomer **51**.

Electrophile	Solvent	Temp	Time	Other reactants	Result
D	MeOH-d ₄	reflux	15 min	—	No exchange
D	MeOH-d ₄	reflux	15 min	(Me ₂ CH) ₂ NH	No exchange
D	MeOH-d ₄	reflux	24 hr	(Me ₂ CH) ₂ NH	No exchange
D	MeOH-d ₄	reflux	15 min	NaOMe	Exchange at α -positions
CH ₃ /CH ₃ I	MeOH	reflux	30 min	NaOMe	Unidentifiable products
CH ₃ /CH ₃ I	MeOH	reflux	1 hr	NaOMe	Unidentifiable products
CH ₃ /CH ₃ I	MeOH	reflux	4 hr	NaOMe	Unidentifiable products
CH ₃ /CH ₃ I	MeOH	reflux	24 hr	NaOMe	Unidentifiable products
CH ₃ /CH ₃ I	CDCl ₃	RT	24 hr	—	Methylation on phosphorus
—	CDCl ₃	RT	15 min	H ₂ SO ₄ (1 drop)	Unidentifiable products
D	MeOH-d ₄	reflux	15 min	H ₂ SO ₄ (1 drop)	Unidentifiable products
D	MeOH-d ₄	reflux	15 min	H ₂ SO ₄ (10 drops)	Unidentifiable products

of the reaction mixture as white needles upon cooling and was air stable.

Scheme 2.8

The ^1H NMR spectrum of **65** in benzene- d_6 showed only half of the signals expected for this PN compound, implying symmetrical positions for the carbomethoxy and dimethylaminophenyl substituents, and for H_6 and H_8 . Four broad doublets between 6 and 9 ppm were observed indicating that the phenyl protons are magnetically inequivalent as a result of restricted rotation about the C–C bond. This was confirmed by variable temperature ^1H NMR experiments ranging from 20 to 70 °C (Figure 2.5). The signals of the *meta*-protons between 6 and 7 ppm gradually collapsed and coalesced at 60 °C, whereas the *ortho*-proton signals required higher temperatures to reach coalescence. The ^{31}P NMR spectrum showed a single peak at 8.4 ppm, and the IR spectrum was dominated by two carbonyl stretches at 1712 and 1733 cm^{-1} corresponding to the ketone and ester groups respectively.

Crystals of PN compound **65** were grown by the slow evaporation of a C_6D_6 solution and the X-ray crystal structure was determined (Figure 2.6). The solid state crystal structure shows a perfect mirror symmetrical chair-chair conformation with the carbomethoxy, dimethylaminophenyl, Me and Bu^t substituents in equatorial sites (Figure 2.7(a)). This conformation is favourable as the ligand is set up for metal complexation *via* both donor atoms to form a stable tricyclic quasi-adamantane structure. The 6,8-dimethylaminophenyl groups are constrained by the bicyclic framework to be in close proximity to

Figure 2.5. Variable temperature ^1H NMR spectra of PN compound **65** shown as expanded-scale display of the aromatic region, *ortho*-protons (**H**), *meta*-protons (**H**), C_6D_6 , 300 MHz.

Figure 2.6. ORTEP diagram of PN compound **65** (30% thermal ellipsoids). Hydrogen atoms omitted for clarity.

the metal (Figure 2.7(b)). This could lead to unusual coordination chemistry. Furthermore, the *X*-ray crystal structure also shows the unique out-of-plane protection that would be provided by the dimethylaminophenyl groups for coordinated metals. The crystallographic dimensions of PN compound **65** are very similar to its phenyl analogue **37**.⁴⁸ For example, the intramolecular distance between the phosphorus and nitrogen donor atoms is 2.9 Å in both PN compounds. This distance is also the same as the average NN distance in bispidinone compounds.³³ Some selected bond lengths and angles are given in Table 2.6, and the crystallographic parameters are summarised in Table 2.7.

Mannich reaction of phosphorinanone isomer **54**

The Mannich reaction of the enol phosphorinanone isomer **54** with formaldehyde and methylamine in ethanol gave highly unexpected results (Scheme 2.9). Removal of ethanol and washing the resulting yellow residue with diethyl ether several times yielded the symmetrical PN compound **65** (26%). The ether wash still contained small amounts of **65**. Taking the ether wash to dryness and washing the residue with hexane successfully separated the other products. The hexane-insoluble solid was identified as a new six-membered phosphorus-nitrogen compound (**66**) produced in very small yields (13%) and contaminated with compound **65**. Although PN compound **66** is air stable, the use of flash column chromatography for its purification was not successful as it decomposed on the column. It could, however, be further purified by washing several times with small volumes of ethyl acetate which dissolved most of PN compound **65** along with small amounts of **66**. The hexane wash contained the *E/Z* (**67**) isomers of 3-(*p*-dimethylaminophenyl)methyl-2-propenoate (37%), with the *E* isomer being dominant.

PN compound **66** was characterised by IR and NMR spectroscopy and mass spectrometry. Elemental analysis could not be performed due to contamination

Figure 2.7. Different views of PN compound **65** as determined by *X*-ray diffraction. The molecule lies on a crystallographic mirror plane through P, N and the central carbonyl group.

Table 2.6. Selected bond distances (Å) and angles (°) for PN compound **65**.

Bond distances (Å)		Bond angles (°)	
P1–C6	1.878(2)	C6–P1–C16	100.8(1)
P1–C16	1.907(2)	C5–C6–P1	114.0(1)
C6–C12	1.513(2)	C12–C6–P1	111.7(1)
C5–C6	1.572(2)	C8–C5–C6	110.9(1)
C5–C8	1.529(2)	C8–C5–C18	105.5(1)
C5–C13	1.533(2)	C13–C5–C18	108.7(1)
C5–C18	1.545(2)	C13–C5–C6	109.7(1)
N3–C15	1.458(3)	N3–C18–C5	109.1(1)
N3–C18	1.456(2)	C15–N3–C18	111.8(1)
O2–C8	1.211(3)	C12–C6–C5	112.0(1)

Table 2.7. Crystallographic data of PN compound **65**.

Empirical formula	$\text{C}_{32}\text{H}_{44}\text{N}_3\text{O}_5\text{P}$
Formula weight	581.67
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
a/Å	12.631(1)
b/Å	22.509(2)
c/Å	10.961(1)
$\alpha = \beta = \gamma /$	90
V/Å ³	3116.0
Z	4
Cell determination reflections	6817
Cell determination range, $\theta_{\min} - \theta_{\max} /$	2.46 — 25.13
Temperature/K	93(2)
Radiation type	Mo K α
Radiation (λ)/Å	0.71073
Crystal size/ mm	0.70 x 0.40 x 0.20
$D_{\text{calc}}/\text{g cm}^{-3}$	1.240
F(000)	1248
$\rho_{\text{calc}}/\text{mm}$	0.132
$T_{\max}, T_{\min}$	1.000, 0.881
Reflections collected	14215, $R_{\text{equiv}} = 0.0216$
Index range h	-15 — 14
Index range k	-26 — 17
Index range l	-12 — 13
$\Delta\rho_{\text{calc}}/\text{range}/$	2.46 — 25.17
Independent reflections	2868
Reflections [$I \geq 2\sigma(I)$]	2497
Restraints/parameters	0/286
GOF	0.822
$R [I \geq 2\sigma(I)]$	0.038
wR2 [$I \geq 2\sigma(I)$]	0.15
R [all data]	0.045
wR2 [all data]	0.18

Scheme 2.9

with **65**, but HRESIMS analysis confirmed the molecular formula of compound **66**. The IR spectrum of **66** showed a carbonyl stretch at 1744 cm^{-1} and an amide stretch at 1655 cm^{-1} . The phosphorus atom in **66** resonated at -3.5 ppm in the ^{31}P NMR spectrum in CDCl_3 . In the ^1H NMR spectrum, the axial and equatorial protons of the CH_2 group each appeared as a doublet of doublets at 2.84 and 3.03 ppm with J_{HH} of 14.5 Hz . The phosphorus coupling constants were vastly different between the two protons; 18.0 Hz for proton at 3.03 ppm and only 2.6 Hz for its geminal partner. The protons in positions 5 and 6 were in a diaxial arrangement with a J_{HH} of 12.8 Hz indicating that the carbomethoxy and dimethylaminophenyl groups are in equatorial positions. The *t*-butyl group is expected to occupy an equatorial position for reasons discussed in Section 2.1.4. The preferred orientation of the N-methyl substituent should also be equatorial

since its ^{13}C chemical shift (36.6 ppm) is in agreement with equatorial disposition of N-substituents in piperidinone rings.⁷⁶

The results obtained from the Mannich reaction of phosphorinanone isomer **54** are abstruse. Firstly, the use of an asymmetric phosphorinanone such as isomer **54** in the Mannich reaction was hoped to produce an asymmetric PN compound. As this was not the case, formation of the symmetric PN compound **65** implies that some sort of isomerisation about the stereogenic centres in phosphorinanone **54** had taken place during the double Mannich reaction. Secondly, formation of compound **66** suggests that a side reaction was occurring under the Mannich conditions, which had not been observed before. Thirdly, the observation of the *E/Z* isomers of compound **67** could be the result of the side reaction, or perhaps the result of the complete decomposition of phosphorinanone **54** under such reaction conditions. Consequently, the behaviour of phosphorinanone isomer **54** under the Mannich conditions used is very difficult to understand.

2.3 Concluding remarks

The synthesis of bicyclic phosphorus-nitrogen compounds *via* the Mannich condensation reaction of a phosphorinanone, an amine and two equivalents of an aldehyde proved to be challenging. The nature of the substituents at the α -positions to the central carbonyl group in the phosphorinanone compounds had a great effect on the success of the double Mannich reaction. This was demonstrated by the 2,6-diester phosphorinanone system, from which the only PN bicyclic compound was produced. The electron-withdrawing ester groups enhanced the acidic character of the α -CH protons, and also resonance stabilised the enol form of the phosphorinanones. The presence of methyl substituents at the α -positions was detrimental to the success of the Mannich reaction, as

illustrated by the 2,6-dimethyl phosphorinanone system. The lack of reactivity can be attributed to the electron-donating nature of the methyl groups and their inability to stabilise the enol form of the phosphorinanones. The remaining 3,5-diphenyl and 4-phenyl phosphorinanone systems had no α -substituents, but ascertaining whether the synthesis of any bicyclic PN compounds had been achieved was still difficult. Overall, these results suggest that a combination of steric and electronic factors govern the success of a double Mannich reaction in the different phosphorinanone systems examined in this project.

The newly synthesised bicyclic PN compound **65** adopted a rigid chair-chair conformation both in solution and the solid state. This structural feature presets a bidentate capability and ensures that the nitrogen donor group remains in close proximity to the metal centre in non-chelating situations. The coordination chemistry of the novel PN ligand will be explored with transition metals.

Chapter 3

Transition Metal Complexes of Phosphorus-Nitrogen Ligands

The coordination chemistry of the phosphorus nitrogen ligand 7-*t*-butyl-1,5-di(carbomethoxy)-6,8-bis(*p*-dimethylaminophenyl)-3-methyl-3-aza-7-phosphabicyclo[3.3.1]nonan-9-one (**65**) was explored extensively through a series of complexation reactions with rhodium, palladium and platinum metal precursors. The PN ligand is capable of chelating to the metal centres by binding through both donor atoms, or it can coordinate *via* only the phosphorus atom depending on the nature of the metal and the ancillary ligands. All reactions were studied by NMR spectroscopy, and where feasible the *X*-ray crystal structures were determined.

3.1 Metal(II) complexes

Platinum methyl compound

Metal alkyls constitute some of the earliest examples of organometallic complexes. They are of intrinsic importance in catalysis as they represent key intermediates in many catalytic reactions involving hydrocarbons and transition

metals.⁷⁹

The reaction of the PN ligand **65** with $[\text{PtMe}_2(1,5\text{-hexadiene})]$ in benzene at room temperature resulted in the quantitative formation of the square planar complex $[\text{PtMe}_2(\mathbf{65})]$ (**68**) as an off-white solid (Scheme 3.1). Two carbonyl stretches were observed in the IR spectrum at 1743 and 1721 cm^{-1} , corresponding to the ketone and ester groups respectively. These values are slightly higher than the corresponding values in the ligand itself.

Scheme 3.1

The ^1H NMR spectrum of complex **68** showed half the expected signals for the coordinated PN ligand **65**, indicating that it has retained its plane of symmetry upon complexation to platinum. Restricted rotation of the aryl rings was still observed as it resulted in four aromatic resonances in the ^1H NMR spectrum. This was the case in all the coordination compounds of PN ligand **65**.

The most dramatic change in the ^1H NMR spectrum of PN ligand **65** upon complexation was the pronounced downfield shift of one set of the *ortho*-protons of the dimethylaminophenyl groups. The *ortho*-protons shifted from 8.17 ppm in the free ligand to 10.32 ppm in complex **68**. This effect was attributed to the close proximity of the *ortho*-protons to the metal centre. The *ortho*-protons of the other set were less affected by the metal as they resonated at 7.04 ppm (*cf.* 7.27 ppm in the free ligand). Complex **68** had a ^{31}P signal at 26.6 ppm with a relatively small J_{PtP} of 1882 Hz, indicating that the phosphorus nucleus is *trans* to a ligand with a strong *trans*-influence, i.e. a methyl group.

The NMR signals for the methyl groups were differentiated as a result of

being *trans* to the different donor atoms: the methyl group *trans* to phosphorus resonated as a doublet at 1.38 ppm (J_{PH} 7.4 Hz) with platinum coupling of 65 Hz, whereas the *cis* methyl appeared as a doublet at 1.59 ppm (J_{PH} 6.7 Hz) but with a slightly larger coupling to platinum (J_{PtH} 92 Hz). The effects of the inherently different donor atoms on the respective *trans*-positions on the metal were more pronounced in the ^{13}C NMR chemical shifts of the methyl groups: the methyl *trans* to phosphorus appeared as a doublet at 13.7 ppm with a very large phosphorus coupling constant of 112.6 Hz and J_{PtP} of 711 Hz, whereas the methyl group *trans* to nitrogen was observed at -23.0 ppm with a small J_{PC} of 3.8 Hz, but a larger platinum coupling constant of 782 Hz. Therefore, the NMR data strongly suggests that PN ligand **65** is bonded to platinum *via* both donor atoms in complex **68** as the two methyl groups are in very distinct chemical environments. This in turn implies that PN ligand **65** has maintained its chair-chair conformation upon metal coordination and that no dynamic processes are occurring in solution at room temperature.

Palladium chloro compound

Halide ligands are ubiquitous in coordination chemistry. Transition metal halide complexes are important both in catalysis and as synthetic precursors for the construction of new molecules. Some halide complexes also have medicinal applications, for example the anti-cancer drug cisplatin (*cis*-[PtCl₂(NH₃)₂]).⁸⁰

Treatment of [PdCl₂(NCMe)₂] with PN ligand **65** in dichloromethane afforded the complex [PdCl₂(**65**)] (**69**) in good yield (Scheme 3.2). The ^1H NMR spectrum of **69** showed half a set of signals for PN ligand **65** indicating a plane of symmetry, with a pronounced downfield shift of one set of the aromatic *ortho*-protons to 9.70 ppm due to close proximity to the palladium metal centre. The IR spectrum showed two carbonyl stretches at 1744 and 1728 cm⁻¹, and the phosphorus atom resonated at 27.0 ppm in the ^{31}P NMR spectrum.

Scheme 3.2

The crystal structure of **69** was determined from crystals obtained by the slow diffusion of diethyl ether into a dichloromethane-benzene solution (Figure 3.1). Some bond lengths and angles are summarised in Table 3.1 and other crystallographic parameters are compiled in Table 3.2. The structure shows a square planar complex (Figure 3.2) and a perfectly symmetrical PN ligand, which supports the evidence from the ¹H NMR spectrum. It also shows the out-of-plane protection for the metal centre provided by the dimethylaminophenyl groups. The effect of the different donor atoms on the respective *trans*-positions on the metal is very evident in the Pd–Cl bond lengths. The Pd–Cl bond *trans* to phosphorus (2.361(3) Å) is comparatively longer than the Pd–Cl bond *trans* to nitrogen (2.269(3) Å). The degree of ligand rigidity and preorganisation is retained upon complexation to the palladium metal as the distance between the phosphorus and nitrogen donor atoms is 3.0 Å, which is very similar to the free ligand (*cf.* 2.9 Å).

In addition to the formation of complex **69**, a minor complex **70** was also observed in solution. Based on peak intensity in the ³¹P NMR spectrum, the minor complex formed in a 1:3 ratio to complex **69** and exhibited similar NMR features. For example, the ³¹P NMR signal was observed at 25.2 ppm compared to 27.0 ppm for complex **69**. One significant difference between the two complexes was found in the ¹³C NMR spectrum: no carbonyl signal for **70** was apparent, and a peak at 94.5 ppm was observed instead. HMBC

Figure 3.1. ORTEP diagram of $[\text{PdCl}_2(\mathbf{65})]$ complex (**69**) (30% thermal ellipsoids). Hydrogen atoms omitted for clarity.

Table 3.1. Selected bond distances ($\text{\AA}$) and angles ($^\circ$) for complex $[\text{PdCl}_2(\mathbf{65})]$ (**69**).

Bond distances ($\text{\AA}$)		Bond angles ($^\circ$)	
Pd1–Cl1	2.361(3)	P1–Pd1–N1	86.1(2)
Pd1–Cl2	2.269(3)	Cl1–Pd1–Cl2	86.3(1)
Pd1–N1	2.142(6)	P1–Pd1–Cl1	171.8(1)
Pd1–P1	2.238(2)	P1–Pd1–Cl2	93.0(1)
P1–C2	1.853(7)	N1–Pd1–Cl1	95.5(2)
N1–C15	1.48(1)	N1–Pd1–Cl2	173.3(1)
C15–C4	1.52(1)	C2–P1–C2	101.9(3)
C2–C4	1.54(1)	C15–N1–C15	111.2(6)
C4–C7	1.54(1)	C4–C7–C4	112.5(7)
C7–O2	1.18(1)		

Table 3.2. Crystallographic data of complex [PdCl₂(**65**)] (**69**).

Empirical formula	C ₃₂ H ₄₄ N ₃ O ₅ PCl ₂ Pd
Formula weight	758.97
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.453(1)
b/Å	12.746(1)
c/Å	17.665(2)
$\alpha/^\circ$	70.026(3)
$\beta/^\circ$	84.257(3)
$\gamma/^\circ$	70.217(3)
V/Å ³	2081.3
Z	2
Cell determination reflections	7938
Cell determination range, $\theta_{\min}$ — $\theta_{\max}/^\circ$	2.26 — 30.49
Temperature/K	131(2)
Radiation type	Mo K α
Radiation (λ)/Å	0.71073
Crystal size/ mm	0.75 x 0.75 x 0.28
D _{calc} /g m ⁻³	1.211
F(000)	784
ρ_{calc} /mm	0.65
T _{max} , T _{min}	1.000, 0.667
Reflections collected	14667, $R_{\text{equiv}} = 0.0334$
Index range h	-14 — 14
Index range k	-18 — 14
Index range l	-24 — 24
range/ hkl	1.80 — 30.60
Independent reflections	10441
Reflections [$I \geq 2\sigma(I)$]	6768
Restraints/parameters	0/407
GOF	1.436
R [$I \geq 2\sigma(I)$]	0.12
wR2 [$I \geq 2\sigma(I)$]	0.32
R [all data]	0.18
wR2 [all data]	0.35

Figure 3.2. Different views of complex $[\text{PdCl}_2(\mathbf{65})]$ (**69**) as determined by *X*-ray diffraction.

correlations to this carbon atom were observed from two signals in the ^1H NMR spectrum in CDCl_3 : from 6.56 ppm (overlapping with the *meta*-aromatic protons) and a sharp singlet at 6.64 ppm. The two ^1H NMR signals lacked direct C–H correlations in the ^1H – ^{13}C HSQC spectrum, indicating that they were bound to a heteroatom. Further HMBC correlations were observed from the new ^1H NMR resonances to the quaternary α -carbon atom at 57.5 ppm. A third HMBC correlation was also observed from the resonance at 6.64 ppm to the ester carbonyl groups at 170.9 ppm. These NMR results indicate that the central carbonyl group in ligand **65** had been hydrated to a geminal diol upon complexation to palladium to produce the hydrated minor complex **70**. The ^{13}C resonance at 94.5 ppm corresponds to the hydrated carbon atom and the two ^1H NMR signals at 6.56 and 6.64 ppm are the hydroxylic protons (Figure 3.3). The two OH groups are expected to be in different chemical environments, and the hydroxylic protons have the possibility of hydrogen bonding to the ester carbonyl groups to form stable six-membered rings. The IR spectrum of complex **70** further supported the presence of the hydroxyl groups as a broad OH peak was observed at 3423 cm^{-1} .

To further confirm the presence of the hydroxyl groups, a drop of D_2O

Figure 3.3. HMBC correlations for the hydrated analogue of complex $[\text{PdCl}_2(\mathbf{65})]$ (**70**). Correlations from only the OH proton at 6.64 ppm are shown for clarity.

was added to a NMR sample containing both the ketone and hydrate forms of $[\text{PdCl}_2(\mathbf{65})]$ and the ^1H NMR spectrum was recorded (Figure 3.4). The spectrum showed the disappearance of the sharp peak at 6.64 ppm, while small changes were noted for the overlapping signals at 6.56 ppm. This experiment demonstrated the exchangeability of the two hydroxylic protons with deuterium ions, and hence their disappearance from the ^1H NMR spectrum.

Formation of the hydrated complex **70** was surprising as the reaction and all manipulations were done under an inert atmosphere using freshly distilled solvents. The volume of water required to hydrate one third of 100 mg of $[\text{PdCl}_2(\mathbf{65})]$ was calculated to be 0.8 μL , which equates to 0.013% in 6 cm^3 of CH_2Cl_2 . Such a small volume of water could still be present in the distilled solvent or on the surface of the glassware being used. The ketone and hydrate complexes were separable in the solid state as the crystal selected for *X*-ray crystallography consisted only of ketone molecules. However, no crystals of the hydrate were isolated.

To study the relationship between the ketone (**69**) and hydrate (**70**) forms of $[\text{PdCl}_2(\mathbf{65})]$, a NMR experiment was carried out in which water was added to a NMR sample containing both complexes. The 3:1 ketone to hydrate ratio did

Figure 3.4. ^1H NMR spectra of the ketone (**69**) and hydrate (**70**) forms of $[\text{PdCl}_2(\mathbf{65})]$ complex, shown as expanded-scale displays of the aromatic regions, CDCl_3 , 600 MHz: (a) experimental spectrum; (b) with D_2O .

not change, suggesting that the two complexes are not in equilibrium.

Hydrate formation upon complexation to metal ions is well known in bispidinone coordination chemistry. Numerous examples of palladium, platinum and first-row transition metal complexes containing bispidinone ligands in which the central carbonyl group has been hydrated to the corresponding geminal diol have been reported.^{31–33} In addition, if the complexation reaction is carried out in methanolic solutions then the carbonyl group is converted into a hemiacetal ($\text{MeO}-\text{C}-\text{OH}$) functionality.^{81,82} Hydration of coordinated bispidinone ligands is generally observed if the complexation reactions are not performed under strictly water-free conditions. Furthermore, hydration only seems to occur for

bispidinone ligands with ester substituents at the α -positions to the carbonyl group. Bispidinone ligands with Ph, SPh and Me groups at the α -positions form only the keto-complexes. This observation is very apparent from studies by Comba *et al.*,³³ but is somewhat ambiguous from results published by Black and co-workers.³¹ The latter reported twelve bispidinone complexes, half of which contain varying amounts of water that is treated as water of crystallisation. As no crystal structures or ^{13}C NMR data are given for the complexes in question, the nature of the interaction between water and the bispidinone complexes is difficult to determine.

Since free bispidinone ligands do not undergo voluntary hydration, metal coordination must considerably enhance the reactivity of the carbonyl group. This might involve an increase of the electron deficit at the carbonyl carbon atom *via* an inductive effect. If this is the case, then the nucleophilic addition of water to the carbonyl carbon atom followed by a series of proton transfers would result in the formation of the geminal diol.⁶³ Furthermore, the presence of ester substituents at the α -positions to the carbonyl group would further stabilise the OH groups through hydrogen bonding. Thus, trace amounts of water in the reaction medium or on the surface of glassware could lead to the formation of hydrated complexes. Hydration of the bispidinone ketone group appears to have negligible effect both experimentally and computationally on the geometry and, more importantly, the electronic structure and relative energies of the resultant metal complexes.^{33,83}

As no hydration of the central carbonyl group in the free PN ligand **65** has been observed, formation of the hydrated complex **70** could be attributed to similar reasons as for the hydrated bispidinone complexes. Interestingly, complete hydration of bispidinone ligands occurs upon metal complexation, whereas only a third of the PN ligand was hydrated to form complex **70**.

3.2 Rhodium complexes

Rhodium containing compounds are important in homogeneous catalysis. Examples of Rh(I) catalysts include Wilkinson’s catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$, for the hydrogenation of unhindered alkenes, and rhodium complexes bearing chiral phosphine ligands for asymmetric hydrogenation reactions.⁸⁴ The coordination chemistry of PN ligand **65** with Rh(I) was studied as rhodium has many similarities to platinum and palladium.

The addition of the PN ligand **65** to $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ in dichloromethane in a 2:1 ratio at room temperature resulted in no reaction (Scheme 3.3), but abstraction of the chloride ions with AgSbF_6 afforded the four-coordinate complex $[\text{Rh}(\text{cod})(\textbf{65})]\text{SbF}_6$ (**71**). The ^{31}P NMR spectrum of **71** showed a doublet at 21.9 ppm due to rhodium coupling (J_{RhP} 149.4 Hz). The PN ligand retained its plane of symmetry upon complexation as evident by the simple ^1H NMR spectrum and the downfield shift of one set of the *ortho*-protons to 9.72 ppm. The COD NMR resonances reflected the rigidity of the PN ligand and the asymmetry imposed by the different donor atoms on the metal centre as two sets of COD–CH signals were observed. The CH protons resonated as doublets at 4.54 (J_{PH} 2.4 Hz) and 5.68 ppm (J_{PH} 2.6 Hz), while the respective carbon atoms appeared at 73.5 (d, J 11.3 Hz) and 105.1 ppm ($J_{\text{PC}} + J_{\text{RhC}}$ 14.9 Hz). The latter ^{13}C NMR signal at 105.1 ppm was an apparent triplet due to the overlap of two doublets from which the exact magnitude of each coupling constant was difficult to determine, hence the sum of the two coupling constants is reported. Since both phosphorus and rhodium nuclei are NMR active ($I = 1/2$), the couplings exhibited by the COD–CH ^{13}C NMR resonances are not distinguishable as they could be due to either nuclide.

The COD NMR data are consistent with **71** being a four-coordinate Rh(I) complex containing a bidentate phosphorus-nitrogen ligand.²³ Comparison may be made with the PTN ligand **10** as it has a similar carbon framework

Scheme 3.3

to PN ligand **65**. PTN forms the complexes $[\text{RhCl}(\text{cod})(\text{PTN})]$ (**15**) and $[\text{Rh}(\text{cod})(\text{PTN})]\text{BAr}^{\text{F}}$ (**72**) ($\text{BAr}^{\text{F}} = \text{B}[3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3]_4$) (Scheme 3.4).²³ The formation of the monodentate PTN complex **15** is possible due to the considerably smaller size of the PTN ligand compared with PN ligand **65**. As in complex **71**, one set of the COD–CH groups in the PTN complex **72** was also shifted upfield to 3.56 ppm ($\delta_{\text{C}} 71.0$ ppm), while the other group resonated at 5.30 ppm ($\delta_{\text{C}} 109.1$ ppm). The upfield chemical shifts in complex **72** were attributed to the ring current generated by the π -system of the phenyl substituent on phosphorus resulting in shielding of one of the COD–CH groups. However, this explanation cannot be valid for PN complex **71** as there is no phenyl group on the phosphorus donor atom. A more plausible explanation for the disparity in the chemical shifts of the two COD–CH groups is the different *trans*-influence of the phosphorus and nitrogen donor atoms.

The minor hydrated analogue (**73**) of complex **71** was also observed in solution. Complex **73** formed in a 1:3 ratio and had similar NMR data as **71**. For example, a ^{31}P NMR signal was observed at 20.3 ppm with J_{RhP} of 146.2 Hz. The different COD–CH groups resonated at 4.44 ($J_{\text{PH}} 2.4$ Hz) and 5.55 ppm (J_{PH}

Scheme 3.4

2.8 Hz). The respective COD–CH ^{13}C NMR signals were observed at 72.6 and 103.7 ppm, and the hydrated carbon atom resonated at 94.5 ppm. Hydroxylic protons were observed in the ^1H NMR spectrum at 6.38 and 6.42 ppm, which also displayed ^1H – ^{13}C HMBC correlations to the hydrated carbon atom at 94.5 ppm and the quaternary β -carbon atom at 57.4 ppm. Finally, an absorption at 3434 cm^{-1} was observed in the IR spectrum consistent with the presence of the OH groups in complex **73**.

3.3 Alkene complexes

Transition metal alkene complexes are the oldest class of organometallic compounds known and they have been extensively studied. The most famous example, Zeise’s salt ($\text{K}[\text{Pt}(\eta - \text{C}_2\text{H}_4)\text{Cl}_3]$),⁸⁵ was first reported in 1830, and is considered the prototype for the classic Dewar-Chat-Duncanson model for bonding in transition metal alkene complexes.⁸⁶ Metal alkene complexes are used as precursors for the synthesis of new coordination compounds, as well as being important in homogeneous catalysis as they represent key catalytic intermediate species.

Reaction with tris(norborn-2-ene)platinum

Addition of PN ligand **65** to a solution of $[\text{Pt}(\text{norb})_3]$ in benzene afforded the 16-electron complex $[\text{Pt}(\text{norb})(\textbf{65})]$ (**74**) (Scheme 3.5) in high yields. The ^1H and ^{13}C NMR spectra in CD_2Cl_2 were simple, indicating that the PN ligand is in a symmetrical environment as a result of dynamic behaviour, such as free rotation about the Pt–alkene bond. In the ^1H NMR spectrum, one set of the phenylic *ortho*-protons gave rise to a distinctive doublet at 9.26 ppm, and the norborn-2-ene olefinic protons appeared at 2.08 ppm as a broad singlet with J_{PtH} of 77 Hz. Surprisingly, the ^1H and ^{13}C signals for the NMe group showed coupling to phosphorus as well. The methyl protons appeared as a doublet at 3.71 ppm, J_{PH} 1.9 Hz, and the carbon atom was observed at 62.9 ppm with J_{PC} of 4.5 Hz. This is the only instance in which the NMe group displayed phosphorus coupling and it must reflect the unusual bonding in complex **74**.

The ^{13}C NMR signal for the contact carbon atoms of the coordinated alkene resonated at 46.7 ppm as a doublet, due to phosphorus coupling through the metal centre (J_{PC} 27.8 Hz), with J_{PtC} of 469 Hz. A similar coupling pattern was observed for the carbon atom of the non-bridgehead CH_2 groups in norborn-

Scheme 3.5

2-ene at 30.2 ppm with J_{PC} of 5.5 Hz and J_{PtC} of 77 Hz. The ^{31}P NMR spectrum of **74** showed a single resonance at 47.5 ppm with ^{195}Pt coupling of 3559 Hz. All attempts at crystallisation failed partly due to complex **74** being very fragile in solution even under an inert atmosphere. As a solid, complex **74** is air stable but cannot be stored for prolonged periods of time.

Reaction with tris(ethene)platinum

Treatment of an ethene-saturated solution of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ with PN ligand **65** in benzene- d_6 immediately formed $[\text{Pt}(\text{C}_2\text{H}_4)(\textbf{65})]$ complex (**75**) (Scheme 3.6). After 10 minutes at room temperature, a second ethene complex (**76**) was observed, which will be discussed in detail in section 3.5. Monitoring the reaction mixture by ^1H and ^{31}P NMR showed that the initial ethene complex **75** was slowly converting into **76**, and that the conversion process was complete after one day. Consequently, complex **75** was never isolated for analysis without any conversion occurring. The conversion process between the two ethene complexes ceases at -10°C .

The ^1H and ^{31}P NMR spectra of complex **75** recorded at -10°C were similar to spectra recorded within 10 minutes of reaction at room temperature. Thus, the ^1H NMR spectrum at room temperature showed a symmetrical PN ligand with a characteristic downfield shift of one set of the aromatic *ortho*-protons to 9.78 ppm. Only one signal was observed for the ethene protons at 3.22 ppm,

Scheme 3.6

which appeared as a doublet (J_{PH} 1.9 Hz, J_{PtH} 16 Hz) and integrated for four protons. This indicated the presence of only one coordinated ethene unit in complex **75**, which is rotating freely about the Pt–alkene bond. A ^{13}C NMR spectrum was also obtained at -10°C in which the coordinated ethene carbon atoms resonated at 64.7 ppm as a broad singlet with no distinguishable ^{195}Pt satellites due to the weak spectrum. Complex **75** had a ^{31}P NMR signal at 47.5 ppm with platinum coupling of 3727 Hz.

Reaction with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$

Reaction of PN ligand **65** with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ in benzene resulted in the formation of the 16-electron complex $[\text{Pd}(\text{dba})(\text{65})]$ (**77**) (Scheme 3.7). The by-product from this reaction, free dba, could not be completely removed despite all purification efforts. Thus, complex **77** was always contaminated with free dba. The dba complex is remarkably air stable both as a solid and in solution,

Scheme 3.7

and is readily soluble in polar solvents but only moderately soluble in benzene and toluene. Complex **77** had a signal in the ^{31}P NMR spectrum at 33.6 ppm.

The ^1H and ^{13}C NMR spectra (Table 3.3) of complex $[\text{Pd}(\text{dba})(\mathbf{65})]$ showed that the coordinated PN ligand had no plane of symmetry. Furthermore, the observation of both coordinated and free alkene signals suggested that the dba ligand was bound to palladium through only one of the double bonds, and that no interchange was occurring between the coordinated and non-coordinated dba double bonds at room temperature on the NMR time scale. This in turn destroyed the symmetrical mirror plane found in metal-bound PN ligand **65**.

Table 3.3. NMR data of the olefinic positions of coordinated dba ligand in complex $[\text{Pd}(\text{dba})(\mathbf{65})]$ (**77**) and free dba.*

$$\text{Ph}-\underset{\beta}{\text{HC}}=\underset{\alpha}{\text{CH}}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{HC}=\text{CH}-\text{Ph}$$

	α		β	
$\text{HC}=\text{CH}$	^1H	^{13}C	^1H	^{13}C
coordinated	5.51 (d, 10.0 Hz)	59.8 (br s)	4.99 (br s)	66.9 (m)
non-coordinated	7.25 (m)	128.5 (s)	8.12 (d, 15.6 Hz)	137.2 (s)
free dba	6.88 (d, 15.9 Hz)	126.1 (s)	7.80 (d, 15.9 Hz)	142.7 (s)

*Spectra obtained in C_6D_6 . Chemical shifts in ppm. Multiplicity and coupling constants given in parentheses.

The ^1H NMR resonances of the coordinated dba double bond were found at 5.51 ppm for the β -proton and 4.99 ppm for the α -proton, while those of free dba appeared at 6.88 and 7.80 ppm respectively. The upfield shift of the β - and α -protons reflects the shielding effect of the palladium metal upon complexation. Conversely, the olefinic protons of the non-coordinated dba double bond were deshielded as their resonances were observed at 7.25 and 8.12 ppm respectively. The effect of metal coordination to only one of the dba double bonds was also evident in the ^{13}C NMR signals. The carbon atoms of the coordinated dba double bond resonated upfield at 59.8 and 66.9 ppm, while the other olefinic

carbon atoms were only affected to a small degree as they appeared at 128.5 and 137.2 ppm. The latter ^{13}C NMR signals are similar to the values in free dba (126.1 and 142.7 ppm). Moreover, the ^{13}C NMR resonance of the dba carbonyl group at 188.8 ppm showed unusual coupling (J_{PC} 2.2 Hz) to phosphorus through the metal *via* three bonds.

Two downfield signals at 8.99 and 9.57 ppm were observed for one set of the *ortho*-protons of the dimethylaminophenyl groups, which also had two non-equivalent methyl singlets at 2.46 and 2.50 ppm. In total, eight aromatic proton signals were observed owing to the absence of a symmetry plane in PN ligand **65**. Variable temperature ^1H and ^{31}P NMR studies were conducted in toluene- d_8 from -40 to 80 °C to explore any dynamic processes in **77**. No major changes were observed at low temperatures except for some signal broadening. On increasing the temperature, all PN ^1H NMR signals achieved coalescence to give an average spectrum of a symmetric PN ligand at 80 °C. Higher temperatures were required to observe the coalesced average dba ^1H NMR signals as up to 80 °C they only broadened until they were indistinguishable from the baseline. The signals of the free dba already present in the solution of **77** were unaffected by the temperature change. The ^{31}P NMR signal of **77** was unaltered over the entire temperature range. These results show that free dba is not involved in any dynamic processes, and that only one isomer of complex **77** is formed as low temperature NMR spectra showed no new signals. Furthermore, an intramolecular alkene exchange between the coordinated and non-coordinated double bonds of the bound dba ligand in complex **77** occurs at higher temperatures. This exchange, together with rotation about the Pd–dba bond, account for the averaged PN NMR signals.

The formation and behaviour of complex **77** is different from other palladium-dba compounds containing chelating PN ligands. For example, complex **78** containing the ligand PhPN exhibits one ^{31}P NMR signal at room temperature,

but two signals are observed at -13 °C indicating that two isomers are formed that are involved in a fast equilibrium at room temperature (Scheme 3.8).⁸⁷ The contrasting behaviour of PN ligand **65** could be due to its large size, which is selectively directing the coordination of dba through one double bond to form one isomer of [Pd(dba)(**65**)].

Scheme 3.8

3.4 Palladium allyl complexes

Transition metal allyl complexes are intrinsically important in organometallic chemistry and in homogeneous catalysis as they represent key reaction intermediates.^{88–90} The allyl ligand can coordinate to metal centres through η or η^3 bonding modes. An asymmetric limit of the η^3 bonding mode has also been described as a σ -allyl coordination.^{89,91} The η^3 coordination mode is the most general in Pd-allyl chemistry.

The reaction of PN ligand **65** with $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})]_2$ in dichloromethane afforded a new allyl chloro Pd(II) complex (Scheme 3.9). The spectroscopic NMR data collected at 600 MHz at room temperature suggest that an η^3 -allyl complex (**79**) is observed in solution, which can be

formed by the dissociation of the chloride ligand from **80**.

Scheme 3.9

Only four allyl signals were observed in the ^1H NMR spectrum. The CH_2 group *cis* to phosphorus resonated at 3.35 ppm (d, J_{HH} 9.4 Hz), while two dd were observed for the syn and anti protons of the *trans* CH_2 group at 5.26 and 4.75 ppm respectively. The anti proton exhibited large coupling constants to the central allylic proton (J_{HH} 14.1 Hz) and to phosphorus (J_{PH} 9.6 Hz), whereas the syn proton had almost equal couplings (J_{PH} 7.4 and J_{HH} 7.3 Hz) hence its dd had the appearance of a triplet. A complex multiplet at 6.26 ppm was observed for the central allylic proton.

The appearance of the syn and anti protons of the *cis* CH_2 group as a single resonance is consistent with an $\eta^3\text{-}\eta$ allyl isomerisation through selective dissociation of the $\text{Pd-CH}_2\text{-CH}$ bond *trans* to the phosphorus atom. This reflects the larger *trans*-effect of the P donor compared to the nitrogen donor atom. The different influences of P and N donor atoms were also observed in the ^{13}C NMR chemical shifts. The *cis* CH_2 carbon atom resonated as a doublet

at 49.5 ppm (J_{PC} 4.8 Hz), while the *trans* CH₂ carbon atom was observed at 88.1 ppm (J_{PC} 26.9 Hz). The central allylic carbon atom appeared as a doublet at 122.3 ppm with J_{PC} of 6.2 Hz.

Looking now at the coordinated PN ligand, the ¹H and ¹³C NMR spectra indicated a symmetrical molecule as only one set of signals was observed. This implies that the η^3 -allyl ligand is fluxional at room temperature. In the hope of observing the η -allyl complex **80**, the ¹H and ¹³C NMR spectra were recorded at -80 °C. At such temperature no change was observed in the allylic signals suggesting that the fluxional η^3 -allyl complex is still the dominant species. In contrast, palladium-allyl complexes containing bidentate oxazoline-based PN ligands exhibit the η^3 bonding mode at low temperatures as indicated by ¹H and ¹³C NMR data.^{92–95} Upon raising the temperature, the chemical shifts progressively move toward those of a static η -allyl structure, which is always *trans* to the nitrogen donor atom. For example, at -96 °C (CD₂Cl₂) the allyl fragment adopts an η^3 bonding mode in complex **81** (Scheme 3.10).⁹³ Increasing the temperature results in the formation of complex **82**, in which the allyl ligand is coordinated in an η fashion. Moreover, the *X*-ray structure of **82** confirmed the η -allyl bonding mode and its *cis* arrangement with the phosphorus atom.

Scheme 3.10

The ³¹P NMR spectrum of the allyl complex showed two signals in a

3:1 ratio at 38.7 and 39.9 ppm for the ketone (**79**) and hydrate (**83**) forms respectively. The hydrated complex had very similar ^1H and ^{13}C NMR chemical shifts to the ketone complex with respect to the PN and allyl ligands. For example, a complex multiplet was also observed for the central allylic proton at approximately 5.94 ppm. This particular proton is expected to couple to both the *cis*- and *trans*-CH₂ allylic protons and the phosphorus donor atom. A phosphorus-decoupled ^1H NMR spectrum of complexes **79** and **83** showed no change in the coupling pattern of the central allylic proton in both complexes, thus suggesting a lack of coupling between the central allylic proton and the phosphorus atom. To further confirm the absence of phosphorus coupling, the coupling pattern of the central allylic proton in the hydrate analogue **83** was calculated using the spectral simulation programme gNMR.⁹⁶ The calculated coupling pattern matched exactly the experimental data, hence corroborating the lack of phosphorus coupling (Figure 3.5). Consequently, the coupling pattern of the central allylic proton in complexes **79** and **83** is a dtd.

The hydrated analogue also had an OH stretch at 3408 cm⁻¹ in the IR spectrum. To obtain more insight into hydrate formation, a few drops of water were added to a sample containing both the ketone and hydrate complexes and the sample was monitored by ^1H and ^{31}P NMR over a period of one month.

Figure 3.5. ^1H NMR spectra of the hydrate form of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mathbf{65})]\text{Cl}$ complex (**83**) shown as an expanded-scale display of the central allylic proton signal: (a) experimental spectrum, CD_2Cl_2 , 600 MHz; (b) calculated spectrum obtained with gNMR.

The NMR spectra showed no change in the ratio between the two forms of the $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mathbf{65})]\text{Cl}$ complex. This suggests that the ketone and hydrate forms are not in equilibrium and that no aqua complex was formed.

In addition, abstraction of the chloride ions from the ketone (**79**) and hydrate (**83**) forms of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mathbf{65})]\text{Cl}$ using AgSbF_6 produced very similar η^3 -allyl complexes. The new $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mathbf{65})]\text{SbF}_6$ complexes also formed in a 3:1 ketone (**84**) to hydrate (**85**) ratio. Complexes **84** and **85** exhibited similar NMR features, which in turn resembled the spectroscopic data for complexes **79** and **83** respectively. For example, the ^{31}P chemical shift for the ketone

form **84** was observed at 38.8 ppm (*cf.* 38.7 ppm in complex **79**), while the ^{31}P NMR signal for the hydrate analogue **85** appeared at 37.7 ppm (*cf.* 39.9 ppm in complex **83**).

3.5 Metallation reactions

Cyclometallated compounds describe transition metal complexes in which the ligand has undergone an intramolecular metallation to form a chelate ring containing a metal–carbon σ -bond.^{97,98} Metallation of phenyl-substituted ligands at the *ortho*-position of the ring is termed *ortho*-metallation and is very common in coordination complexes. Cyclometallated compounds can undergo a variety of reactions, for example ligand exchange and insertion reactions, and are of interest in organic synthesis.

Ethene complexes

As discussed previously in section 3.3, the reaction of PN ligand **65** with tris(ethene)platinum under an ethene atmosphere in benzene- d_6 initially produced $[\text{Pt}(\text{C}_2\text{H}_4)(\textbf{65})]$ (**75**). After 10 minutes of reaction at room temperature, complex **75** started to convert into a second ethene complex (**76**). The

conversion between the two ethene complexes was complete after one day and was accompanied by the formation of ethane, which was observed at 0.78 ppm in the ^1H NMR spectrum. The ^{31}P NMR signal for the new complex shifted dramatically from 47.5 ppm in complex **75** to 73.8 ppm with platinum coupling of 3965 Hz. Extensive analysis of the spectroscopic data showed that **76** was in fact a dimetallated complex in which cyclometallation had occurred at the *ortho*-positions of both of the dimethylaminophenyl groups (Scheme 3.11). The eliminated *ortho*-protons were in turn used to hydrogenate some of the dissolved ethene gas to form ethane.

Scheme 3.11

The aromatic regions of the ^1H NMR spectra show the differences between complexes $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65})]$ (**75**) and $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65-2H})]$ (**76**) very clearly (Figure 3.6). The signal for one set of the *ortho*-protons at 9.78 ppm disappears in complex **75** as the metal inserts into the aromatic C–H bonds. Consequently, the *meta*-protons at 6.50 and 6.92 ppm now exhibit platinum coupling of 61 and 26 Hz respectively. The effect of cycloplatination was also felt by the PCH protons, which are normally found between 3.9 and 4.5 ppm, as they shifted downfield to 5.07 ppm and displayed coupling to platinum of 25 Hz. Coordinated ethene protons were observed at 4.02 ppm with J_{PtH} of 55 Hz, while the olefinic carbon atoms resonated as a singlet at 62.5 ppm. Two significant changes were observed in the ^{13}C NMR spectrum of the dimetallated complex: (i) the aromatic

Figure 3.6. Expanded-scale aromatic regions of the ^1H NMR spectra of: (a) $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65})]$ (**75**) and (b) $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65-2H})]$ (**76**). The nitrogen group in complex **75** is not shown to be coordinated for clarity. 300 MHz, C_6D_6 .

ipso-carbon atoms, which typically resonate between 118 and 120 ppm, were observed at 143.6 ppm as a doublet with a large phosphorus coupling of 18 Hz; (ii) the metallated *ortho*-carbon atoms were observed at 161.2 ppm as a small doublet (J_{PC} 2.4 Hz). The spectroscopic data reflect the close proximity of the metal as the proton and carbon atoms are shifted downfield. No platinum coupling was observed in the ^{13}C NMR spectrum due to a weak sample. Large scale synthesis and isolation of complex **76** was not successful as the complex decomposed into an unidentifiable brown residue.

COD complexes

In view of the formation of the dimetallated ethene complex **76**, the reaction of PN ligand **65** with bis(cycloocta-1,5-diene)platinum in benzene at room temperature was studied. This reaction was much slower than the reaction of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ with PN ligand **65**. The ^{31}P NMR resonance of the expected

product $[\text{Pt}(\text{cod})(\mathbf{65})]$ (**86**) was observed initially at 45.0 ppm with J_{PtP} of 3621 Hz. Subsequently, a new ^{31}P NMR signal appeared at 70.4 ppm with a slightly larger platinum coupling of 3787 Hz as **86** converted into a new (**87**) COD complex (Scheme 3.12). After a period of one day at room temperature, the reaction mixture contained predominately complex **87** and trace amounts of **86**. The isolation and characterisation of the initial COD complex **86** was not possible.

The phosphorus chemical shift of the second COD complex **87** is similar to the dimetallated ethene complex **76** (73.8 ppm). This suggests that complex **87** also contains a metallated PN ligand. Detailed analysis of the NMR spectra revealed that cyclometallation had occurred at the *ortho*-position of only one of the dimethylaminophenyl groups, and that the COD ligand had undergone major changes. The NMR data showed that the COD ligand was bonded to platinum *via* a 1-3- η -allyl system to form a C_8H_{13} fragment.

Scheme 3.12

Due to the asymmetric binding of the PN ligand in complex **87**, two sets of NMR signals were observed. Three signals were observed for the metallated aryl ring protons at 6.66, 7.34 and 8.28 ppm, whereas only two signals were noted

for the other dimethylaminophenyl ring: a sharp doublet integrating for two *meta*-protons at 6.52 ppm and a very broad peak at 7.50 ppm, which sharpened into a doublet upon increasing the temperature to 40 °C, representing the *ortho*-protons. This was quite an unusual observation as the aromatic groups normally exhibit restricted rotation, resulting in four distinct proton environments at room temperature. Upon lowering the temperature to -30 °C and recording the ^1H NMR spectrum in toluene- d_8 four signals were observed. This implies that at room temperature, the signals for the *meta*-protons had already coalesced but the *ortho*-protons had only collapsed and needed higher temperatures to achieve coalescence. Furthermore, the averaging of the signals at room temperature must be a consequence of the asymmetric binding mode of PN ligand **65** to platinum, which presumably shifts the five-membered metallacycle slightly to one side allowing the non-metallated ring to rotate freely.

Broad peaks were also observed in the ^{13}C NMR spectrum for the *ortho*- and *meta*-carbon atoms of the free dimethylaminophenyl ring, while the other ring showed evidence of metallation. The metallated carbon atom appeared as a small doublet (J_{PC} 1.9 Hz) at 157.6 ppm with a very large platinum coupling of 1188 Hz. All the other carbon atoms displayed platinum couplings ranging from 55 to 75 Hz, except for the *para*-carbon atom with respect to the metallated position.

Looking at the C_8H_{13} ligand, three allyl signals were observed at 3.75, 4.29 and 5.08 ppm and five CH_2 groups were identified. This suggests that the C_8H_{13} ligand is asymmetrically bound to the metal. The ^{13}C NMR spectrum supported this observation as the terminal carbon atoms were found to be inequivalent, giving rise to signals at 65.1 and 73.0 ppm, while the central allylic carbon atom was observed at 107.3 ppm. Moreover, the carbon atom at 65.1 ppm exhibited large phosphorus (49.6 Hz) and platinum (237 Hz) couplings, implying that it is in a transoid position to phosphorus. The above observations could also

suggest that the σ , π -bonding model is more appropriate than the 1-3- η -allyl description as a consequence of the larger *trans*-influence of the metallated carbon donor atom as compared with phosphorus.

3.6 Protonation reactions

The presence of a transition metal in an alkyl complex imparts properties to the alkyl group that are unprecedented in normal organic chemistry. As a result, the normally relatively inert C–H bonds of an appended ligand can form significant interactions with the metal centre. Agostic interactions describe the coordination of an alkyl ligand to a metal in an η fashion, which involves the simultaneous bonding of a hydrogen atom to both a carbon and a metal atom.^{99–101} Such interactions are of prime significance in organometallic chemistry and catalysis as they feature heavily in catalytic intermediates.

The comparative reactions of ethene and COD platinum precursors with PN ligand **65** showed that the close proximity of the dimethylamionphenyl substituents to the metal had led to cycloplatination, and that depending on the nature and size of the other ligands, one or both of the aromatic rings were metallated. The same reactions were therefore studied with the addition of strong protic acids.

The fluorocarbon acids $\text{CH}_2(\text{SO}_2\text{CF}_3)_2$ and $\text{CHPh}(\text{SO}_2\text{CF}_3)_2$ were chosen for the protonation studies. They were reported by Koshar and Mitsch¹⁰² in 1973, and have since been used in the protonation reactions of organometallic complexes.^{103–106} These acids were selected because they possess a combination of unique properties. They are strong non-oxidising acids as the $\text{p}K_{\text{a}}$ of bis(trifluoromethylsulfonyl)methane was estimated to be about -1. Both acids are crystalline solids and can be handled easily in the air as they are not hygroscopic. They are soluble in apolar, non-donor solvents such as

dichloromethane and toluene, and their conjugate bases are essentially non-coordinating.

COD complexes

In the reaction of $[\text{Pt}(\text{cod})_2]$ with PN ligand **65** and $\text{CH}_2(\text{SO}_2\text{CF}_3)_2$ in dichloromethane, an anionic complex (**88**) containing a $1-\sigma,4-5-\eta-\text{C}_8\text{H}_{13}$ ligand was obtained as an air-stable white solid. Examination of the NMR spectra showed that no metallation of **65** had occurred as protonation probably involved direct attack on the COD ligand in precursor **86**. Complex **88** had a ^{31}P NMR signal at 18.1 ppm with platinum coupling of 4304 Hz. Two sets of NMR signals for the coordinated PN ligand **65** were observed due to the binding mode of the C_8H_{13} ligand. The η -bonded olefinic protons resonated at 6.38 and 6.45 ppm, and the corresponding carbon atoms were observed at 113.3 and 110.2 ppm as doublets (J_{PC} 10.8 and 8.7 Hz respectively). An upfield signal at 18.0 ppm with J_{PtC} 601 Hz was assigned to the carbon-platinum σ bond, and its proton was located at 3.08 ppm. The above data are in accordance with other complexes containing an identical C_8H_{13} ligand.¹⁰⁷ Moreover, the non-coordinated anion $\text{CH}(\text{SO}_2\text{CF}_3)_2^-$ was observed at -81.0 ppm in the ^{19}F NMR spectrum. In addition, the hydrated analogue of complex **88** was also observed. The hydrated complex formed in a 1:3 ratio to the ketone form and had a ^{31}P NMR signal at 16.1 ppm (J_{PtP} 4220 Hz).

Furthermore, the $1-\sigma,4-5-\eta-\text{C}_8\text{H}_{13}$ ligand in complex **88** rearranged slowly

over time into a 1-3- η -C₈H₁₃ fragment to give complex **89**. The ³¹P NMR signal for the new complex was observed at 30.7 ppm (*J*_{PtP} 4010 Hz), and its hydrated analogue (**90**) at 28.4 ppm (*J*_{PtP} 3928 Hz).

The C₈H₁₃ ligand in complex **89** is static at room temperature as the spectroscopic data showed three allylic and five CH₂ signals. This resulted in an asymmetric PN ligand. The central allylic proton resonated at 5.85 ppm as a triplet (*J*_{HH} 8.4 Hz) with platinum coupling of 64 Hz, while the other CH protons appeared at 5.55 and 4.20 ppm. Their ¹³C chemical shifts reflected the asymmetry of the platinum-bonded allyl system: the central and one of the terminal CH carbon atoms exhibited double bond character as they resonated at 109.6 and 91.9 ppm respectively, whereas the other CH group was found upfield at 49.4 ppm with large coupling to platinum (270 Hz). In view of the above observations, the bonding mode of the C₈H₁₃ ligand in complex **89** is closer to a σ , interaction, and is similar to the C₈H₁₃ ligand in complex **87**.

Ethene complexes

Protonation studies of the ethene system proved to be much more challenging. Five products were obtained from the reaction of [Pt(C₂H₄)₃] with PN ligand **65** and CH₂(SO₂CF₃)₂ in benzene. The protonation precursor [Pt(C₂H₄)(**65**)] (**75**) could not be made first and then added to the acid as it converted to the dimetallated ethene complex **76**.

Three of the products were identified from the ³¹P NMR signals (10.0, 21.5 and 24.3 ppm) as being derived from the PN ligand alone as their ³¹P resonances

lacked platinum coupling and were all observed in a control experiment between the PN ligand and acid only. The structure of one of these species (**91**), the compound with δ_P 21.5 ppm, was elucidated by NMR spectroscopy. Analysis revealed that compound **91** is a protonated form of PN ligand **65**, and that the protonation was at the phosphorus atom as a doublet of triplets was observed at 8.42 ppm with J_{PH} 563 Hz and J_{HH} 10.7 Hz in the 1H NMR spectrum. The formation of compound **91** suggests that the reaction of the acid with PN ligand **65** is much faster than either the formation of $[Pt(C_2H_4)(\mathbf{65})]$ and/or its reaction with the acid. Unfortunately, the structures of the other two compounds could not be determined.

Most of the fourth product (**92**) crystallised out of solution as air-stable long fine colourless needles. The complex had a ^{31}P NMR signal at 33.4 ppm with J_{PtP} 3768 Hz. An IR stretch at 2250 cm^{-1} and an upfield signal at -20.26 ppm with J_{PtH} 1285 Hz in the 1H NMR spectrum confirmed the existence of a hydride ligand. The magnitude of the platinum coupling places the hydride *trans* to the nitrogen donor atom rather than phosphorus as the latter would result in a smaller platinum coupling due to its larger *trans*-influence. Analysis of the spectroscopic data showed no coordinated ethene-type signals. This was puzzling as to what ligand was occupying the fourth coordination site on the metal. The nature of the fourth ligand in complex **92** was elucidated from two NMR signals: a doublet at 5.37 ppm (J_{PH} 6.4 Hz) with platinum coupling of 64 Hz observed

in the ^1H NMR spectrum, which was attached to a carbon atom at 67.6 ppm, which also resonated as a doublet with very large phosphorus (65.9 Hz) and platinum (469 Hz) couplings. These NMR chemical shifts are consistent with a $\text{CH}(\text{SO}_2\text{CF}_3)_2$ ligand covalently bonded to platinum, as observed for, *cis*- and *trans*- $[\text{PtH}\{\text{HC}(\text{SO}_2\text{CF}_3)_2\}(\text{Ph}_3\text{P})_2]$ complexes.¹⁰⁴ This was further supported by a signal at -74.9 ppm with platinum coupling of 24 Hz in the ^{19}F NMR spectrum which is indicative of a coordinated $\text{CH}(\text{SO}_2\text{CF}_3)_2$ group, as the free anion resonates at -81.0 ppm with no ^{195}Pt coupling.

92

To prevent the formation of complex **92**, i.e. coordination of the anion $[\text{CH}(\text{SO}_2\text{CF}_3)_2]^-$ to the metal, the bulky phenyl analogue $[\text{CHPh}(\text{SO}_2\text{CF}_3)_2]^-$ was used. Indeed, no product similar to complex **92** containing a metal-bound $\text{CPh}(\text{SO}_2\text{CF}_3)_2$ group was observed. However, multiple products were also formed in this reaction, including compounds derived from the PN ligand only.

The final product (**93**) from the protonation reaction of the ethene system had a ^{31}P NMR signal at 11.3 ppm with a very large ^{195}Pt coupling of 5424 Hz. This was the lowest observed ^{31}P NMR chemical shift for a transition metal complex containing PN ligand **65**. The ^1H NMR spectrum showed a triplet at 1.22 ppm (J_{HH} 7.5 Hz) and a quartet at 1.91 ppm (J_{HH} 6.7 Hz) in a 3:2 ratio. Based on the NMR data, **93** could either be a 14-electron 3-coordinate complex containing an ethyl ligand, or alternatively an agostic complex with a three-centre, two-electron $\text{Pt}-\text{H}-\text{C}$ (π -agostic) interaction (Figure 3.7). The triplet resonance represents the CH_3 group of the 14-electron complex, or the

agostic and C protons which are interchanging at room temperature. The quartet signal corresponds to the CH₂ unit. The magnitude of the Pt–P coupling constant is appropriate for both of the proposed chemical structures of complex **93**. The CH(SO₂CF₃)₂ group is not coordinated to the metal as a signal at -81.0 ppm was observed in the ¹⁹F NMR spectrum. The ¹³C chemical shifts of the ethyl ligand could not be obtained from the NMR spectra recorded at room temperature. Variable-temperature NMR studies on complex **93** revealed no useful information about the C₂H₅ moiety.

Figure 3.7. Possible structures of complex **93**

The agostic form of complex **93** is the expected product from the protonation reaction of complex [Pt(C₂H₄)₂(**65**)] (**75**). Previous work has shown that ethyl agostic complexes are in equilibrium with the alkene/hydride forms and that several factors influence the position of the equilibrium, such as the nature of the complex and the ancillary ligands present.^{99,108,109} The ethyl agostic moiety in platinum complexes containing bis-phosphine ligands show facile scrambling of all five protons and both carbon atoms such that sharp averaged signals are observed in the NMR spectra at room temperature.¹⁰⁸ These observations are attributed to rapid intramolecular rearrangement processes involving both the alkyl form, for which methyl rotation is rapid, and the alkene/hydride form, in which ethene rotation is facile (Scheme 3.13). In contrast, cobalt complexes of the type [Co(η -C₅Me₅)Et(PR₃)] show one ¹H NMR signal for the agostic methyl protons and two resonances for the methylene protons at room temperature.¹¹⁰ Thus, the agostic form of complex **93** resembles the cobalt complexes as two distinct ¹H NMR signals were observed at 1.22 and 1.91 ppm

for the ethyl group.

Scheme 3.13

The alkene-hydride form of **93** was not observed at room temperature, but it could well be the precursor to complex **92** by simple substitution of the coordinated ethene molecule with the anion $\text{CH}(\text{SO}_2\text{CF}_3)_2^-$. Due to the numerous products formed, accurate elemental analytical data could not be obtained for complex **93** but its molecular weight was confirmed by mass spectrometry.

Norbornene complexes

The protonation reaction of $[\text{Pt}(\text{norb})\mathbf{65}]$ (**74**) with $\text{CH}_2(\text{SO}_2\text{CF}_3)_2$ acid was also studied. This reaction produced only two products. The minor product was identified as $[\text{PtH}(\text{CH}(\text{SO}_2\text{CF}_3)_2)(\mathbf{65})]$ (**92**), suggesting that the $[\text{CH}(\text{SO}_2\text{CF}_3)_2]^-$ anion has the propensity to coordinate to platinum in such reactions. The major product had a very similar ^{31}P signal to **92** at 34.8 ppm (*cf.* 35.5 ppm, J_{PtP} 3724) but with very large platinum coupling of 6013 Hz, which indicates that the phosphorus atom is *trans* to a weakly bound ligand such as an agostic C–H bond. A broad doublet of doublets signal in the ^1H NMR spectrum at -1.02 ppm supported this observation, as it corresponded to the agostic proton being coupled to phosphorus (J_{PH} 50.3 Hz) and its geminal partner (J_{HH} 13.6 Hz). However, no platinum-proton coupling was observed. Since this protonation reaction produced the desired agostic norbornyl complex in high yields, the reaction was repeated with $\text{CHPh}(\text{SO}_2\text{CF}_3)_2$ to completely eliminate the formation of **92**. This indeed was the case and the agostic complex **94** was

obtained in 71% yield, of which 10% was in the hydrated form (**95**). The ^{31}P NMR chemical shift of complex **94** was slightly different due to the different acid and was observed at 33.8 ppm (J_{PtP} 6008 Hz), while the ^{31}P NMR signal for the hydrate analogue resonated at 31.6 ppm (J_{PtP} 5886 Hz).

The inward diffusion of diethyl ether into a dichloromethane solution yielded crystals suitable for single crystal *X*-ray diffraction. The particular crystal that was examined contained a molecule each of the ketone (**94**) and hydrate (**95**) forms of $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]\text{CPh}(\text{SO}_2\text{CF}_3)_2$ in the asymmetric unit (Figure 3.8). A summary of the crystallographic data are compiled in Table 3.4.

Looking at the ketone form **94**, the solid-state structure of $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]$ shows that the norbornyl ligand is bound *via* both a σ -bond to the α -carbon and a π -agostic interaction. Consequently, the carbon atom C33 is within the normal σ -bond distance to platinum (2.02(1) Å), whereas C34 is more remote (2.37(1) Å) due to its bonding mode and the strong *trans*-influence of phosphorus, but is still close enough to interact with the metal (Table 3.5). The agostic proton was located directly (Pt–H1 2.05, C34–H1 1.16 Å) and lies in the coordination plane defined by Pt, P1 and N1. The rigidity of the coordinated PN ligand in both the ketone and hydrate forms of $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]$ is reflected in the distance between the phosphorus and nitrogen donor atoms as it is 3.0 Å, which is very similar to the free ligand (*cf.* 2.9 Å) and the same as in the dichloro-complex **69**. In addition, in both the ketone and hydrate *X*-ray crystal structures, the agostic interaction is *trans*

(a)

(b)

Figure 3.8. ORTEP diagrams of $[\text{Pt}(\eta - \text{C}_7\text{H}_{11})(\mathbf{65})]$: (a) ketone form **94** and (b) hydrate form **95** (30% thermal ellipsoids). Most hydrogen atoms and the $\text{CPh}(\text{SO}_2\text{CF}_3)_2$ anions are omitted for clarity.

Table 3.4. Crystallographic data of norbornyl agostic complexes **94** and **95**.

Empirical formula	$\text{C}_{96}\text{H}_{122}\text{N}_6\text{O}_{19}\text{P}_2\text{S}_4\text{F}_{12}\text{Pt}_2^*$
Formula weight	1227.17
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> /Å	13.313(1)
<i>b</i> /Å	14.961(1)
<i>c</i> /Å	16.193(1)
α /	91.528(2)
/	97.270(2)
/	114.749(2)
<i>V</i> /Å ³	2894.0
<i>Z</i>	2
Cell determination reflections	9822
Cell determination range, $\theta_{\min}$ — $\theta_{\max}$ /	2.28 — 30.89
Temperature/K	119(2)
Radiation type	Mo <i>K</i> α
Radiation (λ)/Å	0.71073
Crystal size/ mm	0.46 x 0.41 x 0.38
<i>D</i> _{calc} /g m ⁻³	1.408
<i>F</i> (000)	1240
mm	2.59
<i>T</i> _{max} , <i>T</i> _{min}	0.747, 0.585
Reflections collected	88313, <i>R</i> _{equiv} = 0.0393
Index range <i>h</i>	-20 — 21
Index range <i>k</i>	-22 — 23
Index range <i>l</i>	-25 — 24
range/	2.55 — 35.21
Independent reflections	40129
Reflections [<i>I</i> ≥ 2 (<i>I</i>)]	33422
Restraints/parameters	3/1296
GOF	1.054
<i>R</i> [<i>I</i> ≥ 2 (<i>I</i>)]	0.047
<i>wR</i> ² [<i>I</i> ≥ 2 (<i>I</i>)]	0.13
<i>R</i> [all data]	0.060
<i>wR</i> ² [all data]	0.14

*Combined formulae of ketone and hydrate molecules.

Table 3.5. Selected interatomic distances (Å) and interbond angles (°) for the ketone (**94**) and hydrate (**95**) forms of $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]$.

Bond distances (Å)			Bond angles (°)		
	94	95		94	95
Pt–P1	2.197(3)	2.197(3)	P1–Pt–N1	86.1(2)	85.3(2)
Pt–N1	2.18(1)	2.20(1)	C33–Pt–C34	40.1(3)	39.3(4)
Pt–C33	2.02(1)	2.04(1)	P1–Pt–C33	111.2(2)	111.2(3)
Pt–C34	2.37(1)	2.36(1)	P1–Pt–C34	150.2(2)	149.6(2)
C33–C34	1.54(1)	1.50(1)	N1–Pt–C33	162.6(3)	163.3(3)
Pt–H1	2.05	*	N1–Pt–C34	122.7(2)	124.3(3)
C34–H1	1.16	*	Pt–C34–H1	59.6	*
C33–H2	0.98	0.98	Pt–H1–C34	91.2	*
C7–O1	1.19(1)	—	C34–Pt–H1	29.3	*
C7–O1a	—	1.29(1)	P1–Pt–H1	178.4	*
C7–O1b	—	1.47(1)	N1–Pt–H1	94.1	*
C34–C35	1.52(1)	1.50(1)	Pt–P1–C5	110.1(3)	109.7(3)
C35–C36	1.56(1)	1.49(1)	Pt–N1–C2	113.9(5)	112.2(6)
C36–C37	1.53(2)	1.58(2)	C5–P1–C6	99.6(4)	101.8(4)
C37–C38	1.57(2)	1.51(1)	C2–N1–C3	108.9(7)	112.8(7)
C33–C38	1.52(1)	1.54(2)	C1–C7–C4	110.4(7)	113.1(7)
C38–C39	1.55(2)	1.53(2)	Pt–C33–C34	82.4(5)	81.7(5)
C35–C39	1.51(1)	1.53(2)	Pt–C34–C33	57.4(5)	59.0(4)
			C33–C34–C35	103.4(8)	105.0(8)
			C34–C33–C38	103.7(8)	102.6(9)

*Not observed.

to the phosphorus donor atom. This could be a consequence of the stronger *trans*-influence of the phosphorus atom, which places the strong σ -bond *trans* to the nitrogen donor atom. This situation is very similar to the PN palladium-allyl systems in which the $\eta\text{-allyl}$ ligand is always *trans* to nitrogen, while the chloride ion is *trans* to phosphorus making it labile and able to form the corresponding $\eta^3\text{-allyl}$ complexes (Section 3.4).

The crystallographic dimensions of the ketone **94** and hydrate **95** forms of $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]\text{CPh}(\text{SO}_2\text{CF}_3)_2$ are very similar as shown in Table 3.5, suggesting that the hydrate form is chemically equivalent to the dominant ketone form (Figure 3.9). The agostic hydrogen atom could not be located in the hydrate

form but both of the OH hydrogens were found. The hydroxylic H4 proton was found to be hydrogen bonded to the ester carbonyl oxygen O2, whereas no such interaction was possible for H3. The C–O bond lengths however were found to be anomalous: the C7–O1a bond was very short (1.29(1) Å) for a C–O single bond and almost like a C=O double bond, while the C7–O1b bond was significantly longer (1.47(1) Å). These bond distances are also different from other metal complexes containing hydrated bispidinone ligands, in which the average C–O bond lengths were 1.394 and 1.404 Å.³³ The anomaly suggests that the crystallographic position of the C7 carbon atom is not entirely correct in complex **95**, and that it could be due to some crystallographic artifact. Nonetheless, the C–O bond distances should be compared with other metal complexes containing similar hydrated PN ligands when they become available to obtain a more general idea about such complexes and how they differ from their bispidinone counterparts.

Furthermore, the crystallographic parameters of the norbornyl ligand in **94** were compared (Table 3.6) with [Pt(C₇H₁₁)(L–L)]BF₄ (**96**), [L–L = Bu^t₂P(CH₂)₂PBu^t₂], reported by Spencer and co-workers.¹¹¹ Although the parameters are similar, they do indicate that the agostic interaction in **94** is weaker. This was concluded from longer Pt–C and Pt–H bond lengths (2.37(1) and 2.05 Å respectively), which in turn resulted in appreciably shorter Pt–P1 and C–H bond distances (2.197(3) and 1.16 Å respectively). As a consequence, the norbornyl carbon atoms bonded to the metal are now more sp³ in character than sp, as in complex **96**, as the C–C bond is much longer (1.54(1) Å, *cf.* 1.480(6) Å). The weaker agostic interaction in complex **94** was further supported by the very large J_{PtP} coupling constant of 6013 Hz, which is appreciably larger than 4909 Hz in complex **96**.

Wholly consistent with the solid-state structure, the solution NMR data of the agostic complex **94** showed that the norbornyl ligand is bound to the

Figure 3.9. Crystallographic views of (a) ketone form (**94**) and (b) hydrate form (**95**) of the norbornyl agostic complex $[\text{Pt}(\eta\text{-C}_7\text{H}_{11})(\mathbf{65})]$.

Table 3.6. Comparison between the agostic bond distances (Å) in complexes **94** and **96**.

Bond distances (Å)	94	96
<p>The figure shows two chemical structures, 94 and 96, illustrating agostic interactions. Structure 94 shows a platinum atom (Pt) coordinated to a norbornyl ligand (C1, C2) and a phosphine ligand (P1). A dashed line indicates an agostic interaction between the Pt atom and a hydrogen atom (H) on the norbornyl ligand. Structure 96 shows a platinum atom (Pt) coordinated to a norbornyl ligand (C1, C2) and two phosphine ligands (P1, P2). Dashed lines indicate agostic interactions between the Pt atom and hydrogen atoms (H) on the norbornyl ligand.</p>		
Pt–P1	2.197(3)	2.256(1)
Pt–N1/P2	2.18(1)	2.311(1)
Pt–C1	2.37(1)	2.309(5)
Pt–C2	2.02(1)	2.096(4)
Pt–H	2.05	1.90(7)
C1–C2	1.54(1)	1.480(6)
C1–H	1.16	1.28(6)

metal through both σ -alkyl and π -agostic interactions. The β -carbon and its proton were located at 38.7 and 3.12 ppm respectively, whereas the α -carbon resonated at 26.3 ppm and the non-agostic proton at 1.37 ppm. The presence of such an agostic bond would be expected to manifest itself in a substantially diminished $^1J_{\text{CH}}$ coupling constant for the agostic hydrogen atom, due to the reduced C–H bond order in the two-electron, three-centre C–H–M bond.⁹⁹ This was indeed the case as the β -carbon atom showed proton couplings of 70 and 173 Hz. Although only six, rather than seven, ^{13}C NMR resonances were noted for the agostic norbornyl ligand as the signals for the CH_2 groups overlapped, the NMR data showed that the agostic complex **94** did not undergo any dynamic behaviour at room temperature. This is in contrast with complex **96**, in which the agostic hydrogen is rapidly transferred to the metal to give an intermediate alkene-hydride species for which rotation about the metal-alkene bond is facile (Scheme 3.14). This results in a time-averaged NMR spectrum for the agostic norbornyl ligand such that only four carbon environments are discerned.

Scheme 3.14

Due to the asymmetric nature of the agostic interaction of the C_7H_{11} ligand, two sets of NMR signals were observed for the coordinated PN ligand as its symmetry plane was destroyed. In general, the ketone and hydrated analogues

exhibited similar NMR features except for the presence of a hydrated carbon atom at 94.1 ppm. The counterion $\text{CPh}(\text{SO}_2\text{CF}_3)_2$ had a signal at -78.6 ppm in the ^{19}F NMR spectrum indicating that it is a free anion. Finally, complex **94** represents the first example of an agostic norbornyl interaction stabilised by a phosphorus-nitrogen ligand.

3.7 Hydroxo-bridged platinum complexes

Dinuclear platinum complexes represent an important class of compounds because of their potential in homogeneous catalysis and for the synthesis of mixed ligand mononuclear platinum complexes.¹¹² For example, bis-hydroxo-bridged dimers of platinum promote the Baeyer-Villiger (BV) oxidation of cyclic and acyclic ketones in the presence of H_2O_2 to give esters and lactones respectively.^{113,114} For these reasons, understanding the structure and properties of dimeric platinum complexes is important.

In view of the formation of the dimetallated complex $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65})]$ (**76**) from the reaction of tris(ethene)platinum with PN ligand **65**, its hydrogenation reaction was studied. The reaction was studied on a NMR scale in benzene- d_6 and monitored by both ^1H and ^{31}P NMR. The pale yellow solution of **76** darkened over time and a fine black suspension formed. The reaction was rather slow as the signals for the dimetallated complex gradually decreased and then disappeared after a period of 20 days at room temperature. The expected products from the hydrogenation reaction of **76** were $[\text{PtH}_2(\mathbf{65})]$ (**97**) and ethane (Scheme 3.15), but the ^1H and ^{31}P NMR spectra clearly showed that **97** had not been formed. No signal corresponding to ethane or ethene was observed in the ^1H NMR spectrum under the experimental conditions used.

The ^{31}P NMR spectrum showed two peaks in about 1:1 ratio at 47.8 and 49.9 ppm, both with very similar couplings to platinum of 4874 and 4851 Hz

Scheme 3.15

respectively. Two doublets integrating for one proton each were observed in the ^1H NMR spectrum at -0.62 (J_{PH} 3.1 Hz) and 0.06 ppm (J_{PH} 1.9 Hz). The phosphorus couplings were confirmed by a phosphorus-decoupled ^1H NMR spectrum in which the two doublets resonated as singlets. Moreover, the two protons were not attached to carbon atoms as they were absent from the HSQC spectrum. Even though these signals resonate at unique chemical shifts typical for hydrogen atoms interacting closely with a metal, they are not likely to correspond to Pt–H because such hydride resonances would be expected at very high field with large platinum coupling. Interestingly, HMBC correlations were observed from the hydride-like signals at -0.62 and 0.06 ppm to carbon atoms at 138.3 and 138.2 ppm respectively.

Extensive analyses of the 2D NMR spectra revealed that two very similar compounds had been formed in which the PN ligand was asymmetric. Two C=O ^{13}C NMR signals were observed at 205.3 and 205.9 ppm indicating that both compounds were in the ketone form, thus eliminating the formation of a hydrated analogue. In both compounds, the NMR data showed that something unusual had happened to one of the dimethylaminophenyl groups as only one *ortho*- and two *meta*-protons were located along with their corresponding carbon atoms. The other *ortho*-CH group remained elusive. Beside the two hydride-

like peaks and the two ^{13}C signals at 138.2 and 138.3 ppm, every resonance in the ^1H and ^{13}C spectra had been accounted for as belonging to the coordinated PN ligand **65**. If the dimethylaminophenyl group was *ortho*-metallated, then the metallated carbon atom would be expected to resonate downfield above 155 ppm in the ^{13}C NMR spectrum as in complexes **76** and **87**. As no such ^{13}C NMR signals were observed, the nature of the other ligand(s) on the metal remained ambiguous. Furthermore, no platinum coupling was observed in either the ^1H or the ^{13}C NMR spectra.

The same two compounds were also obtained from the reaction of $[\text{Pt}(\text{Ph}_2\text{C}_2)_2]$ and $[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{cod})]$ with PN ligand **65**. These observations suggest that the formation of these two similar compounds is independent of the other ligands on platinum metal. To shed some light on the identity of the other ligands, two NMR experiments were performed with oxygen gas and water. The reaction of complex **76** with water resulted in no change at all, whereas the reaction with oxygen produced some other unidentifiable products.

The NMR scale hydrogenation reaction was scaled up many times using Schlenk techniques but most of the product decomposed to give a dark brown residue. Finally, the reaction was repeated in a Fischer-Porter vessel to try and minimise the decomposition. This experimental set-up was indeed a success as enough material for crystallisation was produced, although some brown residue was deposited at the bottom of the reaction vial. The slow diffusion of diethyl ether into a benzene solution of the two compounds at 5 °C yielded small and large yellow cubic crystals and some pale brown amorphous solid. Samples of each type of solid were analysed by ^1H and ^{31}P NMR: the large crystals contained the complex with the proton signal at 0.06 ppm and the ^{31}P resonance at 47.8 ppm; the small crystals were mainly of the other complex which had a ^{31}P signal at 49.9 ppm; and finally the brown residue was a mixture of the latter complex plus some unidentifiable organic compounds. These results suggested

that the two complexes had crystallised separately to give different crystals and that one of them did not crystallise well under these conditions. No further analyses were done on the small crystals due to their limited quantity, but a complete analysis including *X*-ray diffraction was performed on the large crystals.

The *X*-ray crystal structure obtained from a single large crystal showed that the mysterious complex (**98**) was a platinum dimer bridged by hydroxyl groups (Scheme 3.16). The PN ligand is bonded through the phosphorus donor atom and a carbon atom from the dimethylaminophenyl ring in which *ortho*-metallation had occurred (Figure 3.10). The solid-state structure of $[\text{Pt}_2(\mu\text{-OH})_2(\mathbf{65}\text{-H})_2]$ clearly shows that the nitrogen donor atom is not bonded to platinum. The dimer has a C_2 symmetry axis at the midpoint of the two

Scheme 3.16

platinum atoms. A summary of crystallographic parameters of complex **98** are given in Table 3.7, and some selected bond distances and angles are given in Table 3.8.

The NMR data of complex **98** is in accordance with the *X*-ray crystal structure. Due to the asymmetric binding of PN ligand **65**, all its proton and carbon atoms resonated in different chemical environments. The unique ^1H NMR resonance at 0.06 ppm is probably due to the bridging hydroxylic hydrogen atoms, which also had a HMBC correlation to the unassigned carbon atom at 138.2 ppm. This suggests that the latter ^{13}C NMR signal corresponds to the Pt–C carbon atom in the metallated dimethylaminophenyl ring, which is more shielded than the metallated carbon atoms in complexes **76** and **87** (*cf.* 161.2 and 157.6 ppm respectively). The absence of any observable coupling to platinum could be due to peak overlap. Moreover, a sharp OH stretch was observed in the IR spectrum at 3564 cm^{-1} confirming the presence of the bridging hydroxyl groups.

The coordination sphere around each metal atom is square planar, and the dihedral angle between the two O1–C13–P1–O1 planes is 21° . This results in a slightly bent structure according to the possible molecular conformation reported by Aullón *et al.* for binuclear complexes with monosubstituted bridges.¹¹⁵ The hydroxylic hydrogens at the bridging atoms were found (O–H $0.72\text{ \AA}$) but their positions could not be refined. Their relative orientation to the coordination core in complex **98** was *exo* to give a bent, *exo* (**be**) structure (Figure 3.11). Such orientation is probably the result of the lone pair of electrons on the bridging oxygen atoms occupying more space than the bonding O–H electron pair. There is no interaction between the two bridging oxygen atoms as the distance between them is $2.56\text{ \AA}$. The O1–Pt1–O1 angle is $75.4(2)^\circ$, while the Pt1–O1–Pt1 angle is $100.6(2)^\circ$.

Although the nitrogen donor atom is not coordinated to platinum metal

(a)

(b)

Figure 3.10. ORTEP diagrams of hydroxo-bridged platinum complex (**98**):
 (a) complete dimer (b) half dimer (30% thermal ellipsoids). Hydrogen atoms
 omitted for clarity.

Table 3.7. Crystallographic data of hydroxo-bridged platinum complex **98**.

Empirical formula	$\text{C}_{64}\text{H}_{88}\text{N}_6\text{O}_{12}\text{P}_2\text{Pt}_2$
Formula weight	1553.52
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	15.356(1)
b/Å	16.572(1)
c/Å	27.816(2)
$\alpha/^\circ$	90
$\beta/^\circ$	105.768(5)
$\gamma/^\circ$	90
V/Å ³	6812.8
Z	8
Cell determination reflections	9952
Cell determination range, $\theta_{\min}$ — $\theta_{\max}/^\circ$	2.46 — 23.20
Temperature/K	296(2)
Radiation type	Mo K α
Radiation (λ)/Å	0.71073
Crystal size/mm	0.41 x 0.35 x 0.32
$D_{\text{calc}}/\text{g cm}^{-3}$	1.515
F(000)	3120
$\rho_{\text{calc}}/\text{mm}$	4.21
$T_{\max}, T_{\min}$	0.746, 0.572
Reflections collected	82218, $R_{\text{equiv}} = 0.0670$
Index range h	-21 — 21
Index range k	-22 — 23
Index range l	-38 — 39
range/ $^\circ$	2.57 — 30.17
Independent reflections	10011
Reflections [$I \geq 2\sigma(I)$]	6441
Restraints/parameters	0/402
GOF	1.076
R [$I \geq 2\sigma(I)$]	0.057
wR2 [$I \geq 2\sigma(I)$]	0.12
R [all data]	0.10
wR2 [all data]	0.14

Table 3.8. Selected bond distances (Å) and angles (°) for hydroxo-bridged platinum complex **98**.

Bond distances (Å)		Bond angles (°)	
Pt1–P1	2.179(2)	Pt1–O1–Pt1	100.6(2)
Pt1–C13	1.999(7)	O1–Pt1–O1	75.4(2)
Pt1–O1	2.074(5)	P1–Pt1–C13	83.2(2)
Pt1–O1	2.110(5)	Pt1–P1–C1	107.1(3)
Pt1–Pt1	3.221(1)	P1–C1–C12	104.6(4)
P1–C1	1.86(1)	C1–C12–C13	119.5(6)
P1–C6	1.87(1)	C12–C13–Pt1	122.3(6)
C1–C12	1.52(1)	O1–Pt1–C13	96.3(3)
C12–C13	1.41(1)	O1–Pt1–P1	104.8(2)

in complex **98**, the bound PN ligand still maintains its rigid chair-chair conformation. The distance between the phosphorus and nitrogen donor atoms is slightly longer as expected at 3.2 Å (*cf.* 3.0 Å in complexes containing a coordinated nitrogen donor atom). In contrast, the Pt–N distance is very long at 3.8 Å. This is longer than in complex [AuCl(**37**)] (**41**) (3.1 Å) in which the nitrogen atom was also not bound to the metal.⁶² This could be due to the different metal atoms used and the fact that complex **98** contains a cyclometallated dimethylaminophenyl group. Interestingly, the cyclometallation did not have a significant impact on the bond distances within the phenyl ring as they are similar to the bond lengths of the other non-metallated aryl group.

The stronger *trans*-influence of the carbon donor atom is clearly reflected

Figure 3.11. Molecular conformation of the coordination core in hydroxo-bridged platinum complex **98**

in the respective *trans* Pt–O bond being longer (2.110(5) Å) than the other Pt–O bond *trans* to phosphorus (2.074(5) Å). Both bond distances fall within the expected range of Pt–O bonds in hydroxo-bridged platinum complexes.¹¹⁶ The two platinum atoms in the dimer are not bonded as the distance between them is 3.221 Å.¹¹⁷ This explains the lack of a second smaller platinum coupling in the ³¹P NMR spectrum as the effect of the second platinum atom was not felt by the coordinated phosphorus as the two platinum atoms were too far apart.

All the crystallographic parameters of complex **98** agree very well with other similar bis-hydroxo-bridged dimers of platinum(II) as shown by a search performed on 37 structures in the Cambridge Crystallographic Database. Most complexes were planar with a square planar geometry around each platinum atom, and only five complexes showed a slight bend between the two metal coordination planes. Examples of such dimers are **99** and **100**, which contain phosphorus and carbon ligands.^{118,119} Both complexes have *C*₂ symmetry and a similar *trans*-influence was observed for the Pt–O bonds due to the different donor atoms.

The formation of the platinum dimer **98** was probably the consequence of adding one molecule of adventitious water to the dimetallated ethene platinum complex **76** to form a highly reactive 14-electron species (Scheme 3.17). This intermediate in turn dimerised to form the hydroxo-bridged complex. The presence of the hydrogen gas is necessary for the formation of complex **98** presumably to hydrogenate the complexed ethene ligand to release it.

Scheme 3.17

During the dimerisation process there are two orientations in which the 14-electron reactive intermediates can combine together: if a double OH bridge is formed between two P–C fragments where one unit had rotated by 180° C, complex **98** is formed; however, a new configurational isomer can be produced if no rotation occurs. This could explain the observation of a similar complex to dimer **98** under all the reaction conditions used. The second dimer (**101**) was observed at 49.9 ppm in the ^{31}P NMR, and it crystallised as small yellow crystals from the benzene-diethyl ether mixture. Although complex **101** possesses a vertical symmetry plane across the bridging atoms, the two OH hydrogen atoms should still be different and would be expected to give two OH resonances in the ^1H NMR spectrum. Since only one signal was observed at -0.62 ppm, perhaps the two hydroxylic protons are exchanging rapidly on the NMR time scale.

3.8 Bis(phosphorus-nitrogen) ligand complexes

Reactions of PN ligand **65** with three platinum precursors in a 2:1 ligand to metal ratio were carried out in an attempt to prepare bis(PN)metal complexes. The ligand was reacted with $[\text{Pt}(\text{norb})_3]$, $[\text{Pt}(\text{cod})_2]$ and $[\text{Pt}(\text{Ph}_2\text{C}_2)_2]$ metal precursors in C_6D_6 on a NMR scale at room temperature. The products from all three reactions were the same as the products obtained from the respective 1:1 ligand to metal syntheses, i.e. $[\text{Pt}(\text{norb})(\mathbf{65})]$ (**74**) (Section 3.3), $[\text{Pt}(1\text{-}3\text{-}\eta\text{-C}_8\text{H}_{13})(\mathbf{65}\text{-H})]$ (**87**) (Section 3.5) and *trans*- and *cis*- $[\text{Pt}_2(\mu\text{-OH})_2(\mathbf{65}\text{-H})_2]$ (**98**, **101**) (Section 3.7). Such results suggest that PN ligand **65** is too bulky to form 2:1 complexes in which the ligand is coordinated through both donor atoms, or *via* only the phosphorus atom in a monodentate fashion. In contrast, the similar but considerably smaller PTN ligand **10** can act as either a mono- or bidentate PN ligand and form 2:1 ligand to metal complexes.^{23,24}

3.9 Ligand hydration

The formation of hydrated complexes was an intriguing characteristic of the coordination chemistry of PN ligand **65**. In such complexes, the central carbonyl group at position 9 was hydrated to form a geminal diol. Interestingly, hydration of the PN ligand only occurred upon metal complexation, despite the use of dry solvents and inert atmosphere, and was only observed for complexes prepared in CDCl_3 , CD_2Cl_2 and CH_2Cl_2 . No hydration occurred for complexes synthesised in benzene, toluene or their respective deuterated analogues. These observations suggest that the hydration of the central carbonyl group in complexed PN ligand **65** could be due to the presence of the metal and the acidic character of the chlorinated solvents. The precise effect of metal coordination is not well understood as the hydration is taking place at a site remote from the

reaction centre. The oxidation state of the metal could be a contributing factor considering that all hydrated complexes contain M(I) or M(II) metals.

Furthermore, hydrated analogues generally formed in a 1:3 ratio to the ketone forms of the PN metal complexes. The ketone and hydrate forms are not in equilibrium, as might be expected, because their relative ratios remained unchanged regardless of how much water was added to the product mixtures. The hydrated analogues appear to have similar chemical characteristics to their ketone counterparts both in solution and the solid state.

3.10 Coordination chemistry of PN ligand **66**

Despite the small quantity of PN ligand **66** isolated and the fact that it was only about 80% pure as it was contaminated with PN ligand **65** and 3-(4-dimethylaminophenyl)methyl-2-propenoate **67**, some preliminary complexation studies were conducted. A NMR scale experiment was performed with [PtMe₂(1,5-hexadiene)] in a 2:1 ratio in benzene-d₆ at room temperature. PN ligand **66** cannot act as a bidentate ligand because the angle between the phosphorus and nitrogen donor atoms is too small. The expected product from the reaction was *cis*-[PtMe₂(**66**)₂] (**102**), but the ³¹P NMR spectrum clearly showed that complex **102** had not been formed.

The ³¹P NMR spectrum showed an AB pattern with δ_A 28.1 ppm, $J(\text{PtP}_A)$ 3066 Hz and δ_B 59.4 ppm, $J(\text{PtP}_B)$ 3204 Hz and $J(\text{P}_A\text{P}_B)$ 429 Hz. This is consistent with the formation of a *trans* complex in which cyclometallation has occurred on one of the coordinated phosphine ligands. The signal at 28.1 ppm is assigned to the monodentate phosphine and the low-field ³¹P chemical shift at 59.4 ppm corresponds to the internally metallated phosphine.¹²⁰ Moreover, methane was observed at 0.14 ppm in the ¹H NMR spectrum indicating the hydrogenolysis of one of the coordinated methyl groups. The ¹H NMR spectrum

also showed a triplet at -0.17 ppm (J_{PH} 5.5, J_{PtH} 49 Hz) corresponding to the other methyl group bonded to platinum which is coupling to two phosphorus atoms. Two doublets at 0.80 (J_{PH} 13.8 Hz) and 1.25 ppm (J_{PH} 13.3 Hz) were also observed due to the non-equivalent *t*-butyl groups. The doublet at 0.80 ppm was slightly broader possibly due to coupling with the other phosphorus nucleus.

Potential cyclometallated complexes of ligand **66** are shown in Figure 3.12. These include metallation at the methylene (**103**) or the methine (**104**) carbons on either side of the phosphorus atom to form 3-membered rings, or metallation at an *ortho*-position of the dimethylaminophenyl ring (**105**) or on the N-methyl substituent (**106**) to produce 5-membered metallacycles. A 4-membered ring can also be formed through metallation at the activated α -position to the ketone (**107**). Internal metallation on a methyl group of the *t*-butyl substituent can be ruled out as two *t*-butyl doublets were observed in the ^1H NMR spectrum.

Figure 3.12. Possible metallaphosphabicyclic complexes of PN ligand **66**.

To determine exactly the cycloplatination position in ligand **66**, NMR spectra were recorded on a 500 MHz NMR instrument. However, these revealed that the metallated complex had decomposed at room temperature within hours of its formation. For this reason, the NMR scale experiment was repeated in toluene- d_8 so that NMR spectra could be recorded at $-20\text{ }^{\circ}\text{C}$ to avoid decomposition. Cooling the reaction mixture down to $-20\text{ }^{\circ}\text{C}$ in a 300 MHz NMR instrument straight after combining the reactants together at room temperature ceased the cyclometallation reaction of ligand **66** and allowed the observation of the intermediate *cis*-dimethyl complex **102** in the ^{31}P NMR spectrum at 33.9 ppm with J_{PtP} of 1830 Hz (Scheme 3.18). As PN ligand **66** is chiral, it is possible to form the *meso* and *rac* diastereoisomers of **102**. However, the observation of one signal in the ^{31}P NMR spectrum indicates the dominance of only one species.

Scheme 3.18

Small quantities of the cyclometallated complex were also present indicating that the cycloplatination reaction is very facile at room temperature. NMR analysis of the spectra recorded at $-20\text{ }^{\circ}\text{C}$ to characterise complex **102** and possibly also the *trans*-complex proved to be inconclusive. The spectra acquired were of low resolution and broad due to short acquisition time and low acquisition temperature, and they were further complicated by peaks due to compounds **65** and **67**. Consequently, the NMR spectra were recorded at room temperature on a 600 MHz NMR instrument which should produce high resolution spectra

over short periods of time before much decomposition had taken place. After an extensive examination of the highly complex spectra, no definite conclusions could be made about the metallation position of ligand **66**. However, some other useful NMR data were obtained, for example the ^{13}C chemical shift for the methyl group was at -21.0 ppm.

Although the NMR data were not conclusive about the metallation position of the coordinated ligand **66**, the ^{31}P chemical shift (59.4 ppm) of the metallated ligand could give some insight into the ring size being formed. Looking at the possible metallated complexes in Figure 3.12, compounds **103** and **104** both have 3-membered rings and compound **107** has a 4-membered ring after cyclometallation. The ^{31}P NMR chemical shifts of phosphine ligands become very shielded upon formation of 3- and 4-membered metallacycles.¹²⁰ For example, a similar phosphine ligand (**108**) resonates at 17.1 ppm in the ^{31}P NMR spectrum (Scheme 3.19).⁶¹ Upon its reaction with $[\text{PtCl}_2(\text{cod})]$, a [3.1.1]metallaphosphabicyclic product (**109**) is formed in which the phosphorus atom in the 4-membered ring has a ^{31}P NMR signal at -13.0 ppm. Therefore, complexes **103**, **104** and **107** can be ruled out as the ^{31}P chemical shift of the metallated ligand **66** was very deshielded as compared to the free ligand (*cf.* -3.5 ppm).

Scheme 3.19

The ^{31}P NMR resonances of phosphine ligands tend to become deshielded when metallation results in a 5-membered ring.¹²⁰ Since the ^{31}P NMR chemical

shift of the metallated ligand is at 59.4 ppm, it is therefore more consistent with the formation of a 5-membered ring as in complexes **105** and **106**. Of these two, complex **105** represents the most likely structure as *ortho*-metallation at the dimethylaminophenyl group has been observed in the coordination chemistry of PN ligand **65**. Nevertheless, further experimental studies are required to determine the exact structure of the *trans*-metallated complex as well as to explore the coordination chemistry of PN ligand **66**.

3.11 Concluding remarks

The coordination chemistry of bicyclic PN ligand **65** was explored extensively with rhodium, palladium and platinum. Generally, the ligand coordinated *via* both the phosphorus and nitrogen donor atoms, to form stable and well defined metal complexes. This showed that the degree of ligand preorganisation was transferred to the resulting metal complexes. Coordination compounds containing 2:1 ligand to metal ratio were never observed, possibly due to the large size of PN ligand **65**. Moreover, the ligand favoured bidentate binding as no metal complexes containing monodentate PN ligands were confirmed. The effect of the different donor atoms on the respective *trans*-positions on the metal was clearly evident both in solution and the solid state structures.

Complexation of PN ligand **65** to a metal was generally characterised by a large downfield shift of the dimethylaminophenyl *ortho*-protons in the ^1H NMR spectrum. This was attributed to the close proximity of the aryl groups (which were constrained by the ligand backbone) to the metal. In extreme cases, *ortho*-metallation was observed with platinum insertion into one or both of the dimethylaminophenyl rings. In such metallated complexes, the nitrogen donor group was not bound to the metal. Instead, the PN ligand coordinated through the phosphorus and the metallated *ortho*-carbon atoms. Moreover,

further reaction of some metallated compounds led to the formation of new complexes.

Another feature of the coordination chemistry of PN ligand **65** was hydration of the central carbonyl group into a geminal diol upon metal complexation. Hydrated analogues were only observed for M(I) and M(II) complexes prepared in chlorinated solvents. The relative ratio between the ketone and hydrate forms remained constant at 3:1 regardless of the amount of water present in solution. This suggests that the ketone and hydrate forms are not in equilibrium. The precise factors controlling the hydration of the remote carbonyl group are not well understood.

In addition, protonation studies using the fluorocarbon acid $\text{CH}_2(\text{SO}_2\text{CF}_3)_2$ revealed that the $\text{CH}(\text{SO}_2\text{CF}_3)_2^-$ anion has the propensity to coordinate to the metal centre in platinum complexes containing PN ligand **65**, even though it is often considered to be a non-coordinating species.

Overall, the coordination chemistry of PN ligand **65** has revealed that the combination of the bicyclic framework, the phosphorus and nitrogen donor atoms, the dimethylaminophenyl groups and the central ketone functionality gives this ligand interesting chemical properties. A total of 24 complexes were prepared and fully characterised by spectroscopic methods in solution and, where possible, by *X*-ray diffraction in the solid state. Among these coordination compounds are hydroxo-bridged dimers containing a metallated PN ligand and the first examples of agostic ethyl and norbornyl complexes stabilised by a phosphorus-nitrogen ligand. The PN metal complexes also featured different coordination modes of the nitrogen donor atom, which were studied by ^{15}N NMR spectroscopy and will be further discussed in Chapter 4.

Chapter 4

Nitrogen NMR Spectroscopy of Transition Metal Complexes

The importance of nitrogen in all branches of chemistry makes nitrogen nuclear magnetic resonance an attractive means of gaining insight into bonding and the nature of interactions in molecules. Inversely detected ^{15}N NMR experiments at the natural abundance level of the ^{15}N nuclide were used to measure the ^{15}N chemical shifts of PN ligand **65** and its various metal complexes. The results provided valuable information about the coordination behaviour of the ligand nitrogen arm in the PN metal complexes.

4.1 Nitrogen NMR spectroscopy

The utilisation of ^{15}N NMR as a structural probe is highly desirable as nitrogen-containing compounds are ubiquitous in chemistry.^{121,122} It represents a powerful technique to study the molecular structures and electronic properties of molecules. This branch of molecular spectroscopy is experimentally more difficult than the NMR of other commonly occurring elements such as hydrogen, carbon, phosphorus and fluorine for several reasons: (1) both ^{14}N and ^{15}N isotopes have low gyromagnetic ratios resulting in low sensitivity; (2) the more

abundant (99.6%) but quadrupolar ($I = 1$) ^{14}N nuclide yields very broad NMR signals; (3) the other isotopic form, ^{15}N , has no quadrupole moment ($I = 1/2$) but is only 0.37% abundant. Therefore, the NMR spectroscopy of the ^{15}N nucleus is preferred but its direct detection at natural abundance is very difficult. Commonly, samples enriched with ^{15}N are used, but these can be costly and time consuming to prepare.

The development of inversely-detected NMR experiments, the use of powerful superconducting magnets and major advances in probe design have made it possible to overcome the difficulties associated with ^{15}N NMR. In this study, ^{15}N chemical shifts were obtained from ^1H – ^{15}N Heteronuclear Multiple Bond Correlation (HMBC) experiments¹²³ since the PN ligand **65** has no direct N–H bonds. The ^{15}N NMR data were recorded on a 600 MHz NMR spectrometer and were referenced to nitromethane for which the ^{15}N chemical shift is taken to be zero. Thus, resonances observed upfield of nitromethane are assigned negative chemical shifts, while downfield signals are assigned positive values. For ^{15}N , the range of chemical shifts for organic compounds spans *ca* 900 ppm,¹²¹ while the range for transition metal complexes containing nitrogen ligands extends over 1500 ppm.¹²² This is significantly larger than the ranges for ^1H and ^{13}C nuclei.

4.2 ^{15}N NMR of PN compounds

Two different ^{15}N chemical shifts were observed for PN compound **65**, at -337 and -353 ppm. The HMBC correlations that determined the ^{15}N chemical shifts are shown in Figure 4.1. Correlations from the methyl groups and the *meta*-protons established the ^{15}N chemical shift of the nitrogen atom in the dimethylaminophenyl group, while correlations from the methylene protons and the methyl substituent established the signal for the nitrogen arm in PN compound **65**.

Figure 4.1. ^1H – ^{15}N HMBC correlations for PN compound **65**.

The negative sign of the signals imply that the nitrogen atoms in **65** are more shielded than in nitromethane, and that the nitrogen arm is in turn more shielded than the NMe_2 groups. The NMe resonance is in the expected range for compounds with the same bicyclic framework, for example bispidinone compounds (Figure 4.2).¹²⁴ The nitrogen groups in the bispidinone compounds are deshielded due to the electron-withdrawing substituents. The ^{15}N chemical shifts of PN compound **66** were also measured. The NMe_2 group resonated at the same chemical shift of -337 ppm, but the NMe group was observed at -279 ppm. Due to the limited quantity of **66** isolated and the short life of its platinum complexes, this compound was not investigated further by ^{15}N NMR.

Figure 4.2. ^{15}N NMR chemical shifts of bispidinone compounds.

4.3 ^{15}N NMR of metal complexes

Nitrogen NMR spectroscopy is a sensitive structural probe to detect changes upon coordination of nitrogen-containing ligands to metal ions. ^{15}N NMR data reported for coordinated nitrogen ligands in transition metal complexes are rare,^{121,122,125–127} and to our knowledge no such data have been reported for metal complexes containing PN ligands. Since the nitrogen arm in PN ligands has the potential to be hemilabile, ^{15}N NMR can be particularly useful in studying its coordination mode in metal complexes.

The ^{15}N chemical shifts of almost all metal complexes containing PN ligand **65** were obtained and are summarised in Table 4.1. The ^{15}N chemical shifts will be influenced by many factors including the nature of the metal and its oxidation state, the bonding mode of the PN ligand itself and finally the nature of the co-ligands. The ^{15}N chemical shift of the dimethylamino (NMe_2) group in all metal complexes studied does not reflect major changes upon ligand complexation as expected since it is far from the reaction site. As for the NMe group, there appears to be no straightforward correlation between the ^{15}N chemical shifts and the nitrogen binding mode of the PN ligand in the metal complexes. Therefore, the ^{15}N NMR data has to be interpreted carefully with the aid of chemical understanding of the individual structures and the information obtained from X-ray crystallography, even though the solution structure may not necessarily be reflected in the solid state.

The largest differences in the ^{15}N chemical shifts of the NMe group in PN ligand **65** were observed for complexes $[\text{PtMe}_2(\text{PN})]$ (-377 ppm), $[\text{PdCl}_2(\text{PN})]$ (-377 ppm), and $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{PN})]\text{SbF}_6$ (-372 ppm) as the nitrogen group became very shielded. The bidentate coordination of the PN ligand in $[\text{PdCl}_2(\text{PN})]$ was confirmed by its X-ray crystal structure, and from the NMR data for complex $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{PN})]\text{SbF}_6$. In $[\text{PtMe}_2(\text{PN})]$, as well as the differences in the NMR data for the two methyl ligands, $^1\text{H}-^{15}\text{N}$ HMBC correlations from both

Table 4.1. ^{15}N NMR chemical shifts of PN compound **65** and metal complexes thereof, 600 MHz, referenced to CH_3NO_2 .

Compound	#	Solvent	^{15}N NMe ₂	^{15}N NMe
PN	65	C_6D_6	-337	-353
$[\text{PtMe}_2(\text{PN})]$	68	C_6D_6	-335	-377
$[\text{Pt}(\text{norb})(\text{PN})]$	74	CD_2Cl_2	-336	-362
$[\text{Pt}(\text{C}_2\text{H}_4)(\text{PN})]$	75	C_6D_6	-336	-363
$[\text{Pt}(\text{C}_2\text{H}_4)(\text{PN-2H})]$	76	C_6D_6	-336	-362
$[\text{Pt}(1-3- \text{---} \text{C}_8\text{H}_{13})(\text{PN-H})]$	87	C_6D_6	-336 -339	-354
$[\text{Pt}(1- \text{---}, 4-5- \text{---} \text{C}_8\text{H}_{13})(\text{PN})]\text{CH}(\text{SO}_2\text{CF}_3)_2$	88	CDCl_3	-331	-356
$[\text{Pt}(1-3- \text{---} \text{C}_8\text{H}_{13})(\text{PN})]\text{CH}(\text{SO}_2\text{CF}_3)_2$	89	CDCl_3	-331	-369
$[\text{PtH}\{\text{CH}(\text{SO}_2\text{CF}_3)_2\}(\text{PN})]$	92	CD_2Cl_2	-332	-367
$[\text{Pt}(\text{C}_7\text{H}_{11})(\text{PN})]\text{CPh}(\text{SO}_2\text{CF}_3)_2$	94	CD_2Cl_2	-332	-355
<i>trans</i> - $[\text{Pt}_2(\text{---OH})_2(\text{PN-H})_2]$	98	C_6D_6	-333	-355
<i>cis</i> - $[\text{Pt}_2(\text{---OH})_2(\text{PN-H})_2]$	101	C_6D_6	-339	-354
$[\text{PdCl}_2(\text{PN})]$	69	CD_2Cl_2	-331	-377
$[\text{Pd}(\text{dba})(\text{PN})]$	77	C_6D_6	-335	-359
$[\text{Pd}(\text{---}^3\text{-C}_3\text{H}_5)(\text{PN})]\text{Cl}$	79	CD_2Cl_2	-331	-369
$[\text{Pd}(\text{---}^3\text{-C}_3\text{H}_5)(\text{PN})]\text{SbF}_6$	84	CD_2Cl_2	-332	-363
$[\text{Rh}(\text{C}_8\text{H}_{12})(\text{PN})]\text{SbF}_6$	71	CDCl_3	-331	-372

of the methyl groups to the metal-bound nitrogen donor atom were observed (Figure 4.3). These observations confirmed the bonding between the platinum metal and the nitrogen atom.

Similarly, the nitrogen donor atom in complex $[\text{PtH}\{\text{CH}(\text{SO}_2\text{CF}_3)_2\}(\text{PN})]$ resonated at -367 ppm, and an HMBC correlation was observed from the hydride ligand to the nitrogen atom. This is consistent with the other NMR data, which indicated that both donor atoms in PN ligand **65** were bonded to platinum.

Although the ^{15}N chemical shift of the norbornyl agostic complex **94** at -355 ppm is very similar to the free ligand (-353 ppm), the nitrogen donor atom is definitely bonded to platinum as shown by the *X*-ray crystal structure. In

Figure 4.3. $^1\text{H}-^{15}\text{N}$ HMBC correlations for $[\text{PtMe}_2(\text{PN})]$ complex.

this instance, the change in the chemical environment around the nitrogen group was not reflected by the ^{15}N NMR signal. In contrast, the ^{15}N chemical shift of the PN ligand in the *trans* hydroxo-bridged platinum complex **98** at -355 ppm certainly demonstrated that the nitrogen donor atom was not coordinated to the metal as was shown by the solid state structure. Moreover, the same assumption can be made for the *cis* platinum dimer **101**, in which the NMe group resonated at -354 ppm. These results clearly show that many factors influence the ^{15}N chemical shifts of the coordinated PN ligand.

The ^{15}N chemical shifts of the alkene complexes were not very informative as to the binding mode of the nitrogen arm in PN ligand **65**. Complexes $[\text{Pt}(\text{norb})(\text{PN})]$ and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PN})]$ had very similar ^{15}N NMR signals at -362 and -363 ppm respectively, while the nitrogen donor atom in $[\text{Pd}(\text{dba})(\text{PN})]$ complex resonated at -359 ppm. These chemical shifts are only slightly different from the free ligand and no $^1\text{H}-^{15}\text{N}$ HMBC correlations were observed, thus making these results difficult to interpret. However, as the metal centres are in the zero oxidation state, the expected chemical structures of these complexes require the coordination of the nitrogen donor atom to give 16-electron complexes. Without nitrogen binding, electron deficient complexes would form, which might be expected to be too reactive to observe and isolate. In contrast, despite the similarity of the ^{15}N chemical shift of the second ethene complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PN-2H})]$ at -362 ppm, the NMe group is unlikely to be coordinated to the metal because the PN ligand is doubly metallated. This would place the

nitrogen donor atom out of bonding distance to the metal as was the case for the hydroxo-bridged complex *trans*-[Pt₂(μ-OH)₂(PN-H)₂], in which the Pt–N distance was 3.8 Å.

The above conclusion about ligand metallation could also apply to complex [Pt(1-3-η-C₈H₁₃)(PN-H)] in which the PN ligand was singly metallated. In the other two COD complexes [Pt(1-σ,4-5-η-C₈H₁₃)(PN)]CH(SO₂CF₃)₂ and [Pt(1-3-η-C₈H₁₃)(PN)]CH(SO₂CF₃)₂, and the allyl complexes [Pd(η³-C₃H₅)(PN)]Cl and [Pd(η³-C₃H₅)(PN)]SbF₆, the nitrogen group is expected to coordinate to form stable 16-electron complexes. Moreover, the NMR data for each complex were consistent with the proposed structures involving bidentate binding by the PN ligand.

4.4 Concluding remarks

The ¹⁵N chemical shifts obtained from ¹H–¹⁵N HMBC NMR spectra were analysed extensively in an effort to determine the binding mode of the nitrogen donor atom in PN ligand **65** in various transition metal complexes. The NMR data showed no obvious correlation between the ¹⁵N chemical shifts and the coordination mode of the nitrogen group. Thus, structural information obtained from other NMR data and X-ray crystallography was utilised to propose chemical structures in which the nitrogen donor atom was coordinated to the metal centres in some cases and non-coordinated in other instances.

Chapter 5

Conclusion

Phosphorus-nitrogen (PN) compounds represent an important class of ligands in coordination chemistry. These ligands combine the individual characteristics of the donor atoms to display an interesting mode of coordination to metal centres. Such ligands can also be hemilabile as the weakly bound nitrogen group plays the role of an intramolecular solvent molecule assuring the stability of the metal complexes in catalytic reactions.

In this study, the synthesis of phosphorus-nitrogen ligands based on a bicyclo[3.3.1]nonan-9-one backbone was attempted *via* the Mannich reaction using four different classes of phosphorinanone compounds. Reaction of the symmetric 2,6-diester phosphorinanone isomer **53** with methylamine and formaldehyde produced the bicyclic PN compound **65** in 75% yield. In contrast, many products were obtained from the Mannich reaction of the asymmetric isomer **54**. These included PN compound **65** but in low yield (26%), a new six-membered compound containing phosphorus and nitrogen atoms (**66**) and the *E/Z* isomers of 3-(*p*-dimethylaminophenyl)methyl-2-propenoate (**67**). These results were surprising and difficult to interpret.

The Mannich reaction of the 2,6-dimethyl phosphorinanones **50** and **51** was not successful possibly due to the decreased acidity of the α -protons caused by

the electron-donating methyl substituents at these positions. The remaining 3,5-diphenyl (**44**, **45**) and 4-phenyl (**42**) phosphorinanones had no β -substituents, yet the products obtained from their respective Mannich reactions could not be identified. Therefore, it was difficult to determine if the Mannich reaction was successful in these two cases.

PN ligand **65** adopted a chair-chair conformation both in solution and the solid state ensuring a preset bidentate capability. The coordination chemistry of PN ligand **65** was comprehensively explored with rhodium, palladium and platinum metals. A range of complexes were synthesised in which the ligand was coordinated *via* both the phosphorus and nitrogen donor atoms. The contrasting *trans*-influence of the phosphorus and nitrogen donor atoms were clearly exhibited by the ligands in the respective *trans*-positions on the metal. For example, in complex $[\text{PdCl}_2(\mathbf{65})]$ (**69**), the Pd–Cl bond *trans* to phosphorus was longer than the *cis* bond as determined from the *X*-ray crystal structure.

Cyclometallated platinum complexes were also observed. Depending on the nature of the complex, metallation occurred at the *ortho*-position of one or both of the dimethylaminophenyl groups. In such complexes, the nitrogen donor atom was not coordinated as the PN ligand was bound through the phosphorus atom and the *ortho*-carbon atom in the aryl rings only. This ligand binding mode was confirmed by *X*-ray crystallography for the hydroxo-bridged platinum complex *trans*- $[\text{Pt}_2(\mu\text{-OH})_2(\mathbf{65}\text{-H})_2]$ (**98**).

Protonation of the alkene complexes $[\text{Pt}(\text{C}_2\text{H}_4)(\mathbf{65})]$ (**75**) and $[\text{Pt}(\text{norb})(\mathbf{65})]$ (**74**) with the fluorocarbon acid $\text{CH}_2(\text{CF}_3\text{SO}_2)_2$ resulted in the formation of the hydride complex $[\text{PtH}\{\text{CH}(\text{SO}_2\text{CF}_3)_2\}(\mathbf{65})]$ (**92**), in which the anion was coordinated to the metal. The use of the sterically bulky analogue $\text{CHPh}(\text{CF}_3\text{SO}_2)_2$ eliminated the formation of such hydride complexes, and produced the respective ethyl (**93**) and norbornyl (**94**) agostic complexes. The agostic interaction in complex **94** was confirmed by *X*-ray crystallography, and

this compound represents the first example of an agostic complex containing a phosphorus-nitrogen ligand.

Hydration of the central carbonyl group in PN ligand **65** to a geminal diol upon metal complexation was also observed. This was partially attributed to the acidic character of the solvents used and the high oxidation state of the metal. Hydrated complexes possessed similar chemical properties to their ketone counterparts.

The coordination mode of the nitrogen donor atom in coordinated PN ligand **65** was studied by ^{15}N NMR. Inversely-detected $^1\text{H}-^{15}\text{N}$ HMBC experiments were used to measure the ^{15}N NMR chemical shifts of the PN ligand and its various metal complexes. The NMR data showed no direct correlation between the ^{15}N chemical shift and the binding mode of the nitrogen group.

In summary, incorporating phosphorus and nitrogen donor atoms in the bicyclo[3.3.1]nonan-9-one framework gave rise to a highly rigid and preorganised bicyclic PN ligand. The structure of the free ligand matched closely the ligand conformation in the PN metal complexes. The ligand framework constrained the dimethylaminophenyl substituents causing them to be in close proximity to the metal centres. This sometimes led to the formation of cyclometallated platinum complexes under mild conditions, in which the nitrogen donor group was not coordinated.

As part of future work, the catalytic activity of the different PN metal complexes should be evaluated through a series of catalytic reactions. Such studies would shed light on the catalytic potential of such complexes, and also on the hemilability of the nitrogen donor group. The possibility of synthesising chiral PN ligands containing the bicyclic framework is also feasible. Metal complexes of such ligands could potentially be used in asymmetric catalysis.

Chapter 6

Experimental

General procedures

All reactions and manipulation of products and reagents were carried out under an inert nitrogen atmosphere using standard Schlenk line techniques unless otherwise stated. Analytical grade reagents and high purity solvents were degassed and purged with nitrogen before use, except for diethyl ether and tetrahydrofuran which were dried by refluxing over sodium/benzophenone ketyl. NMR spectra were recorded using a Varian Unity Inova 300 (300 MHz for ^1H , 75 MHz for ^{13}C , 121 MHz for ^{31}P and 282 MHz for ^{19}F), a Varian Unity Inova 500 (500 MHz for ^1H and 125 MHz for ^{13}C), or a Varian DirectDrive 600 (600 MHz for ^1H , 150 MHz for ^{13}C and 60 MHz for ^{15}N) spectrometers. The 600 MHz instrument was equipped with a Varian inverse-detected triple-resonance HCN cold probe operating at 25 K. All direct-detected ^1H and ^{13}C chemical shifts were referenced to the residual solvent peak.¹²⁸ Indirectly-detected ^{15}N chemical shifts were referenced to the unified TMS scale with Ξ ratio of 10.136767, and an uncertainty of ± 2 ppm.¹²⁹ NMR samples were prepared under an inert nitrogen atmosphere unless otherwise stated using C_6D_6 , CDCl_3 , CD_2Cl_2 and toluene- d_8 . All NMR solvents were degassed before use. Variable

temperature NMR was carried out in toluene- d_8 or CD_2Cl_2 using Varian Unity Inova 300 MHz NMR spectrometer. Infrared spectra were recorded with a PerkinElmer Spectrum One FT-IR spectrophotometer using pressed KBr discs. Microanalyses were performed by The Campbell Microanalytical Laboratory at Otago University. Melting points were recorded on a Gallenkamp Melting Point Apparatus under vacuum unless otherwise stated. Single crystal *X*-ray diffraction data were recorded by the *X*-ray Crystallography Laboratory at the University of Canterbury. Electrospray ionisation mass spectra were either recorded on a PE Biosystem Mariner 5158 TOF mass spectrometer at Victoria University, or performed by the GlycoSyn QC laboratory at Industrial Research Limited using a Waters Q-TOF Premier Tandem mass spectrometer. Calculated 1H NMR spectra were obtained from gNMR spectral simulation programme, version 5.0.6.0 written by P. H. M. Budzelaar, IvorySoft 2006.

Crystallography

Diffraction data* (see Tables 2.7, 3.2, 3.4, 3.7 for details) were collected using Bruker CCD diffractometers with Mo K α radiation (0.71073 Å) from fine-focus sealed tubes with graphite monochromators, using phi and omega scans. Multi-scan absorption corrections were applied. The structures were solved by direct methods and full-matrix least squares refinement, with anisotropic thermal parameters for all non-H atoms.¹³⁰ Hydrogen atoms are in calculated positions and refined using a riding model with SHELXL defaults. The agostic hydrogen atom in Pt–H–C interaction was located and its position refined, and all relevant bond distances and angles were calculated using Mercury, version 1.4.2. Molecular drawings were made using ORTEP3.¹³¹

*Bruker SMART (Version 5.054), SADABS (Version 2.03), and SAINT (Version 6.02A), Bruker AXS Inc., Madison, Wisconsin, USA, 1997.

G. M. Sheldrick, SHELX-97. Programmes for the Solution and Refinement of Crystal Structures, 1997.

2,4 - Di(carbomethoxy) - 1,5 - bis(*p* - dimethylaminophenyl) - penta-1,4-dien-3-one (38)

Dimethyl 1,3-acetonedicarboxylate (3.5 g, 0.02 mol), *p*-dimethylaminobenzaldehyde (6.0 g, 0.04 mol), piperidine (0.45 cm³, 4.6 mmol) and glacial acetic acid (0.30 cm³, 5.2 mmol) were combined in benzene (60 cm³) in a 250 cm³ round bottom flask in the air. The flask was equipped with a Dean-Stark trap to measure the volume of water being eliminated during the course of the reaction. The trap was in turn equipped with a condenser, and the reaction mixture was heated under reflux for 1 day. About 0.7 cm³ of water were collected in the Dean-Stark trap indicating that the reaction was complete. The solvent was removed *in vacuo* to yield a dark red oil. The oil was washed with petroleum ether several times then taken up in benzene. The mixture was stirred at room temperature for several hours during which yellow crystalline solid precipitated out as the oil slowly dissolved. The solid was filtered, washed with benzene and dried in the air (7.5 g, 86%); mp 124.5-124.8 °C (from benzene); (Found: C, 69.2; H, 6.5; N, 6.4. C₂₅H₂₈N₂O₅ requires C, 68.8; H, 6.5; N, 6.4%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1732, 1719, 1701, 1693, 1572, 1526, 1373, 1189 and 1158; $\delta_{\text{H}}(300 \text{ MHz}; \text{C}_6\text{D}_6; \text{Me}_4\text{Si})$ 2.18 (6 H, s, NMe₂), 2.19 (6 H, s, NMe₂), 3.43 (3 H, s, OMe), 3.69 (3 H, s, OMe), 6.12 (2 H, d, J_{HH} 9.0, *m*-H), 6.23 (2 H, d, J_{HH} 9.0, *m*-H), 7.31 (2 H, d, J_{HH} 9.0, *o*-H), 7.62 (2 H, d, J_{HH} 9.0, *o*-H), 7.88 (1 H, s, CH=CH) and 8.32 (1 H, s, CH=CH); $\delta_{\text{C}}(75 \text{ MHz}; \text{C}_6\text{D}_6; \text{Me}_4\text{Si})$ 39.15 (2 C, s, NMe₂), 39.17 (2 C, s, NMe₂), 51.8 (1 C, s, OMe), 52.0 (1 C, s, OMe), 111.8 (1 C, s, *m*-C₆H₄), 112.1 (1 C, s, *m*-C₆H₄), 120.9 (2 C, s, C₆H₄), 121.2 (2 C, s, C₆H₄), 132.5 (2 C, s,

o-C₆H₄), 133.2 (2 C, s, *o*-C₆H₄), 143.7 (1 C, s, *p*-C₆H₄), 143.9 (1 C, s, *p*-C₆H₄), 166.5 (1 C, s, COO), 169.3 (1 C, s, COO) and 193.8 (1 C, s, CO); *m/z* (ESI) 459.1000 ([M + Na]⁺. C₂₅H₂₈N₂O₅Na requires 459.1896).

2,4-Dimethyl-1,5-diphenyl-1,4-pentadien-3-one (46)

Compound **46** was made by a literature method,⁶⁸ in which two side products (**47**⁶⁹ and **48**) were produced.

Compound 48:

¹H (600 MHz; CDCl₃; Me₄Si) 0.90 (3 H, s, Me-10), 0.91 (3 H, d, *J*_{HH} 6.5, Me-5), 1.68 (3 H, s, Me-6), 3.10 (2 H, dq, *J*_{HH} 13.0, 6.5, CH-2), 3.53 (2 H, d, *J*_{HH} 13.4, CH-3), 4.32 (1 H, br s, CH-9), 6.72 (2 H, d, *J*_{HH} 7.3, Ph) and 7.09-7.45 (13 H, m, Ph); ¹³C (150 MHz; CDCl₃; Me₄Si) 12.8 (1 C, s, Me-6), 13.0 (2 C, s, Me-5), 13.9 (1 C, s, Me-10), 44.3 (2 C, s, CH-2), 58.8 (1 C, s, C4), 59.3 (2 C, s, CH-3), 127.1 (1 C, s, Ph), 127.3 (1 C, s, Ph), 128.0 (1 C, s, CH-9), 128.1 (1 C, s, Ph), 129.0 (2 C, s, Ph), 135.7 (1 C, s, Ph), 138.2 (1 C, s, C8), 138.6 (2 C, s, Ph), 211.5 (1 C, s, CO-1) and 213.0 (1 C, s, CO-7).

4 - *t* - Butyl - 2,6 - di(carbomethoxy) - 3,5 - bis(*p* - dimethyl - aminophenyl)-4-phosphacyclohexanone (**53**, **54**, **57**)

Dibenzylideneacetone derivative **38** (3.6 g, 8.2 mmol) was dissolved in pyridine (30 cm³). To the solution, *t*-butylphosphine (1.1 g, 12.3 mmol) was quickly added. The reaction mixture was stirred at room temperature for 1 day in a closed vessel to prevent Bu^tPH₂ from escaping. Over time a white solid precipitated out. The solid was filtered in the air, washed with diethyl ether then dried *in vacuo* to give the first batch of phosphorinanone isomer **53**. The filtrate was reduced to dryness *in vacuo* to give a yellow foam. Washing the foam with diethyl ether yielded a second batch of compound **53** as a white solid.

The diethyl ether wash was reduced to dryness *in vacuo* and the yellow solid was recrystallised from hot methanol in the air to produce white crystalline fine needles of **54**. The yield can be increased by several cycles of crystallisations of the filtrates from hot methanol. Sometimes residual **53** co-crystallised with **54** as off-white balls, which could be physically separated from the needles. The final mother liquor contained small amounts of **53**, **54**, **57** and several other isomers as shown by ¹H and ³¹P NMR spectra. It was impractical to separate the remaining isomers any further.

Compound **53**:

(2.4 g, 55%); decomposition at 200 °C (from pyridine); (Found: C, 66.2; H, 7.7; N, 5.4. C₂₉H₃₉N₂O₅P requires C, 66.1; H, 7.5; N, 5.3%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1755, 1707, 1610, 1520; δ_{H} (500 MHz; CDCl₃; Me₄Si) 0.63 (9 H, d, J_{PH} 10.7, Bu^t),

2.91 (12 H, s, NMe₂), 3.51 (6 H, s, OMe), 3.59 (2 H, dd, J_{PH} 12.7, J_{HH} 5.9, PCH), 3.97 (2 H, dd, J_{PH} 12.7, J_{HH} 5.4, PCCH), 6.62 (4 H, d, J_{HH} 8.5, *m*-H) and 7.21 (4 H, d, J_{HH} 8.5, *o*-H); ^1C (125 MHz; CDCl₃; Me₄Si) 28.7 (3 C, d, J_{PC} 10.1, CMe₃), 30.9 (1 C, d, J_{PC} 20.6, CMe₃), 40.6 (4 C, s, NMe₂), 42.3 (2 C, d, J_{PC} 19.7, PCH), 52.1 (2 C, s, OMe), 65.4 (2 C, d, J_{PC} 16.1, PCCH), 112.7 (4 C, s, *m*-C₆H₄), 127.7 (2 C, d, J_{PC} 8.2, C₆H₄), 129.9 (4 C, d, J_{PC} 8.2, *o*-C₆H₄), 149.6 (2 C, s, *p*-C₆H₄), 168.2 (2 C, d, J_{PC} 10.6, COO) and 199.4 (1 C, d, J_{PC} 3.4, CO); ^3P (121 MHz; CDCl₃; H₃PO₄) 13.0 (1 P, s); m/z (ESI) 527.2661 ([M + H]⁺. C₂₉H₄₀N₂O₅P requires 527.2675), 264 (100%).

Compound 54:

(0.64 g, 15%); decomposition at 170 °C (from methanol); (Found: C, 66.3; H, 7.6; N, 5.4. C₂₉H₃₉N₂O₅P requires C, 66.1; H, 7.5; N, 5.3%); ν_{max} (KBr)/cm⁻¹ 3453, 1735, 1644, 1610, 1519; ^1H (600 MHz; CDCl₃; Me₄Si) 0.52 (9 H, d, J_{PH} 11.6, Bu^t), 2.91 (6 H, br s, NMe₂), 2.95 (6 H, br s, NMe₂), 3.62 (3 H, s, OMe), 3.66 (3 H, s, OMe), 3.90 (2 H, m, PCH/PCCH), 4.28 (1 H, d, J_{PH} 5.9, PCH), 6.51 (1 H, br s, *m*-C₆H₄), 6.74 (3 H, br s, *m*-C₆H₄), 6.91 (1 H, br s, *o*-C₆H₄), 7.40 (3 H, br s, *o*-C₆H₄) and 12.84 (1 H, s, OH); ^{13}C (150 MHz; CDCl₃; Me₄Si) 27.6 (3 C, d, J_{PC} 12.3, CMe₃), 30.2 (1 C, d, J_{PC} 21.3, CMe₃), 35.2 (1 C, d, J_{PC} 24.1, PCH), 36.5 (1 C, d, J_{PC} 19.1, PCH), 40.7 (2 C, br s, NMe₂), 40.8 (2 C, br s, NMe₂), 52.4 (1 C, s, OMe), 52.6 (1 C, s, OMe), 57.3 (1 C, d, J_{PC} 17.4, PCCH), 103.8 (1 C, d, J_{PC} 9.0, C=COH), 112.0 (1 C, br s, *m*-C₆H₄), 112.5 (1 C, br s, *m*-C₆H₄), 113.7 (2 C, br s, *m*-C₆H₄), 127.1 (1 C, br s, C₆H₄), 128.5 (1 C, br s,

C₆H₄), 128.9 (1 C, br s, *o*-C₆H₄), 130.6 (3 C, br s, *o*-C₆H₄), 149.1 (1 C, br s, *p*-C₆H₄), 149.7 (1 C, br s, *p*-C₆H₄), 168.3 (1 C, d, J_{PC} 6.2, C=COH), 172.6 (1 C, d, J_{PC} 13.2, COO) and 172.8 (1 C, d, J_{PC} 6.7, COO); ^1P (121 MHz; CDCl₃; H₃PO₄) 6.0 (1 P, s); m/z (ESI) 527.2677 ([M + H]⁺. C₂₉H₄₀N₂O₅P requires 527.2675).

Compound 57:

This phosphorinane isomer was not isolated, ^1H (600 MHz; CDCl₃; Me₄Si) 0.96 (9 H, d, J_{PH} 11.3, Bu^t), 2.90 (12 H, s, NMe₂), 3.58 (3 H, s, OMe), 3.61 (3 H, s, OMe), 3.78 (1 H, dd, J_{HH} 12.6, J_{PH} 3.2, PCH), 4.13 (1 H, s, PCH), 4.42 (1 H, dd, J_{HH} 12.6, J_{PH} 1.0, PCCH) 6.57 (2 H, d, J_{HH} 8.8, *m*-C₆H₄), 6.72 (2 H, m, *m*-C₆H₄), 7.13 (2 H, d, J_{HH} 8.7, *o*-C₆H₄), 7.24 (2 H, m, *o*-C₆H₄) and 13.13 (1 H, s, OH); ^{13}C (150 MHz; CDCl₃; Me₄Si) 29.8 (3 C, d, J_{PC} 13.7, CMe₃), 31.7 (1 C, d, J_{PC} 30.9, CMe₃), 34.3 (1 C, d, J_{PC} 21.3, PCH), 34.5 (1 C, d, J_{PC} 13.5, PCH), 40.0 (4 C, s, NMe₂), 52.0 (2 C, s, OMe), 48.1 (1 C, d, J_{PC} 2.0, PCCH), 99.9 (1 C, d, J_{PC} 2.8, C=COH), 112.0 (4 C, s, *m*-C₆H₄), 126.0 (1 C, d, J_{PC} 6.7, C₆H₄), 130.8 (1 C, d, J_{PC} 11.8, C₆H₄), 128.4 (2 C, d, J_{PC} 5.9, *o*-C₆H₄), 128.7 (2 C, d, J_{PC} 5.9, *o*-C₆H₄), 148.7 (2 C, m, *p*-C₆H₄), 169.9 (1 C, s, C=COH), 172.6 (1 C, d, J_{PC} 6.7, COO) and 173.1 (1 C, s, COO); ^1P (121 MHz; CDCl₃; H₃PO₄) 17.5 (1 P, s).

General procedure for the Mannich reaction of 4-phenylphosphorinanone (**42**)

4-Phenylphosphorinanone⁶⁵ **42** (0.10 g, 0.52 mmol), methylamine (0.05 cm³, 0.52 mmol) and formaldehyde (0.08 cm³, 1.0 mmol) were combined in absolute ethanol (10 cm³). The reaction mixture was heated under reflux for 24 hr. Removal of solvent *in vacuo* gave a pale yellow solid, which could not be identified.

General procedure for the Mannich reaction of phosphorinanone isomers **44** and **45**

A mixture of phosphorinanone isomers^{58,60,61} **44** and **45** (0.10 g, 0.29 mmol), methylamine (0.03 cm³, 0.29 mmol) and formaldehyde (0.04 cm³, 0.58 mmol) were combined in absolute ethanol (10 cm³). The reaction mixture was heated under reflux for the required length of time. Removal of solvent *in vacuo* gave a pale yellow oil, which could not be identified.

General procedure for the Mannich reaction of phosphorinanone isomers **50** and **51**

A mixture of phosphorinanone isomers^{59,60} **50** and **51** (0.10 g, 0.27 mmol), methylamine (0.02 cm³, 0.27 mmol) and formaldehyde (0.04 cm³, 0.54 mmol) were combined in absolute ethanol (10 cm³). The reaction mixture was heated under reflux for the required length of time. Upon cooling down to room temperature, the phosphorinanones crystallised out of the reaction mixture as white needles. These were filtered in the air, washed with cold ethanol and dried *in vacuo* then re-used in subsequent attempts.

General procedure for the exchange reactions of phosphorinanone isomer **51**

Phosphorinanone isomer **51** (0.005 g, 0.01 mmol) and NaOMe (0.001 g, 0.03 mmol) were combined in MeOH- d_4 . The reaction mixture was heated under reflux for 15 min. White solid precipitated out as the mixture cooled down to room temperature. The solvent was decanted and the solid dried *in vacuo*.

7 - *t* - Butyl - 1,5 - di(carbomethoxy) - 6,8 - bis(*p* - dimethylaminophenyl) - 3 - methyl - 3 - aza - 7 - phosphabicyclo[3.3.1] - nonan-9-one (**65**)

Phosphorinanone isomer **53** (1.7 g, 3.2 mmol), methylamine (0.30 cm³, 3.2 mmol) and formaldehyde (0.51 cm³, 6.3 mmol) were combined in absolute ethanol (30 cm³). The reaction mixture was heated under reflux for 1 day. Colourless needles crystallised out of the yellow reaction mixture as it cooled down to room temperature. The needles were filtered in the air, washed with cold ethanol and dried *in vacuo* (1.83 g, 75%); decomposition at 200 °C (from ethanol); (Found: C, 65.7; H, 7.6; N, 7.0. C₃₂H₄₄N₃O₅P requires C, 66.1; H, 7.6; N, 7.2%); $\nu_{\max}$ (KBr)/cm⁻¹ 1733, 1712, 1612, 1521, 1360, 1264; δ_{H} (300 MHz; C₆D₆; Me₄Si) 0.86 (9 H, d, J_{PH} 9.8, Bu^t), 2.30 (3 H, s, NMe), 2.48 (12 H, s, NMe₂), 2.91 (2 H, d, J_{HH} 12.0, CH₂), 3.44 (6 H, s, OMe), 3.56 (2 H, d, J_{HH} 12.5, CH₂), 4.44 (2 H, d, J_{PH} 5.4, PCH), 6.32 (2 H, br d, J_{HH} 7.8, *m*-H), 6.69 (2 H, br d,

J_{HH} 6.7, *m*-H), 7.27 (2 H, br d, J_{HH} 8.1, *o*-H) and 8.17 (2 H, br d, J_{HH} 8.6, *o*-H); ^1C (75 MHz; C_6D_6 ; Me_4Si) 28.1 (3 C, d, J_{PC} 13.4, CMe_3), 31.4 (1 C, d, J_{PC} 27.5, CMe_3), 39.9 (4 C, s, NMe_2), 43.0 (2 C, d, J_{PC} 28.4, PCH), 44.1 (1 C, s, NMe), 51.6 (2 C, s, OMe), 60.7 (2 C, s, CH_2), 65.8 (2 C, d, J_{PC} 1.4, PCHC), 112.2 (2 C, br s, *m*- C_6H_4), 112.4 (2 C, br d, J_{PC} 1.3, *m*- C_6H_4), 132.1 (2 C, br d, J_{PC} 3.4, C_6H_4), 133.1 (2 C, br d, J_{PC} 1.8, *o*- C_6H_4), 133.4 (2 C, br d, J_{PC} 2.0, *o*- C_6H_4), 149.7 (2 C, d, J_{PC} 1.7, *p*- C_6H_4), 169.7 (2 C, d, J_{PC} 2.2, COO) and 205.2 (1 C, d, J_{PC} 2.5, CO); ^1P (121 MHz; C_6D_6 ; H_3PO_4) 8.4 (1 P, s); ^1N (60 MHz; C_6D_6 ; MeNO_2) -337 (2 N, NMe_2) and -353 (1 N, NMe); m/z (ESI) 582.3086 ($[\text{M} + \text{H}]^+$. $\text{C}_{32}\text{H}_{45}\text{N}_3\text{O}_5\text{P}$ requires 582.3096).

Mannich reaction of phosphorinanone isomer **54**

Phosphorinanone isomer **54** (1.0 g, 1.9 mmol), methylamine (0.16 cm³, 1.9 mmol) and formaldehyde (0.28 cm³, 3.8 mmol) were combined in absolute ethanol (100 cm³). The reaction mixture was heated under reflux for 1 day. Big colourless crystals of **65** crystallised out of the yellow reaction mixture as it cooled down to room temperature. The crystals were filtered, washed with ethanol and dried in the air. All solvent was removed from the filtrate to give a yellow solid. Washing the solid with ethanol removed most of the yellow colouration to leave behind **65** as a white solid. Taking the filtrate to dryness again and washing the resulting yellow solid with diethyl ether gave another batch of compound **65** bringing the total yield to 0.29 g, 26%. The yields calculated from this reaction are based on the number of moles of phosphorinanone **54**.

The diethyl ether filtrate was taken to dryness and the resulting yellow residue was washed with hexane. This successfully separated the other products from this reaction. The hexane-insoluble white solid was identified as PN ligand **66** but the solid was contaminated with compound **65**. The white solid can be further purified by washing with small volumes of ethyl acetate to give up to

90% pure sample of compound **66** (0.09 g, 13%). The hexane wash contained the *E/Z* isomers of compound **67** (0.27 g, 37%, *E/Z* 9:1).

4-*t*-Butyl-6-carbomethoxy-5-(*p*-dimethylaminophenyl)-2-methyl-2-aza-4-phosphacyclohexanone (66**):**

Correct melting point and elemental analytical data could not be obtained because of contamination with compound **65**. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1744, 1655, 1612, 1520, 1351, 1164; δ_{H} (500 MHz; C_6D_6 ; Me_4Si) 0.79 (9 H, d, J_{PH} 11.5, Bu^t), 2.45 (6 H, s, NMe_2), 2.68 (3 H, s, NMe), 2.84 (1 H, dd, J_{HH} 14.5, J_{PH} 2.6, CH_2), 3.03 (1 H, dd, J_{PH} 18.0, J_{HH} 14.5, CH_2), 3.32 (3 H, s, OMe), 3.67 (1 H, dd, J_{HH} 12.8, J_{PH} 7.2, PCH), 3.90 (1 H, dd, J_{HH} 12.8, J_{PH} 5.3, PCCH), 6.55 (2 H, d, J_{HH} 8.8, *m*-H) and 7.32 (2 H, d, J_{HH} 8.8, *o*-H); δ_{C} (150 MHz; C_6D_6 ; Me_4Si) 27.4 (3 C, d, J_{PC} 13.0, CMe_3), 29.2 (1 C, d, J_{PC} 18.7, CMe_3), 36.6 (1 C, s, NMe), 39.2 (1 C, d, J_{PC} 17.3, PCH), 40.0 (2 C, s, NMe_2), 43.3 (1 C, d, J_{PC} 27.8, CH_2), 51.7 (1 C, s, OMe), 57.6 (1 C, d, J_{PC} 8.6, PCHC), 112.9 (2 C, s, *m*- C_6H_4), 129.0 (1 C, d, J_{PC} 13.4, C_6H_4), 130.0 (2 C, d, J_{PC} 8.6, *o*- C_6H_4), 149.5 (1 C, d, J_{PC} 1.9, *p*- C_6H_4), 167.6 (1 C, s, CO) and 169.7 (1 C, d, J_{PC} 9.1, COO); δ_{P} (121 MHz; C_6D_6 ; H_3PO_4) -3.5 (1 P, s); δ_{N} (60 MHz; C_6D_6 ; MeNO_2) -337 (1 N, NMe_2) and -279 (1 N, NMe); m/z (ESI) 365.1997 ($[\text{M} + \text{H}]^+$. $\text{C}_{19}\text{H}_{30}\text{N}_2\text{O}_3\text{P}$ requires 365.1994).

Compound 67 - *E* isomer:

^1H (500 MHz; C_6D_6 ; Me_4Si) 2.34 (6 H, s, NMe_2), 3.54 (3 H, s, OMe), 6.28 (2 H, d, J_{HH} 8.9, *m*-H), 6.48 (1 H, d, J_{HH} 15.9, -H), 7.22 (2 H, d, J_{HH} 8.9, *o*-H) and 7.99 (1 H, d, J_{HH} 15.9, -H); ^{13}C (150 MHz; C_6D_6 ; Me_4Si) 39.5 (2 C, s, NMe_2), 50.9 (1 C, s, OMe), 112.1 (2 C, s, *m*- C_6H_4), 113.0 (1 C, s, -C), 122.9 (1 C, s, C_6H_4), 129.9 (2 C, s, *o*- C_6H_4), 145.5 (1 C, s, -C) 151.8 (1 C, s, *p*- C_6H_4) and 167.8 (1 C, s, COO).

Compound 67 - *Z* isomer:

^1H (300 MHz; C_6D_6 ; Me_4Si) 2.36 (6 H, s, NMe_2), 3.44 (3 H, s, OMe), 5.81 (1 H, d, J_{HH} 13.0, -H), 6.44 (2 H, d, J_{HH} 9.1, *m*-H), 6.61 (1 H, d, J_{HH} 13.0, -H) and 8.11 (2 H, d, J_{HH} 8.8, *o*-H).

cis-[PtMe₂(**65**)] (**68**)

PN ligand **65** (0.1 g, 0.17 mmol) and [PtMe₂(1,5-hexadiene)] (0.05 g, 0.17 mmol) were combined in benzene (5 cm³). The colourless reaction mixture was heated at 50 °C for 3 days. Removal of solvent *in vacuo* gave complex **68** as an off-white solid (0.14 g, 98%) decomposition at 130 °C (from benzene); (Found: C, 50.5; H, 6.5; N, 5.3. C₃₄H₅₀N₃O₅PPt requires C, 50.6; H, 6.3; N, 5.2%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1743, 1721, 1610, 1519, 1355, 1259; $\delta_{\text{H}}^{\text{H}}(300 \text{ MHz}; \text{C}_6\text{D}_6; \text{Me}_4\text{Si})$ 0.75 (9 H, d, J_{PH} 12.7, Bu^t), 1.38 (3 H, d, J_{PH} 7.4, J_{PtH} 65, *trans*-Me), 1.59 (3 H, d, J_{PH} 6.7, J_{PtH} 92, *cis*-Me), 2.54 (3 H, br s, NMe), 2.93 (12 H, s, NMe₂), 2.94 (2 H, d, J_{HH} 13.4, CH₂), 3.38 (6 H, s, OMe), 4.22 (2 H, d, J_{HH} 13.9, CH₂), 4.36 (2 H, d, J_{PH} 11.2, PCH), 6.43 (2 H, dd, J_{HH} 8.5, J_{HH} 2.9, *m*-H), 6.63 (2 H, dd, J_{HH} 8.8, J_{HH} 2.7, *m*-H), 7.04 (2 H, dd, J_{HH} 8.5, J_{HH} 2.0, *o*-H) and 10.32 (2 H, dd, J_{HH} 8.8, J_{HH} 2.0, *o*-H); $\delta_{\text{C}}^{\text{C}}(75 \text{ MHz}; \text{C}_6\text{D}_6; \text{Me}_4\text{Si})$ -23.0 (1 C, d, J_{PC} 3.8, J_{PtC} 782, *cis*-Me), 13.7 (1 C, d, J_{PC} 112.6, J_{PtC} 711, *trans*-Me), 27.7 (3 C, d, J_{PC} 2.3, CMe₃), 33.5 (1 C, d, J_{PC} 12.2, CMe₃), 39.6 (4 C, s, NMe₂), 42.6 (2 C, d, J_{PC} 11.4, PCH), 51.7 (2 C, s, OMe), 57.2 (1 C, s, NMe), 64.4 (2 C, br s, CH₂), 65.0 (2 C, d, J_{PC} 3.6, PCHC), 111.7 (2 C, s, *m*-C₆H₄), 112.4 (2 C, s, *m*-C₆H₄), 122.5 (2 C, d, J_{PC} 3.1, C₆H₄), 132.9 (2 C, d, J_{PC} 5.2, *o*-C₆H₄), 133.5 (2 C, d, J_{PC} 6.2, *o*-C₆H₄), 150.1 (2 C, s, *p*-C₆H₄), 168.2 (2 C, d, J_{PC} 8.5, COO) and 203.0 (1 C, d, J_{PC} 1.6, CO); $\delta_{\text{P}}^{\text{P}}(121 \text{ MHz}; \text{C}_6\text{D}_6; \text{H}_3\text{PO}_4)$ 26.6 (1 P, s, J_{PtP} 1882); $\delta_{\text{N}}^{\text{N}}(60 \text{ MHz}; \text{C}_6\text{D}_6; \text{MeNO}_2)$ -335 (2 N, NMe₂) and -377 (1 N, NMe); m/z (ESI) 791.2896 ([PtMe(**65**)]⁺. C₃₃H₄₇N₃O₅PPt requires 791.2901).

cis-[PdCl₂(**65**)] (**69** and **70**)

PN ligand **65** (0.1 g, 0.17 mmol) and [PdCl₂(NCMe)₂] (0.04 g, 0.17 mmol) were dissolved in dichloromethane (6 cm³). The yellow solution was stirred at room temperature for 3 days. Removal of solvent *in vacuo* gave the ketone (**69**) and hydrate (**70**) forms of the title compound in a 3:1 ratio as a pale yellow solid (0.1 g, 77%). *X*-ray quality crystals were obtained by the slow diffusion of diethyl ether into a dichloromethane-benzene mixture; (Found: C, 51.0; H, 5.8; N, 4.8. C₃₂H₄₄N₃O₅PCl₂Pd requires C, 50.6; H, 5.8; N, 5.5%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3423, 1744, 1728, 1608, 1520, 1257; *m/z* (ESI) 740.1848 ([PdCl(**65**) + H₂O]⁺. C₃₂H₄₆N₃O₆PClPd requires 740.1848).

Compound **69**:

¹H (600 MHz; CD₂Cl₂; Me₄Si) 0.93 (9 H, br s, Bu^t), 2.89 (2 H, d, *J*_{HH} 14.1, CH₂), 2.96 (12 H, s, NMe₂), 3.42 (3 H, s, NMe), 3.66 (6 H, s, OMe), 3.89 (2 H, d, *J*_{PH} 16.2, PCH), 4.12 (2 H, d, *J*_{HH} 14.6, CH₂), 6.56 (2 H, m, *m*-H), 6.93 (4 H, m, *m/o*-H) and 9.70 (2 H, dd, *J*_{HH} 8.7, *J*_{HH} 1.3, *o*-H); ¹³C (150 MHz; CD₂Cl₂; Me₄Si) 28.2 (3 C, s, CMe₃), 38.6 (1 C, d, *J*_{PC} 21.0, CMe₃), 40.2 (4 C, s, NMe₂), 41.2 (2 C, d, *J*_{PC} 16.9, PCH), 53.0 (2 C, s, OMe), 61.2 (1 C, s, NMe), 63.6 (2 C, d, *J*_{PC} 2.3, PCHC), 64.1 (2 C, d, *J*_{PC} 3.9, CH₂), 112.3 (2 C, s, *m*-C₆H₄), 113.1 (2 C, s, *m*-C₆H₄), 117.3 (2 C, s, C₆H₄), 131.9 (2 C, d, *J*_{PC} 7.0, *o*-C₆H₄), 132.6 (2 C, d, *J*_{PC} 6.0, *o*-C₆H₄), 150.7 (2 C, s, *p*-C₆H₄), 166.3 (2 C, d, *J*_{PC} 9.9, COO) and 199.4 (1 C, s, CO); ³¹P (121 MHz; CD₂Cl₂; H₃PO₄) 27.0 (1 P, s); ¹⁵N (60 MHz; CD₂Cl₂; MeNO₂) -331 (2 N, NMe₂) and -377 (1 N, NMe).

Compound 70:

^1H (600 MHz; CD_2Cl_2 ; Me_4Si) 0.93 (9 H, br s, Bu^t), 2.77 (2 H, d, J_{HH} 13.4, CH_2), 2.95 (12 H, s, NMe_2), 3.35 (3 H, s, NMe), 3.44 (6 H, s, OMe), 3.79 (2 H, d, J_{HH} 14.4, CH_2), 4.04 (2 H, d, J_{PH} 17.0, PCH), 6.56 (3 H, m, $m\text{-H}$, OH), 6.64 (1 H, s, OH), 6.93 (4 H, m, $m/o\text{-H}$) and 9.78 (2 H, dd, J_{HH} 8.8, J_{HH} 1.1, $o\text{-H}$); ^{13}C (150 MHz; CD_2Cl_2 ; Me_4Si) 28.3 (3 C, s, CMe_3), 38.2 (1 C, d, J_{PC} 22.8, CMe_3), 39.1 (2 C, d, J_{PC} 17.1, PCH), 40.3 (4 C, s, NMe_2), 53.1 (2 C, s, OMe), 57.7 (2 C, d, J_{PC} 2.6, PCHC), 58.2 (2 C, d, J_{PC} 3.9, CH_2), 61.4 (1 C, s, NMe), 94.5 (1 C, s, $\text{C}(\text{OH})_2$), 112.2 (2 C, s, $m\text{-C}_6\text{H}_4$), 113.3 (2 C, s, $m\text{-C}_6\text{H}_4$), 119.1 (2 C, s, C_6H_4), 132.0 (2 C, d, J_{PC} 7.0, $o\text{-C}_6\text{H}_4$), 132.4 (2 C, d, J_{PC} 6.7, $o\text{-C}_6\text{H}_4$), 150.4 (2 C, s, $p\text{-C}_6\text{H}_4$) and 170.9 (2 C, d, J_{PC} 11.3, COO); ^31P (121 MHz; CD_2Cl_2 ; H_3PO_4) 25.2 (1 P, s); ^{15}N (60 MHz; CD_2Cl_2 ; MeNO_2) -331 (2 N, NMe_2) and -379 (1 N, NMe).

[Rh(cod)(65)]SbF₆ (71 and 73)

PN ligand **65** (0.12 g, 0.20 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.05 g, 0.10 mmol) and AgSbF_6 (0.07 g, 0.20 mmol) were combined in dichloromethane (5 cm^3). The yellow reaction mixture was stirred for 1 hr at room temperature and then was filtered and centrifuged to remove AgCl . The yellow filtrate was stirred at room temperature for 1 week, after which hexane was added to precipitate the ketone (**71**) and hydrate (**73**) forms of the title compound in a 3:1 ratio as a yellow solid. The solid was filtered in the air, washed with hexane and dried *in vacuo* (0.09 g, 91%) (Found: C, 46.9; H, 5.6; N, 4.1. $\text{C}_{40}\text{H}_{56}\text{F}_6\text{N}_3\text{O}_5\text{PRhSb}$ requires C,

46.7; H, 5.5; N, 4.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3434, 1741, 1609, 1520, 1259, 658; m/z (ESI) 792.3022 ($[\text{M}]^+$. $\text{C}_{40}\text{H}_{56}\text{N}_3\text{O}_5\text{PRh}$ requires 792.3012).

Compound 71:

^1H (600 MHz; CDCl_3 ; Me_4Si) 0.74 (9 H, d, J_{PH} 13.7, Bu^t), 2.17 (4 H, m, COD- CH_2), 2.59 (2 H, m, COD- CH_2), 2.80 (2 H, m, COD- CH_2), 2.84 (3 H, s, NMe), 2.86 (2 H, d, J_{HH} 14.3, CH_2), 3.01 (12 H, s, NMe_2), 3.63 (6 H, s, OMe), 4.03 (2 H, d, J_{HH} 14.5, CH_2), 4.08 (2 H, d, J_{PH} 14.3, PCH), 4.54 (2 H, d, J_{PH} 2.4, COD- CH_X), 5.68 (2 H, d, J_{PH} 2.6, COD- CH_Y), 6.65 (2 H, m, $m\text{-H}$), 6.96 (4 H, m, $m/o\text{-H}$) and 9.72 (2 H, d, J_{HH} 8.6, $o\text{-H}$); ^{13}C (150 MHz; CDCl_3 ; Me_4Si) 28.9 (5 C, m, CMe_3 , COD- CH_2), 32.2 (2 C, d, J_{PC} 2.8, COD- CH_2), 36.9 (1 C, d, J_{PC} 14.8, CMe_3), 40.3 (4 C, s, NMe_2), 43.1 (2 C, d, J_{PC} 13.8, PCH), 52.98 (2 C, s, OMe), 55.5 (1 C, s, NMe), 63.2 (2 C, d, J_{PC} 3.4, PCHC), 64.6 (2 C, d, J_{PC} 2.3, CH_2), 73.5 (2 C, d, J 11.3, COD- CH_X), 105.1 (2 C, dd, $J_{\text{PC}} + J_{\text{RhC}}$ 14.9, COD- CH_Y), 111.5 (2 C, s, $m\text{-C}_6\text{H}_4$), 112.8 (2 C, s, $m\text{-C}_6\text{H}_4$), 118.7 (2 C, s, C_6H_4), 132.5 (2 C, d, J_{PC} 7.6, $o\text{-C}_6\text{H}_4$), 133.1 (2 C, d, J_{PC} 5.3, $o\text{-C}_6\text{H}_4$), 150.7 (2 C, s, $p\text{-C}_6\text{H}_4$), 166.6 (2 C, d, J_{PC} 9.5, COO) and 200.0 (1 C, s, CO); ^{31}P (121 MHz; CDCl_3 ; H_3PO_4) 21.9 (1 P, d, J_{RhP} 149.4); ^{15}N (60 MHz; CDCl_3 ; MeNO_2) -331 (2 N, NMe_2) and -372 (1 N, NMe).

Compound 73:

^1H (600 MHz; CDCl_3 ; Me_4Si) 0.73 (9 H, d, J_{PH} 12.9, Bu^t), 2.17 (4 H, m, COD- CH_2), 2.59 (2 H, m, COD- CH_2), 2.79 (5 H, m, CH_2 , NMe), 2.80 (2 H, m, COD- CH_2), 3.00 (12 H, s, NMe₂), 3.43 (6 H, s, OMe), 3.67 (2 H, d, J_{HH} 14.1, CH_2), 4.29 (2 H, d, J_{PH} 15.3, PCH), 4.44 (2 H, d, J_{PH} 2.4, COD- CH_X), 5.55 (2 H, d, J_{PH} 2.8, COD- CH_Y), 6.65 (2 H, m, *m*-H), 6.96 (4 H, m, *m/o*-H) and 9.75 (2 H, d, J_{HH} 8.5, *o*-H); ^{13}C (150 MHz; CDCl_3 ; Me_4Si) 27.3 (3 C, br s, CMe₃), 28.9 (2 C, m, COD- CH_2), 32.2 (2 C, d, J_{PC} 2.8, COD- CH_2), 35.3 (1 C, d, J_{PC} 4.7, CMe₃), 40.5 (4 C, s, NMe₂), 41.4 (2 C, d, J_{PC} 13.8, PCH), 53.03 (2 C, s, OMe), 55.7 (1 C, s, NMe), 57.4 (2 C, d, J_{PC} 3.4, PCHC), 58.7 (2 C, s, CH_2), 72.6 (2 C, d, J 10.6, COD- CH_X), 94.5 (1 C, s, C(OH)₂), 103.7 (2 C, dd, $J_{\text{PC}} + J_{\text{RhC}}$ 14.5, COD- CH_Y), 111.7 (2 C, s, *m*-C₆H₄), 113.0 (2 C, s, *m*-C₆H₄), 120.7 (2 C, br s, C₆H₄), 132.7 (2 C, d, J_{PC} 7.5, *o*-C₆H₄), 132.8 (2 C, d, J_{PC} 5.8, *o*-C₆H₄), 150.3 (2 C, s, *p*-C₆H₄) and 170.8 (2 C, d, J_{PC} 10.7, COO); ^{31}P (121 MHz; CDCl_3 ; H_3PO_4) 20.3 (1 P, d, J_{RhP} 146.2).

[Pt(norb)(65)] (74)

PN ligand **65** (0.10 g, 0.17 mmol) and [Pt(norb)₃] (0.08 g, 0.17 mmol) were combined in benzene (6 cm³). The yellow reaction mixture was stirred for 1 week at room temperature. Removal of solvent *in vacuo* gave an off-white solid (0.14 g, 93%) (Found: C, 53.9; H, 6.2; N, 4.5. C₃₉H₅₄N₃O₅PPt requires C, 53.8; H, 6.3; N, 4.8%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1742, 1720, 1610, 1518, 1445, 1254; δ_{H} (600 MHz; CD₂Cl₂; Me₄Si) 0.51 (1 H, d, J_{HH} 8.1, norb-bridge CH₂), 0.58 (9 H, d, J_{PH} 13.7, Bu^t), 1.14 (2 H, d, J_{HH} 5.0, norb CH₂), 1.56 (2 H, d, J_{HH} 7.7, norb CH₂), 1.82 (1 H, d, J_{HH} 7.9, norb-bridge CH₂), 2.08 (2 H, br s, J_{PtH} 77, norb C=CH), 2.57 (2 H, br s, norb CH), 2.92 (2 H, m, CH₂), 2.92 (12 H, s, NMe₂), 3.58 (6 H, s, OMe), 3.71 (3 H, d, J_{PH} 1.9, NMe), 4.05 (2 H, d, J_{HH} 13.7, CH₂), 4.14 (2 H, d, J_{PH} 9.8, PCH), 6.58 (4 H, m, *m*-H), 6.92 (2 H, m, *o*-H) and 9.26 (2 H, d, J_{HH} 8.3, *o*-H); δ_{C} (150 MHz; CD₂Cl₂; Me₄Si) 26.3 (3 C, d, J_{PC} 6.7, CMe₃), 30.2 (2 C, d, J_{PC} 5.5, J_{PtC} 77, norb CH₂), 32.0 (1 C, d, J_{PC} 10.7, CMe₃), 40.0 (4 C, s, NMe₂), 41.8 (1 C, s, norb-bridge CH₂), 43.1 (2 C, s, norb CH), 43.6 (2 C, d, J_{PC} 7.3, PCH), 46.7 (2 C, d, J_{PC} 27.8, J_{PtC} 469, norb C=C), 51.8 (2 C, s, OMe), 62.9 (1 C, d, J_{PC} 4.5, NMe), 63.9 (2 C, s, CH₂), 65.2 (2 C, d, J_{PC} 3.9, PCHC), 111.1 (2 C, s, *m*-C₆H₄), 111.5 (2 C, s, *m*-C₆H₄), 122.7 (2 C, d, J_{PC} 4.2, C₆H₄), 132.2 (2 C, d, J_{PC} 4.5, *o*-C₆H₄), 132.9 (2 C, d, J_{PC} 7.0, *o*-C₆H₄), 149.8 (2 C, s, *p*-C₆H₄), 168.4 (2 C, d, J_{PC} 8.4, COO) and 203.2 (1 C, d, J_{PC} 2.0, CO); δ_{P} (121 MHz; CD₂Cl₂; H₃PO₄) 47.5 (1 P, s, J_{PtP} 3559); δ_{N} (60 MHz; CD₂Cl₂; MeNO₂) -336 (2 N, NMe₂) and -362 (1 N, NMe); m/z (ESI) 871.3917 ([M + H]⁺). C₃₉H₅₅N₃O₅PPt requires 871.3527).

[Pt(C₂H₄)(65**)] (**75**)**

PN ligand **65** (0.02 g, 0.034 mmol) and [Pt(C₂H₄)₃] (0.01 g, 0.034 mmol) were dissolved in either benzene-d₆ or toluene-d₈ (0.5 cm³) in a NMR tube at room temperature under an ethylene atmosphere. Complex **75** formed immediately, but it converted into complex **76** within 1 day at room temperature.

¹H (300 MHz; C₆D₆; Me₄Si) 0.69 (9 H, d, *J*_{PH} 13.8, Bu^t), 2.39 (12 H, s, NMe₂), 2.61 (3 H, br s, NMe), 3.03 (2 H, d, *J*_{HH} 14.3, CH₂), 3.22 (4 H, d, *J*_{HH} 1.9, *J*_{PtH} 16, C₂H₄), 3.39 (6 H, s, OMe), 4.30 (2 H, d, *J*_{HH} 13.7, CH₂), 4.41 (2 H, d, *J*_{PH} 10.7, PCH), 6.43 (2 H, dd, *J*_{HH} 8.5, 2.8, *m*-H), 6.56 (2 H, dd, *J*_{HH} 8.8, 2.8, *m*-H), 7.06 (2 H, dd, *J*_{HH} 8.5, 2.2, *o*-H) and 9.74 (2 H, dd, *J*_{HH} 8.8, 1.7, *o*-H);
¹³C (75 MHz; toluene-d₈; Me₄Si, -10 °C) 27.2 (3 C, br s, CMe₃), 32.6 (1 C, d, *J*_{PC} 11.4, CMe₃), 40.0 (4 C, s, NMe₂), 44.4 (2 C, d, *J*_{PC} 8.6, PCH), 48.3 (1 C, s, NMe), 52.0 (2 C, s, OMe), 60.0 (2 C, s, CH₂), 64.7 (2 C, br s, C₂H₄), 66.0 (2 C, d, *J*_{PC} 3.6, PCHC), 111.8 (2 C, br s, *m*-C₆H₄), 112.3 (2 C, br s, *m*-C₆H₄), 123.4 (2 C, d, *J*_{PC} 4.1, C₆H₄), 133.0 (2 C, br s, *o*-C₆H₄), 134.0 (2 C, br s, *o*-C₆H₄), 150.1 (2 C, s, *p*-C₆H₄), 168.7 (2 C, d, *J*_{PC} 8.6, COO) and 203.2 (1 C, d, *J*_{PC} 1.3, CO);
³¹P (121 MHz; C₆D₆; H₃PO₄) 47.5 (1 P, s, *J*_{PtP} 3727);
¹⁵N (60 MHz; C₆D₆; MeNO₂) -336 (2 N, NMe₂) and -363 (1 N, NMe).

The title compound was obtained from complex **75**. ¹H (300 MHz; C₆D₆; Me₄Si) 0.85 (9 H, d, *J*_{PH} 15.1, Bu^t), 2.10 (3 H, s, NMe), 2.70 (14 H, m, NMe₂ and CH₂), 3.01 (2 H, d, *J*_{HH} 11.7, CH₂), 3.41 (6 H, s, OMe), 4.02 (4 H, d, *J*_{HH} 3.2, *J*_{PtH} 55, C₂H₄), 5.07 (2 H, d, *J*_{PH} 11.5, *J*_{PtH} 25, PCH), 6.50 (2 H, dd, *J*_{HH} 8.3, 2.7, *J*_{PtH} 61, *m*-H), 6.92 (2 H, d, *J*_{HH} 2.7, *J*_{PtH} 26, *m*-H) and 7.34 (2 H, d, *J*_{HH} 8.3, *o*-H); ¹³C (75 MHz; C₆D₆; Me₄Si) 26.0 (3 C, d, *J*_{PC} 3.8, CMe₃), 31.5 (1 C, s, CMe₃), 40.5 (4 C, s, NMe₂), 48.4 (2 C, d, *J*_{PC} 24.0, PCH), 51.7 (1 C, s, NMe), 52.5 (2 C, s, OMe), 59.3 (2 C, s, CH₂), 62.5 (2 C, s, C₂H₄), 63.1 (2 C, d, *J*_{PC} 16.0, PCHC), 110.2 (2 C, s, *m*-C₆H₄), 117.2 (2 C, s, *m*-C₆H₄), 125.8 (2 C, d, *J*_{PC} 16.4, *o*-C₆H₄), 143.6 (2 C, d, *J*_{PC} 18.3, C₆H₄), 149.4 (2 C, s, *p*-C₆H₄), 161.2 (2 C, d, *J*_{PC} 2.4, Pt-C), 169.0 (2 C, d, *J*_{PC} 8.9, COO) and 203.9 (1 C, d, *J*_{PC} 7.0, CO); ³¹P (121 MHz; C₆D₆; H₃PO₄) 73.5 (1 P, s, *J*_{PtP} 3965); ¹⁵N (60 MHz; C₆D₆; MeNO₂) -336 (2 N, NMe₂) and -362 (1 N, NMe).

[Pd(dba)(**65**)] (**77**)

PN ligand **65** (0.10 g, 0.17 mmol) and [Pd₂(dba)₃ · CHCl₃] (0.09 g, 0.09 mmol) were combined in benzene (3 cm³). The dark red reaction mixture was stirred for 40 hr at room temperature. Gradually the colour changed to yellow as free dba was released into solution and some fine solid formed. Removal of solvent *in vacuo* and subsequent washings with hexane in the air removed much of the free dba to give a pale yellow solid (0.10 g, 66%); accurate elemental analytical data could not be obtained due to contamination with free dba; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1740, 1651, 1615, 1519, 1448, 1339, 1258; $\delta_{\text{H}} (300 \text{ MHz; C}_6\text{D}_6; \text{Me}_4\text{Si})$ 0.44 (9 H, d, J_{PH} 13.7, Bu^t), 2.46 (6 H, s, NMe₂), 2.50 (6 H, s, NMe₂), 2.70 (2 H, m, CH₂), 3.78 (3 H, s, NMe), 3.29 (3 H, s, OMe), 3.36 (3 H, s, OMe), 4.02 (2 H, m, CH₂), 4.15 (1 H, d, J_{PH} 11.0, PCH), 4.25 (1 H, d, J_{PH} 11.5, PCH), 4.99 (1 H, br s, coord dba HC=CH), 5.51 (1 H, d, J_{HH} 10.0, coord dba HC=CH), 6.31 (1 H, dd, J_{HH} 8.2, 1.8, *m*-H), 6.47 (1 H, dd, J_{HH} 8.2, 2.1, *m*-H), 6.80 (1 H, m, *m*-H), 6.87 (1 H, d, J_{HH} 8.9, *o*-H), 7.01 (1 H, m, *o*-H), 7.03 (10 H, m, dba-Ph), 7.25 (1 H, m, *m*-H), 7.25 (1 H, m, non-coord dba HC=CH), 8.12 (1 H, d, J_{HH} 15.6, non-coord dba HC=CH), 8.99 (1 H, d, J_{HH} 7.8, *o*-H) and 9.57 (1 H, d, J_{HH} 8.1, *o*-H), $\delta_{\text{C}} (75 \text{ MHz; C}_6\text{D}_6; \text{Me}_4\text{Si})$ 26.9 (3 C, d, J_{PC} 6.9, CMe₃), 32.9 (1 C, s, CMe₃), 39.8 (4 C, s, NMe₂), 43.6 (1 C, br s, PCH), 44.1 (1 C, br s, PCH), 51.7 (2 C, s, OMe), 57.5 (1 C, s, NMe), 59.8 (1 C, br s, coord dba C=C), 64.2 (1 C, br s, CH₂), 64.4 (1 C, br s, CH₂), 65.2 (1 C, br s, PCHC), 65.3 (1 C, br

s, PCHC), 66.9 (1 C, m, coord dba C=C), 111.9 (2 C, s, *m*-C₆H₄), 113.0 (1 C, s, *m*-C₆H₄), 113.3 (1 C, s, *m*-C₆H₄), 122.7 (1 C, br s, C₆H₄), 122.9 (1 C, br s, C₆H₄), 128.0 (12 C, m, dba-Ph), 128.5 (1 C, s, non-coord dba C=C), 132.4 (1 C, br s, *o*-C₆H₄), 132.9 (2 C, m, *o*-C₆H₄), 133.8 (1 C, m, *o*-C₆H₄), 137.2 (1 C, s, non-coord dba C=C), 149.9 (1 C, s, *p*-C₆H₄), 150.4 (1 C, s, *p*-C₆H₄), 167.8 (1 C, br s, COO), 168.1 (1 C, br s, COO), 188.8 (1 C, d, *J*_{PC} 2.2, dba-CO) and 202.4 (1 C, d, *J*_{PC} 1.8, CO); ³¹P (121 MHz; C₆D₆; H₃PO₄) 33.6 (1 P, s); ¹⁵N (60 MHz; C₆D₆; MeNO₂) -335 (1 N, NMe₂), -336 (1 N, NMe₂) and -359 (1 N, NMe); *m/z* (ESI) 686.1985 ([Pd(**65**) - dba - H]⁺. C₃₂H₄₃N₃O₅PPd requires 686.1975).

[Pd(η^3 -C₃H₅)(**65**)]Cl (**79** and **83**)

PN ligand **65** (0.16 g, 0.27 mmol) and [Pd(η^3 -C₃H₅)(μ -Cl)]₂ (0.05 g, 0.14 mmol) were combined in dichloromethane (5 cm³). The pale green reaction mixture was stirred for 1 day at room temperature. The solvent was removed *in vacuo* and the residue was washed with hexane in the air and dried *in vacuo* to give the ketone (**79**) and hydrate (**83**) forms of the title compound in a 3:1 ratio as a white solid (0.15 g, 74%) (Found: C, 50.8; H, 6.4; N, 5.0. C₃₅H₄₉N₃O₅PClPd + CH₂Cl₂ requires C, 50.9; H, 6.1; N, 5.0%); ^{max}(KBr)/cm⁻¹ 3408, 1728, 1609, 1519, 1257; *m/z* (ESI) 728.2464 ([M - Cl]⁺. C₃₅H₄₉N₃O₅PPd requires 728.2444).

Compound 79:

^1H (600 MHz; CD_2Cl_2 ; Me_4Si) 0.70 (9 H, d, J_{PH} 15.4, Bu^t), 2.96 (12 H, s, NMe_2), 3.06 (2 H, d, J_{HH} 14.5, CH_2), 3.35 (2 H, d, J_{HH} 9.4, allylic CH_2 *cis* to P), 3.65 (6 H, s, OMe), 3.68 (3 H, s, NMe), 4.18 (4 H, m, CH_2 and PCH), 4.75 (1 H, dd, J_{HH} 14.1, J_{PH} 9.6, anti allylic CH_2 *trans* to P), 5.26 (1 H, dd, J_{PH} 7.4, J_{HH} 7.3, syn allylic CH_2 *trans* to P), 6.26 (1 H, dtd, J_{HH} 14.1, 9.4, 7.3, allylic CH), 6.64 (2 H, m, *m*-H), 6.81 (2 H, dd, J_{HH} 8.9, 2.7, *m*), 6.98 (2 H, dd, J_{HH} 8.8, 2.2, *o*) and 8.13 (2 H, dd, J_{HH} 8.7, 1.7, *o*); ^{13}C (150 MHz; CD_2Cl_2 ; Me_4Si) 26.78 (3 C, d, J_{PC} 27.4, CMe_3), 33.9 (1 C, d, J_{PC} 14.5, CMe_3), 39.80 (4 C, s, NMe_2), 42.3 (2 C, d, J_{PC} 13.8, PCH), 49.5 (1 C, d, J_{PC} 4.8, allylic CH_2 *cis* to P), 52.6 (2 C, s, OMe), 63.1 (1 C, s, NMe), 64.2 (4 C, m, PCHC and CH_2), 88.1 (1 C, d, J_{PC} 26.9, allylic CH_2 *trans* to P), 111.4 (2 C, s, *m*- C_6H_4), 112.3 (2 C, s, *m*- C_6H_4), 118.4 (2 C, d, J_{PC} 2.0, C_6H_4), 122.3 (1 C, d, J_{PC} 6.2, allylic CH), 130.8 (2 C, d, J_{PC} 8.4, *o*- C_6H_4), 132.6 (2 C, d, J_{PC} 5.3, *o*- C_6H_4), 150.6 (2 C, s, *p*- C_6H_4), 166.5 (2 C, d, J_{PC} 9.8, COO) and 199.4 (1 C, s, CO); ^{31}P (121 MHz; CDCl_3 ; H_3PO_4) 38.7 (1 P, s); ^{15}N (60 MHz; CD_2Cl_2 ; MeNO_2) -331 (2 N, NMe_2) and -363 (1 N, NMe).

Tentatively assigned by comparison to the theoretical gNMR spectrum (see Figure 3.5).

Compound 83:

^1H (600 MHz; CD_2Cl_2 ; Me_4Si) 0.70 (9 H, d, J_{PH} 15.4, Bu^t), 2.94 (12 H, s, NMe_2), 3.13 (4 H, m, CH_2 and allylic CH_2 *cis* to P), 3.49 (3 H, s, NMe), 3.57 (2 H, d, J_{HH} 12.4, CH_2), 3.57 (6 H, s, OMe), 4.26 (1 H, dd, J_{HH} 14.2, J_{PH} 9.4, anti allylic CH_2 *trans* to P), 4.54 (2 H, d, J_{PH} 16.5, PCH), 4.82 (1 H, dd, J_{HH} 7.5, J_{PH} 7.0, syn allylic CH_2 *trans* to P), 5.94 (1 H, dtd, J_{HH} 14.2, 9.4, 7.5, allylic CH), 6.64 (4 H, m, *m*-H), 7.05 (2 H, d, J_{HH} 8.6, *o*) and 7.98 (2 H, d, J_{HH} 8.2, *o*); ^{13}C (150 MHz; CD_2Cl_2 ; Me_4Si) 26.75 (3 C, d, J_{PC} 27.7, CMe_3), 33.5 (1 C, d, J_{PC} 16.9, CMe_3), 39.7 (2 C, d, J_{PC} 14.3, PCH), 39.84 (4 C, s, NMe_2), 47.4 (1 C, d, J_{PC} 5.3, allylic CH_2 *cis* to P), 52.6 (2 C, s, OMe), 58.9 (4 C, m, PCHC and CH_2), 63.8 (1 C, s, NMe), 83.8 (1 C, d, J_{PC} 27.8, allylic CH_2 *trans* to P), 93.8 (1 C, s, $\text{C}(\text{OH})_2$), 111.4 (2 C, s, *m*- C_6H_4), 112.5 (2 C, s, *m*- C_6H_4), 120.4 (1 C, d, J_{PC} 6.2, allylic CH), 120.7 (2 C, d, J_{PC} 2.0, C_6H_4), 130.4 (2 C, d, J_{PC} 8.4, *o*- C_6H_4), 133.0 (2 C, d, J_{PC} 5.9, *o*- C_6H_4), 150.1 (2 C, s, *p*- C_6H_4) and 169.6 (2 C, d, J_{PC} 11.5, COO); ^{31}P (121 MHz; CDCl_3 ; H_3PO_4) 39.9 (1 P, s); ^{15}N (60 MHz; CD_2Cl_2 ; MeNO_2) -333 (2 N, NMe_2) and -364 (1 N, NMe).

Tentatively assigned by comparison to the theoretical gNMR spectrum (see Figure 3.5).

[Pd(η^3 -C₃H₅)(**65**)]SbF₆ (**84** and **85**)

[Pd(η^3 -C₃H₅)(**65**)]Cl (0.21 g, 0.27 mmol) and AgSbF₆ (0.09 g, 0.27 mmol) were combined in dichloromethane (5 cm³). The yellow reaction mixture was stirred for 1 hr at room temperature then was filtered and centrifuged to remove AgCl. The solvent was removed *in vacuo* and the residue was washed with hexane in the air and dried *in vacuo* to give the ketone (**84**) and hydrate (**85**) forms of the title compound in a 3:1 ratio as a creamy solid (0.21 g, 82%) (Found: C, 41.5; H, 5.3; N, 4.1. C₃₅H₄₉N₃O₅F₆PPdSb + CH₂Cl₂ requires C, 41.2; H, 4.9; N, 4.0%); $\nu_{\max}$ (KBr)/cm⁻¹ 3370, 1724, 1702, 1610, 1521, 1250, 661; m/z (ESI) 728.2451 ([M]⁺. C₃₅H₄₉N₃O₅PPd requires 728.2444).

Compound **84**:

¹H (600 MHz; CD₂Cl₂; Me₄Si) 0.709 (9 H, d, J_{PH} 15.4, Bu^t), 2.95 (12 H, s, NMe₂), 3.08 (2 H, d, J_{HH} 13.3, CH₂), 3.37 (2 H, m, allylic CH₂ *cis* to P) 3.56 (3 H, s, NMe), 3.66 (6 H, s, OMe), 4.06 (2 H, d, J_{HH} 14.6, CH₂), 4.23 (2 H, d, J_{PH} 15.4, PCH), 4.47 (1 H, dd, J_{HH} 14.1, J_{PH} 9.7, anti allylic CH₂ *trans* to P), 5.07 (1 H, dd, J_{HH} 7.8, J_{PH} 7.1, syn allylic CH₂ *trans* to P), 6.14 (1 H, dtd, J_{HH} 14.1, 9.4, 7.8, allylic CH), 6.64-6.75 (4 H, m, *m*-H), 7.00 (2 H, m, *o*) and 8.00 (2 H, d, J_{HH} 7.9, *o*); ¹³C (150 MHz; CD₂Cl₂; Me₄Si) 26.7 (3 C, d, J_{PC} 3.4,

Tentatively assigned by comparison to the theoretical gNMR spectrum (see Figure 3.5).

CMe₃), 34.0 (1 C, d, J_{PC} 15.1, **CMe₃**), 39.9 (4 C, s, NMe₂), 42.2 (2 C, d, J_{PC} 13.7, PCH), 49.9 (1 C, d, J_{PC} 4.7, allylic CH₂ *cis* to P), 52.7 (2 C, s, OMe), 63.0 (1 C, s, NMe), 64.0 (2 C, d, J_{PC} 3.4, PCHC), 64.2 (2 C, d, J_{PC} 2.5, CH₂), 86.3 (1 C, d, J_{PC} 27.5, allylic CH₂ *trans* to P), 111.8-112.6 (2 C, m, *m*-C₆H₄), 118.2 (2 C, s, C₆H₄), 121.8 (1 C, d, J_{PC} 6.2, allylic CH), 130.3 (2 C, m, *o*-C₆H₄), 132.7 (2 C, m, *o*-C₆H₄), 150.6 (2 C, s, *p*-C₆H₄), 166.3 (2 C, d, J_{PC} 9.9, COO) and 199.0 (1 C, d, J_{PC} 1.4, CO); ^1P (121 MHz; CD₂Cl₂; H₃PO₄) 38.8 (1 P, s); ^1N (60 MHz; CD₂Cl₂; MeNO₂) -332 (2 N, NMe₂) and -363 (1 N, NMe).

Compound 85:

^1H (600 MHz; CD₂Cl₂; Me₄Si) 0.713 (9 H, d, J_{PH} 15.7, Bu^t), 2.96 (12 H, s, NMe₂), 3.02 (2 H, d, J_{HH} 13.7, CH₂), 3.48 (3 H, s, NMe), 3.50 (6 H, s, OMe), 3.68 (2 H, m, CH₂), 4.31 (1 H, dd, J_{HH} 14.1, J_{PH} 9.5, anti allylic CH₂ *trans* to P), 4.46 (2 H, d, J_{PH} 16.1, PCH), 4.89 (1 H, dd, J_{HH} 7.8, J_{PH} 7.1, syn allylic CH₂ *trans* to P), 5.99 (1 H, dtd, J_{HH} 14.1, 9.4, 7.8, allylic CH), 6.35 (1 H, s, OH) and 6.44 (1 H, s, OH); ^{13}C (150 MHz; CD₂Cl₂; Me₄Si) 26.8 (3 C, d, J_{PC} 3.6, **CMe₃**), 33.7 (1 C, d, J_{PC} 16.6, **CMe₃**), 39.8 (4 C, s, NMe₂), 40.0 (2 C, d, J_{PC} 14.0, PCH), 48.0 (1 C, d, J_{PC} 5.9, allylic CH₂ *cis* to P), 52.8 (2 C, s, OMe), 58.4 (2 C, d, J_{PC} 2.8, PCHC), 58.6 (2 C, s, CH₂), 63.6 (1 C, s, NMe), 84.4 (1

Tentatively assigned by comparison to the theoretical gNMR spectrum (see Figure 3.5).

C, d, J_{PC} 28.3, allylic CH₂ *trans* to P), 94.1 (1 C, s, C(OH)₂), 120.1 (2 C, br s, C₆H₄), 120.8 (1 C, d, J_{PC} 5.9, allylic CH), 150.2 (2 C, s, *p*-C₆H₄) and 170.1 (2 C, d, J_{PC} 11.5, COO); δ_{P} (121 MHz; CD₂Cl₂; H₃PO₄) 37.5 (1 P, s); δ_{N} (60 MHz; CD₂Cl₂; MeNO₂) -331 (2 N, NMe₂) and -364 (1 N, NMe).

[Pt(cod)(65)] (86) and [Pt(1-3- η -C₈H₁₃)(65-H)] (87)

PN ligand **65** (0.14 g, 0.24 mmol) and [Pt(cod)₂] (0.10 g, 0.24 mmol) were combined in benzene (3 cm³). The dark brown reaction mixture was stirred for 1 day at room temperature. Initially complex **86** was formed, but it was not possible to characterise it as it converted into complex **87**. Hexane was added to the reaction mixture to precipitate complex **87** as a creamy solid. The precipitate was filtered in the air, washed with hexane and dried *in vacuo* (0.17 g, 79%); (Found: C, 54.0; H, 6.3; N, 4.6. C₄₀H₅₆N₃O₅PPt requires C, 54.3; H, 6.4; N, 4.8%); ν_{max} (KBr)/cm⁻¹ 1741, 1702, 1612, 1521, 1270; δ_{H} (600 MHz; C₆D₆; Me₄Si) 1.17 (9 H, d, J_{PH} 13.0, Bu^t), 1.25 (2 H, m, C₈H₁₃-CH₂), 1.32 (1 H, m, C₈H₁₃-CH₂), 1.54 (2 H, m, C₈H₁₃-CH₂), 1.72 (1 H, m, C₈H₁₃-CH₂), 1.83 (1 H, m, C₈H₁₃-CH₂), 1.89 (3 H, s, NMe), 2.20 (1 H, m, C₈H₁₃-CH₂), 2.28 (1 H, m, C₈H₁₃-CH₂), 2.48 (6 H, s, NMe₂), 2.71 (1 H, m, C₈H₁₃-CH₂), 2.74 (1 H, d, J_{HH} 12.6, CH₂), 2.78 (6 H, s, NMe₂), 2.80 (1 H, d, J_{HH} 11.4, CH₂), 3.03 (1 H, dd, J_{HH} 11.3, 3.3, CH₂), 3.17 (1 H, dd, J_{HH} 12.4, 3.4, CH₂), 3.30 (3 H, s, OMe),

3.58 (3 H, s, OMe), 3.75 (1 H, m, C₈H₁₃–CH), 4.29 (1 H, m, C₈H₁₃–CH), 4.99 (1 H, d, J_{PH} 13.2, J_{PtH} 52, PCH), 5.08 (1 H, t, J_{HH} 7.9, J_{PtH} 42, C₈H₁₃–CH), 5.15 (1 H, d, J_{PH} 10.8, J_{PtH} 27, PCH), 6.52 (2 H, d, J_{HH} 6.9, *m*-H), 6.66 (1 H, dd, J_{HH} 8.6, 2.5, *m*-H), 7.34 (1 H, d, J_{HH} 8.6, J_{PtH} 18, *o*-H), 7.50 (2 H, br s, *o*-H) and 8.28 (1 H, d, J_{HH} 1.5, *m*-H); ¹³C (150 MHz; C₆D₆; Me₄Si) 24.9 (1 C, br s, C₈H₁₃–CH₂), 27.6 (3 C, d, J_{PC} 5.1, CMe₃), 30.2 (1 C, s, C₈H₁₃–CH₂), 30.7 (1 C, d, J_{PC} 8.6, J_{PtC} 31, C₈H₁₃–CH₂), 33.0 (1 C, d, J_{PC} 5.6, J_{PtC} 34, C₈H₁₃–CH₂), 33.8 (1 C, s, J_{PtC} 20, C₈H₁₃–CH₂), 35.3 (1 C, d, J_{PC} 19.8, J_{PtC} 39, CMe₃), 39.9 (2 C, s, NMe₂), 40.9 (2 C, s, NMe₂), 42.2 (1 C, d, J_{PC} 18.1, J_{PtC} 50, PCH), 43.9 (1 C, s, NMe), 51.2 (1 C, d, J_{PC} 30.2, J_{PtC} 77, PCH), 51.9 (1 C, s, OMe), 52.2 (1 C, s, OMe), 59.5 (1 C, s, CH₂), 59.6 (1 C, s, CH₂), 65.1 (1 C, d, J_{PC} 49.6, J_{PtC} 237, C₈H₁₃–CH), 65.14 (1 C, d, J_{PC} 1.1, PCHC), 65.8 (1 C, d, J_{PC} 1.7, PCHC), 73.0 (1 C, s, J_{PtC} 45, C₈H₁₃–CH), 107.3 (1 C, d, J_{PC} 4.5, C₈H₁₃–CH), 110.7 (1 C, s, *m*-C₆H₄), 123.9 (1 C, d, J_{PC} 14.2, J_{PtC} 55, *o*-C₆H₄), 125.3 (1 C, d, J_{PC} 3.6, C₆H₄), 129.5 (1 C, d, J_{PC} 4.3, J_{PtC} 74, *m*-C₆H₄), 134.0 (2 C, br s, *o*-C₆H₄), 141.5 (1 C, d, J_{PC} 18.8, J_{PtC} 68, C₆H₄), 149.0 (1 C, s, J_{PtC} 75, *p*-C₆H₄), 149.8 (1 C, s, *p*-C₆H₄), 157.6 (1 C, d, J_{PC} 2.0, J_{PtC} 1189, Pt–C), 169.0 (1 C, d, J_{PC} 7.2, COO), 170.2 (1 C, d, J_{PC} 7.5, COO) and 205.6 (1 C, d, J_{PC} 2.8, CO); ³¹P (121 MHz; C₆D₆; H₃PO₄) 70.4 (1 P, s, J_{PtP} 3787); ¹⁵N (60 MHz; C₆D₆; MeNO₂) -336 (1 N, NMe₂), -339 (1 N, NMe₂) and -354 (1 N, NMe); *m/z* (ESI) 885.3686 ([M + H]. C₄₀H₅₇N₃O₅PPt requires 885.3684).

PN ligand **65** (0.14 g, 0.24 mmol), [Pt(cod)₂] (0.10 g, 0.24 mmol) and CH₂(SO₂CF₃)₂ (0.07 g, 0.24 mmol) were combined in dichloromethane (4 cm³). The dark brown reaction mixture was stirred for 2 hr at room temperature. Hexane was added to the reaction mixture to precipitate the ketone (**88**) and hydrate forms in a 3:1 ratio as a white solid. The precipitate was filtered in the air, washed with hexane and dried *in vacuo* (0.23 g, 82%); (Found: C, 44.5; H, 5.0; N, 3.9. C₄₃H₅₈N₃O₉F₆PS₂Pt requires C, 44.3; H, 5.0; N, 3.6%); ν_{max} (KBr)/cm⁻¹ 3441, 1748, 1740, 1610, 1520, 1343, 600; δ_{H} (600 MHz; CDCl₃; Me₄Si) 0.85 (9 H, br s, Bu^t), 1.20 (1 H, m, C₈H₁₃-CH₂), 1.54 (2 H, m, C₈H₁₃-CH₂), 1.91 (1 H, m, C₈H₁₃-CH₂), 2.10 (2 H, m, C₈H₁₃-CH₂), 2.43 (1 H, m, C₈H₁₃-CH₂), 2.61 (1 H, m, C₈H₁₃-CH₂), 2.86 (1 H, m, C₈H₁₃-CH₂), 2.95 (3 H, s, NMe), 2.967 (6 H, s, NMe₂), 2.97 (6 H, s, NMe₂), 3.01 (1 H, d, J_{HH} 14.3, CH₂), 3.04 (1 H, m, C₈H₁₃-CH₂), 3.06 (1 H, d, J_{HH} 14.3, CH₂), 3.08 (1 H, m, Pt-CH), 3.62 (3 H, s, OMe), 3.63 (3 H, s, OMe), 3.91 (1 H, dd, J_{HH} 13.9, 2.1, CH₂), 3.95 (1 H, s, CH(SO₂CF₃)₂), 3.97 (1 H, dd, J_{HH} 14.2, 2.1, CH₂), 4.37 (1 H, d, J_{PH} 14.2, PCH), 4.42 (1 H, d, J_{PH} 13.7, PCH), 6.38 (1 H, m, C₈H₁₃-CH), 6.45 (1 H, m, C₈H₁₃-CH), 6.62 (3 H, m, *m*-H), 6.71 (1 H, dd, J_{HH} 8.8, 2.8, *m*-H), 6.98 (2 H, m, *o*-H) 8.78 (1 H, dd, J_{HH} 8.7, 2.2, *o*-H) and 8.88 (1 H, dd, J_{HH} 8.7, 2.2, *o*-H); δ_{C} (150 MHz; CDCl₃; Me₄Si) 18.0 (1 C, s, J_{PtC} 601, Pt-C), 24.3 (1 C, s, C₈H₁₃-CH₂), 26.1 (1 C, s, C₈H₁₃-CH₂), 28.1 (3 C, s, CMe₃), 31.7 (1 C, s, C₈H₁₃-CH₂), 35.0 (1 C, d, J_{PC} 23.9, CMe₃), 35.8 (1 C, s, C₈H₁₃-CH₂), 39.3 (1 C, s, C₈H₁₃-CH₂), 40.17 (2 C, s, NMe₂), 40.18 (2 C, s, NMe₂), 42.3 (1

C, d, J_{PC} 21.9, PCH), 43.1 (1 C, d, J_{PC} 21.5, PCH), 52.9 (1 C, s, NMe), 52.996 (1 C, s, OMe), 52.999 (1 C, s, OMe), 53.8 (1 C, sept, J_{FC} 2.6, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 63.2 (1 C, d, J_{PC} 1.2, CH_2), 63.4 (1 C, d, J_{PC} 1.7, PCHC), 63.5 (1 C, d, J_{PC} 1.7, PCHC), 63.9 (1 C, d, J_{PC} 1.2, CH_2), 110.2 (1 C, d, J_{PC} 8.7, $\text{C}_8\text{H}_{13}\text{--CH}$), 111.7 (1 C, s, *m*- C_6H_4), 111.8 (1 C, s, *m*- C_6H_4), 112.5 (1 C, s, *m*- C_6H_4), 112.7 (1 C, s, *m*- C_6H_4), 113.3 (1 C, d, J_{PC} 10.8, $\text{C}_8\text{H}_{13}\text{--CH}$), 117.4 (1 C, s, C_6H_4), 118.1 (1 C, s, C_6H_4), 121.3 (2 C, q, J_{FC} 325.7, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 132.0 (1 C, d, J_{PC} 7.8, *o*- C_6H_4), 132.2 (1 C, d, J_{PC} 7.6, *o*- C_6H_4), 133.2 (1 C, d, J_{PC} 5.7, *o*- C_6H_4), 133.3 (1 C, d, J_{PC} 5.9, *o*- C_6H_4), 150.7 (2 C, s, *p*- C_6H_4), 166.47 (1 C, d, J_{PC} 1.8, COO), 166.54 (1 C, d, J_{PC} 1.8, COO) and 199.8 (1 C, s, CO); ^1P (121 MHz; CDCl_3 ; H_3PO_4) 18.1 (1 P, s, J_{PtP} 4304); ^{15}N (60 MHz; CDCl_3 ; MeNO_2) -331 (2 N, NMe_2) and -356 (1 N, NMe); ^{19}F (282 MHz; CDCl_3 ; CCl_3F) -81.0 (6 F, s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$); m/z (ESI) 885.3689 ($[\text{M}]^+$. $\text{C}_{40}\text{H}_{57}\text{N}_3\text{O}_5\text{PPt}$ requires 885.3684).

[Pt(1-3- η - C_8H_{13})(65)] $\text{CH}(\text{SO}_2\text{CF}_3)_2$ (**89** and **90**)

A mixture of the ketone (**88**) and hydrate forms of the complex [Pt(1- σ ,4-5- η - C_8H_{13})(**65**)] $\text{CH}(\text{SO}_2\text{CF}_3)_2$ (0.10 g, 0.09 mmol) was dissolved in dichloromethane (2 cm^3). The colourless solution was stirred for 1 week at room temperature. The solvent was removed *in vacuo* to give the ketone (**89**) and hydrate (**90**) forms of the title compound in a 3:1 ratio as a white solid (0.09 g, 87%); (Found: C, 44.1; H, 5.3; N, 3.5. $\text{C}_{43}\text{H}_{58}\text{N}_3\text{O}_9\text{F}_6\text{PS}_2\text{Pt}$ requires C, 44.3; H, 5.0; N, 3.6%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3422, 1743, 1610, 1521, 1343, 1165, 600; m/z (ESI) 885.3687 ($[\text{M}]^+$. $\text{C}_{40}\text{H}_{57}\text{N}_3\text{O}_5\text{PPt}$ requires 885.3684).

Compound 89:

^1H (600 MHz; CDCl_3 ; Me_4Si) 0.73 (9 H, d, J_{PH} 15.4, Bu^t), 1.58 (3 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 1.73 (2 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 1.83 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 1.91 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 2.08 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 2.30 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 2.83 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 2.92 (6 H, s, NMe_2), 2.96 (6 H, s, NMe_2), 3.23 (2 H, m, CH_2), 3.56 (3 H, s, OMe), 3.64 (3 H, s, OMe), 3.94 (1 H, s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 4.01 (3 H, s, NMe), 4.15 (1 H, dd, J_{HH} 14.3, 1.9, CH_2), 4.20 (2 H, m, CH_2 and $\text{C}_8\text{H}_{13}\text{--CH}$), 4.28 (2 H, dd, J_{PH} 13.8, J_{HH} 2.9, PCH), 5.55 (1 H, m, $\text{C}_8\text{H}_{13}\text{--CH}$), 5.85 (1 H, t, J_{HH} 8.4, J_{PtH} 64, $\text{C}_8\text{H}_{13}\text{--CH}$), 6.53 (2 H, dd, J_{HH} 8.6, 2.6, *m*-H), 6.65 (1 H, dd, J_{HH} 8.9, 2.7, *m*-H), 6.71 (1 H, dd, J_{HH} 8.9, 2.7, *m*-H), 6.88 (2 H, dd, J_{HH} 8.6, 1.9, *o*-H) and 8.15 (2 H, m, *o*-H); ^{13}C (150 MHz; CDCl_3 ; Me_4Si) 24.4 (1 C, s, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 27.2 (3 C, d, J_{PC} 2.7, CMe_3), 27.8 (1 C, d, J_{PC} 5.4, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 28.5 (1 C, s, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 32.6 (1 C, d, J_{PC} 4.4, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 33.3 (1 C, s, $\text{C}_8\text{H}_{13}\text{--CH}_2$), 34.5 (1 C, d, J_{PC} 24.5, CMe_3), 40.1 (2 C, s, NMe_2), 40.23 (2 C, s, NMe_2), 41.4 (1 C, d, J_{PC} 18.4, PCH), 43.0 (1 C, d, J_{PC} 21.7, PCH), 49.4 (1 C, s, J_{PtC} 270, $\text{C}_8\text{H}_{13}\text{--CH}$), 52.94 (1 C, s, OMe), 52.99 (1 C, s, OMe), 53.8 (1 C, sept, J_{FC} 2.5, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 64.0 (1 C, d, J_{PC} 2.6, PCHC), 64.2 (1 C, d, J_{PC} 1.7, PCHC), 64.9 (1 C, d, J_{PC} 2.9, CH_2), 65.3 (1 C, s, CH_2), 66.9 (1 C, s, NMe), 91.9 (1 C, d, J_{PC} 30.7, $\text{C}_8\text{H}_{13}\text{--CH}$), 109.6 (1 C, d, J_{PC} 2.2, $\text{C}_8\text{H}_{13}\text{--CH}$), 112.1 (1 C, s, *m*- C_6H_4), 112.2 (1 C, s, *m*- C_6H_4), 112.7 (1 C, s, *m*- C_6H_4), 112.8 (1 C, s, *m*- C_6H_4), 117.8 (1 C, s, C_6H_4), 118.3 (1 C, s, C_6H_4), 121.3 (2 C, q, J_{FC} 325.5, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 131.3 (2 C, d, J_{PC} 5.2, *o*- C_6H_4), 132.7 (1 C, d, J_{PC} 6.3, *o*- C_6H_4), 132.9 (1 C, d, J_{PC} 5.7, *o*- C_6H_4), 150.6 (1 C, s, *p*- C_6H_4),

150.7 (1 C, s, *p*-C₆H₄), 166.1 (1 C, d, J_{PC} 10.5, COO), 166.6 (1 C, d, J_{PC} 9.9, COO) and 199.0 (1 C, s, CO); $^{\text{P}}$ (121 MHz; CDCl₃; H₃PO₄) 30.7 (1 P, s, J_{PtP} 4010); $^{\text{N}}$ (60 MHz; CDCl₃; MeNO₂) -331 (2 N, NMe₂) and -369 (1 N, NMe); $^{\text{F}}$ (282 MHz; CDCl₃; CCl₃F) -81.0 (6 F, s, CH(SO₂CF₃)₂).

Compound 90:

$^{\text{H}}$ (600 MHz; CDCl₃; Me₄Si) 0.71 (9 H, d, J_{PH} 15.4, Bu^t), 1.58 (3 H, m, C₈H₁₃–CH₂), 1.73 (2 H, m, C₈H₁₃–CH₂), 1.83 (1 H, m, C₈H₁₃–CH₂), 1.91 (1 H, m, C₈H₁₃–CH₂), 2.08 (1 H, m, C₈H₁₃–CH₂), 2.30 (1 H, m, C₈H₁₃–CH₂), 2.83 (1 H, m, C₈H₁₃–CH₂), 2.91 (6 H, s, NMe₂), 2.95 (6 H, s, NMe₂), 3.15 (1 H, d, J_{HH} 13.4, CH₂), 3.23 (1 H, m, CH₂), 3.36 (3 H, s, OMe), 3.46 (3 H, s, OMe), 3.79 (2 H, dd, J_{HH} 13.2, 5.4, CH₂), 3.98 (3 H, s, NMe), 4.11 (1 H, d, J_{HH} 8.5, C₈H₁₃–CH), 4.50 (1 H, d, J_{PH} 14.5, PCH), 4.53 (1 H, d, J_{PH} 14.5, PCH), 5.30 (1 H, m, C₈H₁₃–CH), 5.67 (1 H, t, J_{HH} 8.0, C₈H₁₃–CH), 6.49 (2 H, dd, J_{HH} 8.9, 2.3, *m*-H), 6.52 (1 H, s, OH), 6.57 (1 H, s, OH), 6.61 (1 H, dd, J_{HH} 8.6, 2.7, *m*-H), 6.62 (1 H, dd, J_{HH} 8.6, 2.7, *m*-H), 6.97 (1 H, dd, J_{HH} 8.6, 1.9, *o*-H), 6.99 (1 H, dd, J_{HH} 8.6, 1.9, *o*-H) and 8.39 (2 H, m, *o*-H); $^{\text{C}}$ (150 MHz; CDCl₃; Me₄Si) 24.6 (1 C, s, C₈H₁₃–CH₂), 27.4 (3 C, d, J_{PC} 2.6, CMe₃), 28.0 (1 C, d, J_{PC} 5.4, C₈H₁₃–CH₂), 28.7 (1 C, s, C₈H₁₃–CH₂), 32.5 (1 C, d, J_{PC} 4.4, C₈H₁₃–CH₂), 33.2 (1 C, s, C₈H₁₃–CH₂), 34.1 (1 C, d, J_{PC} 24.5, CMe₃), 39.0 (1 C, d, J_{PC} 18.8, PCH), 40.24 (2 C, s, NMe₂), 40.3 (2 C, s, NMe₂), 40.9 (1 C, d, J_{PC} 21.4, PCH), 48.4 (1 C, s, J_{PtC} 268, C₈H₁₃–CH), 53.0 (1 C, s, OMe), 53.1 (1 C, s, OMe), 58.2 (1 C, d, J_{PC} 2.3, PCHC), 58.4 (1 C, d, J_{PC} 2.5, PCHC),

59.3 (1 C, d, J_{PC} 3.0, CH₂), 59.7 (1 C, s, CH₂), 67.5 (1 C, s, NMe), 90.2 (1 C, d, J_{PC} 29.7, C₈H₁₃–CH), 94.5 (1 C, s, C(OH)₂), 108.6 (1 C, s, C₈H₁₃–CH), 111.36 (1 C, s, *m*-C₆H₄), 111.4 (1 C, s, *m*-C₆H₄), 112.57 (1 C, s, *m*-C₆H₄), 112.6 (1 C, s, *m*-C₆H₄), 119.5 (1 C, s, C₆H₄), 119.9 (1 C, s, C₆H₄), 130.7 (1 C, d, J_{PC} 7.6, *o*-C₆H₄), 131.0 (1 C, d, J_{PC} 7.6, *o*-C₆H₄), 133.2 (2 C, d, J_{PC} 5.2, *o*-C₆H₄), 150.3 (1 C, s, *p*-C₆H₄), 150.4 (1 C, s, *p*-C₆H₄), 170.2 (1 C, d, J_{PC} 11.3, COO) and 170.9 (1 C, d, J_{PC} 11.7, COO); $^{\text{P}}$ (121 MHz; CDCl₃; H₃PO₄) 28.4 (1 P, s, J_{PtP} 3928).

Protonation of [Pt(C₂H₄)₂ **65**] with CH₂(SO₂CF₃)₂ (**91**, **92** and **93**)

A solution of PN ligand **65** (0.16 g, 0.28 mmol) in benzene (2 cm³) was added to a Schlenk tube containing [Pt(C₂H₄)₃] (0.08 g, 0.28 mmol) under an ethene atmosphere. The colourless reaction mixture was stirred for 10 min at room temperature then a solution of CH₂(SO₂CF₃)₂ (0.08 g, 0.28 mmol) in benzene (0.5 cm³) was added to it. Long-fine colourless needles crystallised out after a few days, which were separated by decanting the solvent under a nitrogen atmosphere and drying *in vacuo*. The needles were identified as complex **92** (0.06 g, 20%). The solvent was taken to dryness *in vacuo* to give compounds **91** and **93** as a brown solid.

Compound 91:

^1H (500 MHz; CD_2Cl_2 ; Me_4Si) 0.93 (9 H, d, J_{PH} 16.4, Bu^t), 2.77 (3 H, s, NMe), 3.01 (12 H, s, NMe_2), 3.03 (2 H, d, J_{HH} 13.4, CH_2), 3.13 (1 H, s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 3.55 (2 H, d, J_{HH} 12.9, CH_2), 3.76 (6 H, s, OMe), 4.48 (2 H, dd, J_{PH} 14.1, J_{HH} 10.9, PCH), 6.70 (2 H, dd, J_{HH} 8.8, 2.2, *m*-H), 6.92 (2 H, dd, J_{HH} 8.8, 2.2, *m*-H), 7.10 (2 H, dd, J_{HH} 8.7, 2.3, *o*-H), 7.44 (2 H, dd, J_{HH} 8.9, 2.3, *o*-H) and 7.78 (1 H, dt, J_{PH} 546.1, J_{HH} 10.8, PH); ^{13}C (125 MHz; CD_2Cl_2 ; Me_4Si) 26.3 (3 C, s, CMe_3), 32.6 (1 C, d, J_{PC} 35.0, CMe_3), 38.8 (2 C, d, J_{PC} 42.2, PCH), 39.8 (4 C, s, NMe_2), 44.2 (1 C, s, NMe), 53.0 (2 C, s, OMe), 59.5 (2 C, s, CH_2), 64.8 (2 C, d, J_{PC} 1.4, PCHC), 110.0 (1 C, s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 112.7 (2 C, s, *m*- C_6H_4), 113.0 (2 C, s, *m*- C_6H_4), 114.3 (2 C, br s, C_6H_4), 121.2 (2 C, q, J_{FC} 324.4, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 130.3 (2 C, d, J_{PC} 8.6, *o*- C_6H_4), 132.5 (2 C, d, J_{PC} 8.6, *o*- C_6H_4), 151.2 (2 C, s, *p*- C_6H_4), 166.0 (2 C, d, J_{PC} 13.0, COO) and 199.3 (1 C, d, J_{PC} 2.9, CO); ^{31}P (121 MHz; CD_2Cl_2 ; H_3PO_4) 24.8 (1 P, s); ^{19}F (282 MHz; CD_2Cl_2 ; CCl_3F) -81.0 (6 F, s, $\text{CPh}(\text{SO}_2\text{CF}_3)_2$).

Compound 92:

(Found: C, 40.0; H, 4.7; N, 3.8. $C_{35}H_{46}N_3O_9F_6PS_2Pt$ requires C, 39.8; H, 4.4; N, 4.0%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2250, 1746, 1611, 1261, 802; $\delta_{\text{H}} (600 \text{ MHz; CD}_2\text{Cl}_2; \text{Me}_4\text{Si})$ -20.26 (1 H, br s, J_{PtH} 1285, Pt–H), 0.65 (9 H, d, J_{PH} 16.1, Bu^t), 3.04 (12 H, s, NMe_2), 3.20 (2 H, d, J_{HH} 13.1, CH_2), 3.29 (3 H, s, NMe), 3.63 (6 H, s, OMe), 4.14 (2 H, d, J_{HH} 14.0, CH_2), 4.36 (2 H, d, J_{PH} 13.1, PCH), 5.37 (1 H, d, J_{PH} 6.4, J_{PtH} 64, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 6.89 (2 H, d, J_{HH} 7.7, *m*-H), 6.91 (2 H, d, J_{HH} 8.6, *m*-H), 7.07 (2 H, d, J_{HH} 7.5, *o*-H) and 9.19 (2 H, d, J_{HH} 8.2, *o*-H); $\delta_{\text{C}} (150 \text{ MHz; CD}_2\text{Cl}_2; \text{Me}_4\text{Si})$ 26.2 (3 C, d, J_{PC} 2.5, CMe_3), 32.6 (1 C, d, J_{PC} 31.7, CMe_3), 42.0 (4 C, s, NMe_2), 42.2 (2 C, s, PCH), 52.6 (2 C, s, OMe), 56.3 (1 C, s, NMe), 63.9 (2 C, s, CH_2), 64.2 (2 C, s, PCHC), 67.6 (1 C, d, J_{PC} 65.9, J_{PtC} 469, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 114.0 (2 C, br s, *m*- C_6H_4), 114.6 (2 C, br s, *m*- C_6H_4), 121.0 (2 C, q, J_{FC} 324.8, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 122.9 (2 C, br s, C_6H_4), 132.8 (2 C, d, J_{PC} 5.3, *o*- C_6H_4), 133.4 (2 C, d, J_{PC} 5.9, *o*- C_6H_4), 148.5 (2 C, br s, *p*- C_6H_4), 166.5 (2 C, d, J_{PC} 10.1, COO) and 199.9 (1 C, s, CO); $\delta_{\text{P}} (121 \text{ MHz; CD}_2\text{Cl}_2; \text{H}_3\text{PO}_4)$ 35.5 (1 P, s, J_{PtP} 3724); $\delta_{\text{N}} (60 \text{ MHz; CD}_2\text{Cl}_2; \text{MeNO}_2)$ -332 (2 N, NMe_2) and -367 (1 N, NMe); $\delta_{\text{F}} (282 \text{ MHz; CD}_2\text{Cl}_2; \text{CCl}_3\text{F})$ -74.9 (6 F, s, J_{PtF} 24, $\text{CPh}(\text{SO}_2\text{CF}_3)_2$); m/z (ESI) 777.2739 ($[\text{M}]^+$. $\text{C}_{32}\text{H}_{45}\text{N}_3\text{O}_5\text{PPt}$ requires 777.2744).

Compound 93:

OR

^1H (500 MHz; C_6D_6 ; Me_4Si) 0.53 (9 H, br d, J_{PH} 14.9, Bu^t), 1.22 (3 H, t, J_{HH} 7.5, $\text{Pt}-\text{CH}_3$), 1.91 (2 H, q, J_{HH} 6.7, $\text{Pt}-\text{CH}_2$), 2.45 (3 H, s, NMe), 2.51 (12 H, s, NMe_2), 2.99 (2 H, d, J_{HH} 13.9, CH_2), 3.30 (6 H, s, OMe), 3.42 (1 H, s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 4.28 (4 H, m, CH_2 and PCH), 6.54 (2 H, d, J_{HH} 7.6, $m\text{-H}$), 7.01 (2 H, dd, J_{HH} 8.5, 1.7, $o\text{-H}$), 7.25 (2 H, d, J_{HH} 6.8, $m\text{-H}$) and 9.85 (2 H, d, J_{HH} 8.5, $o\text{-H}$); ^{13}C (125 MHz; C_6D_6 ; Me_4Si) 27.2 (3 C, br s, CMe_3), 32.1 (1 C, d, J_{PC} 35.0, CMe_3), 39.4 (4 C, s, NMe_2), 40.1 (2 C, br s, PCH), 41.0 (1 C, s, NMe), 52.2 (2 C, s, OMe), 54.3 (1 C, br s, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 63.0 (2 C, s, CH_2), 64.5 (2 C, s, PCHC), 112.6 (2 C, s, $m\text{-C}_6\text{H}_4$), 113.5 (2 C, br s, $m\text{-C}_6\text{H}_4$), 120.1 (2 C, br s, C_6H_4), 122.2 (2 C, q, J_{FC} 325.8, $\text{CH}(\text{SO}_2\text{CF}_3)_2$), 133.2 (2 C, d, J_{PC} 5.8, $o\text{-C}_6\text{H}_4$), 133.6 (2 C, d, J_{PC} 5.8, $o\text{-C}_6\text{H}_4$), 150.2 (2 C, br s, $p\text{-C}_6\text{H}_4$), 166.6 (2 C, d, J_{PC} 11.0, COO) and 200.4 (1 C, s, CO); ^3P (121 MHz; C_6D_6 ; H_3PO_4) 11.3 (1 P, s, J_{PtP} 5424); ^{19}F (282 MHz; C_6D_6 ; CCl_3F) -80.6 (6 F, s, $\text{CPh}(\text{SO}_2\text{CF}_3)_2$); m/z (ESI) 805.3057 ($[\text{M}]^+$. $\text{C}_{34}\text{H}_{49}\text{N}_3\text{O}_5\text{PPt}$ requires 805.3057).

[Pt(η -C₇H₁₁)(65**)]CPh(SO₂CF₃)₂ (**94** and **95**)**

[Pt(norb)(**65**)] (**74**) (0.20 g, 0.23 mmol) was dissolved in benzene (5 cm³) and a solution of CPh(SO₂CF₃)₂ (0.08 g, 0.23 mmol) in benzene (1 cm³) was added. Immediately, lots of white solid formed which redissolved within minutes to give a yellow solution with some brown solid. The reaction mixture was stirred at room temperature for 1 day. The solvent was removed *in vacuo* to give a pale brown solid. This was crystallised from CH₂Cl₂/ether to produce a white solid (0.20 g, 71%) consisting of the ketone (**94**) and hydrate (**95**) forms in a 7:1 ratio. (Found: C, 46.2; H, 4.9; N, 3.4. C₄₈H₆₀N₃O₉F₆PS₂Pt requires C, 46.9; H, 4.9; N, 3.4%); $\nu_{\max}$ (KBr)/cm⁻¹ 3424, 1739, 1610, 1521, 1344, 1182, 605; m/z (ESI) 871.3537 ([M]⁺. C₃₉H₅₅N₃O₅PPt requires 871.3527).

Compound 94:

¹H (600 MHz; CD₂Cl₂; Me₄Si) -1.06 (1 H, dd, J_{PH} 50.3, J_{HH} 13.6, PtH), 0.76 (9 H, d, J_{PH} 16.8, Bu^t), 1.20-1.81 (8 H, m, C₇H₁₁-CH₂, C₇H₁₁-CH and C H), 2.48 (1 H, br s, C₇H₁₁-CH), 2.96 (12 H, s, NMe₂), 3.12 (1 H, br s, C H), 3.24 (2 H, d, J_{HH} 13.6, CH₂), 3.63 (3 H, s, OMe), 3.65 (3 H, s, OMe), 3.77 (3 H, br s, NMe), 4.12 (2 H, d, J_{HH} 13.8, CH₂), 4.38 (2 H, m, PCH), 6.61 (1 H, dd, J_{HH} 8.8, 2.4, *m*-H), 6.65 (1 H, dd, J_{HH} 8.8, 2.6, *m*-H), 6.67 (1 H, dd, J_{HH} 8.8, 2.6, *m*-H), 6.70 (1 H, dd, J_{HH} 8.8, 2.4, *m*-H), 7.00 (1 H, d, J_{HH} 7.0, *o*-H), 7.01 (1 H, d, J_{HH} 7.0, *o*-H), 7.28 (3 H, m, CPh(SO₂CF₃)₂), 7.44 (2 H, m, CPh(SO₂CF₃)₂), 8.56 (1 H, d, J_{HH} 9.7, *o*-H) and 8.57 (1 H, d, J_{HH} 9.7, *o*-H); ¹³C (150 MHz; CD₂Cl₂; Me₄Si) 26.3 (1 C, br s, C), 26.7 (3 C, d, J_{PH} 1.7, CMe₃), 27.7 (2 C, br s, C₇H₁₁-CH₂),

28.0 (1 C, br s, C₇H₁₁—CH), 36.4 (1 C, d, J_{PC} 29.8, CMe₃), 38.7 (1 C, s, C), 39.2 (1 C, s, C₇H₁₁—CH₂), 39.8 (4 C, s, NMe₂), 41.1 (1 C, d, J_{PC} 27.0, PCH), 41.2 (1 C, br s, C₇H₁₁—CH), 42.1 (1 C, d, J_{PC} 27.0, PCH), 52.69 (1 C, s, OMe), 52.72 (1 C, s, OMe), 62.8 (1 C, s, NMe), 63.6 (1 C, s, CH₂), 64.0 (2 C, br s, PCHC), 64.1 (1 C, s, CH₂), 69.7 (1 C, sept, J_{FC} 2.5, CPh(SO₂CF₃)₂), 111.1 (1 C, s, *m*-C₆H₄), 112.0 (1 C, s, *m*-C₆H₄), 112.3 (1 C, s, *m*-C₆H₄), 112.5 (1 C, s, *m*-C₆H₄), 121.9 (2 C, q, J_{FC} 328.7, CH(SO₂CF₃)₂), 116.9 (1 C, s, C₆H₄), 117.3 (1 C, s, C₆H₄), 127.4 (2 C, s, CPh(SO₂CF₃)₂), 131.0 (1 C, d, J_{PC} 5.9, *o*-C₆H₄), 131.1 (1 C, d, J_{PC} 6.6, *o*-C₆H₄), 131.6 (1 C, s, CPh(SO₂CF₃)₂), 133.1 (1 C, d, J_{PC} 6.1, *o*-C₆H₄), 133.2 (1 C, d, J_{PC} 6.0, *o*-C₆H₄), 136.2 (2 C, s, CPh(SO₂CF₃)₂), 150.7 (1 C, s, *p*-C₆H₄), 150.8 (1 C, s, *p*-C₆H₄), 166.0 (1 C, d, J_{PC} 10.7, COO), 166.2 (1 C, d, J_{PC} 10.7, COO) and 198.6 (1 C, s, CO); ^1P (121 MHz; CD₂Cl₂; H₃PO₄) 33.8 (1 P, s, J_{PtP} 6008); ^1N (60 MHz; CD₂Cl₂; MeNO₂) -332 (2 N, NMe₂) and -355 (1 N, NMe); ^{19}F (282 MHz; CD₂Cl₂; CCl₃F) -78.6 (6 F, s, CPh(SO₂CF₃)₂).

Compound 95:

^1H (600 MHz; CD₂Cl₂; Me₄Si) -1.18 (1 H, dd, J_{PH} 48.5, J_{HH} 13.0, PtH), 0.75 (9 H, d, J_{PH} 16.5, Bu^t), 1.20-1.81 (8 H, m, C₇H₁₁—CH₂, C₇H₁₁—CH and C H), 2.35 (1 H, br s, C₇H₁₁—CH), 2.95 (12 H, s, NMe₂), 3.06 (1 H, br s, C H), 3.20 (2 H, d, J_{HH} 13.2, CH₂), 3.43 (3 H, s, OMe), 3.46 (3 H, s, OMe), 3.71 (3 H, br s, NMe), 3.75 (2 H, m, CH₂), 4.57 (1 H, d, J_{PH} 14.5, PCH), 4.62 (1 H, d, J_{PH} 14.5, PCH), 6.19 (1 H, s, OH), 6.48 (1 H, s, OH), 6.61 (1 H, dd, J_{HH} 8.8, 2.4, *m*-H), 6.65 (1 H, dd, J_{HH} 8.8, 2.6, *m*-H), 6.67 (1 H, dd, J_{HH} 8.8, 2.6, *m*-H), 6.70

(1 H, dd, J_{HH} 8.8, 2.4, *m*-H), 7.00 (1 H, d, J_{HH} 7.0, *o*-H), 7.01 (1 H, d, J_{HH} 7.0, *o*-H), 7.28 (3 H, m, CPh(SO₂CF₃)₂), 7.44 (2 H, m, CPh(SO₂CF₃)₂), 8.61 (1 H, d, J_{HH} 9.2, *o*-H) and 8.63 (1 H, d, J_{HH} 9.2, *o*-H); ¹³C (150 MHz; CD₂Cl₂; Me₄Si) 25.7 (1 C, br s, C), 26.7 (3 C, d, J_{PH} 1.7, CMe₃), 27.0-28.0 (4 C, m, C₇H₁₁–CH₂ and C₇H₁₁–CH), 36.0 (1 C, d, J_{PC} 29.8, CMe₃), 38.4 (1 C, s, C), 39.1 (1 C, m, PCH), 39.9 (4 C, s, NMe₂), 40.2 (1 C, d, J_{PC} 26.7, PCH), 43.3 (1 C, br s, C₇H₁₁–CH), 52.8 (2 C, s, OMe), 58.0 (1 C, br s, CH₂), 58.3 (1 C, br s, PCHC), 58.5 (2 C, br s, PCHC and CH₂), 63.2 (1 C, s, NMe), 69.7 (1 C, sept, J_{FC} 2.5, CPh(SO₂CF₃)₂), 94.1 (1 C, s, C(OH)₂), 111.1 (1 C, s, *m*-C₆H₄), 112.0 (1 C, s, *m*-C₆H₄), 112.3 (1 C, s, *m*-C₆H₄), 112.5 (1 C, s, *m*-C₆H₄), 118.6 (1 C, s, C₆H₄), 118.9 (1 C, br s, C₆H₄), 121.9 (2 C, q, J_{FC} 328.7, CH(SO₂CF₃)₂), 127.4 (2 C, s, CPh(SO₂CF₃)₂), 131.0 (1 C, d, J_{PC} 5.9, *o*-C₆H₄), 131.1 (1 C, d, J_{PC} 6.6, *o*-C₆H₄), 131.6 (1 C, s, CPh(SO₂CF₃)₂), 133.1 (1 C, d, J_{PC} 6.1, *o*-C₆H₄), 133.2 (1 C, d, J_{PC} 6.0, *o*-C₆H₄), 136.2 (2 C, s, CPh(SO₂CF₃)₂), 150.5 (2 C, br s, *p*-C₆H₄) and 169.9 (2 C, m, COO); ³¹P (121 MHz; CD₂Cl₂; H₃PO₄) 31.6 (1 P, s, J_{PtP} 5886); ¹⁵N (60 MHz; CD₂Cl₂; MeNO₂) -332 (2 N, NMe₂) and -355 (1 N, NMe); ¹⁹F (282 MHz; CD₂Cl₂; CCl₃F) -78.6 (6 F, s, CPh(SO₂CF₃)₂).

trans-[Pt₂(μ-OH)₂(65-H)₂] (**98**) and

cis-[Pt₂(μ-OH)₂(65-H)₂] (**101**)

NMR scale experiment: A solution of PN compound **65** (0.06 g, 0.10 mmol) in benzene-d₆ (0.5 cm³) was added to a Schlenk tube containing [Pt(C₂H₄)₃] (0.03 g, 0.10 mmol) under an ethene atmosphere. The colourless solution was then transferred into a NMR tube and was left at room temperature for 1 day to allow the formation of complex **76**. Hydrogen gas was then bubbled through the pale yellow solution, which darkened overtime and some fine black suspension formed. After 20 days the synthesis of complexes **98** and **101** was complete, in which they formed in a 1:1 ratio. This sample was used to obtain all NMR data.

Large scale experiment: PN compound **65** (0.14 g, 0.25 mmol) and [Pt(C₂H₄)₃] (0.07 g, 0.28 mmol) were combined in benzene (4 cm³) under an ethene atmosphere in a Fischer-Porter vessel. The yellow reaction mixture was stirred at room temperature for 2 days. An aliquot was removed from the reaction mixture and was analysed by ¹H and ³¹P NMR. The spectra indicated that the dimetallated ethene precursor **76** had been formed. Hydrogen gas was then bubbled through the reaction mixture, and the vessel was sealed for 20 days. Another aliquot was taken and analysed by NMR, which indicated the formation of complexes **98** and **101**. The pale yellow reaction mixture was transferred into a Schlenk tube under a nitrogen atmosphere, and the volume was reduced. The slow diffusion of diethyl ether into the benzene solution at 5 °C produced large yellow crystals of complex **98**, which were used for X-ray crystallography, IR and mass spectrometry and elemental analysis. Small yellow crystals and some pale brown solid were also obtained of complex **101**.

Compound 98:

(Found: C, 48.7; H, 5.4; N, 5.1. $C_{64}H_{88}N_6O_{12}P_2Pt_2$ requires C, 48.5; H, 5.6; N, 5.3%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3564, 1739, 1707, 1610, 1521, 1249; $\delta_{\text{H}}(600 \text{ MHz}; C_6D_6; Me_4Si)$ -0.62 (1 H, d, J_{PH} 3.1, OH), 1.47 (9 H, d, J_{PH} 13.6, Bu^t), 1.87 (3 H, s, NMe), 2.37 (6 H, s, NMe_2), 2.63 (6 H, s, NMe_2), 2.71 (1 H, m, CH_2), 2.82 (1 H, m, CH_2), 3.09 (1 H, m, CH_2), 3.26 (3 H, s, OMe), 3.30 (1 H, m, CH_2), 3.48 (3 H, s, OMe), 4.95 (1 H, d, J_{PH} 9.8, PCH), 5.07 (1 H, d, J_{PH} 13.2, PCH), 6.43 (2 H, m, *m*-H), 6.57 (1 H, d, J_{HH} 2.1, *m*-H), 6.64 (1 H, dd, J_{HH} 8.9, 2.7, *m*-H), 6.88 (1 H, d, J_{HH} 8.3, *o*-H), 7.30 (1 H, d, J_{HH} 8.3, *o*-H) and 9.10 (1 H, d, J_{HH} 8.1, *o*-H); $\delta_{\text{C}}(150 \text{ MHz}; C_6D_6; Me_4Si)$ 26.4 (3 C, br s, CMe_3), 35.8 (1 C, d, J_{PC} 32.3, CMe_3), 39.5 (2 C, s, NMe_2), 40.6 (2 C, s, NMe_2), 41.9 (1 C, d, J_{PC} 26.6, PCH), 43.8 (1 C, s, NMe), 47.9 (1 C, d, J_{PC} 33.2, PCH), 52.09 (1 C, s, OMe), 52.4 (1 C, s, OMe), 59.5 (1 C, s, CH_2), 59.8 (1 C, s, CH_2), 65.0 (1 C, d, J_{PC} 2.9, PCHC), 65.1 (1 C, d, J_{PC} 1.0, PCHC), 109.2 (2 C, s, *m*- C_6H_4), 111.5 (1 C, s, *m*- C_6H_4), 115.9 (1 C, s, *m*- C_6H_4), 122.2 (1 C, s, *o*- C_6H_4), 123.1 (1 C, d, J_{PC} 17.7, C_6H_4), 133.1 (1 C, d, J_{PC} 7.5, *o*- C_6H_4), 135.8 (1 C, d, J_{PC} 8.1, *o*- C_6H_4), 138.3 (1 C, d, J_{PC} 4.1, C_6H_4), 138.7 (1 C, d, J_{PC} 15.9, C_6H_4), 147.1 (1 C, s, *p*- C_6H_4), 149.9 (1 C, s, *p*- C_6H_4), 168.8 (1 C, d, J_{PC} 8.1, COO), 170.6 (1 C, d, J_{PC} 8.3, COO) and 205.9 (1 C, d, J_{PC} 6.4, CO); $\delta_{\text{P}}(121 \text{ MHz}; C_6D_6; H_3PO_4)$ 49.9 (1 P, s, J_{PtP} 4851); $\delta_{\text{N}}(60 \text{ MHz}; C_6D_6; MeNO_2)$ -333 (2 N, NMe_2) and -355 (1 N, NMe); m/z (ESI) 1585.5349 ($[M]^+$. $C_{64}H_{89}N_6O_{12}P_2Pt_2$ requires

1585.5308).

Compound 101:

^1H (600 MHz; C_6D_6 ; Me_4Si) 0.06 (1 H, d, J_{PH} 1.9, OH), 1.15 (9 H, d, J_{PH} 13.6, Bu^t), 2.40 (6 H, s, NMe_2), 2.52 (6 H, s, NMe_2), 2.60 (3 H, s, NMe), 2.94 (1 H, m, CH_2), 3.18 (1 H, m, CH_2), 3.30 (1 H, m, CH_2), 3.35 (3 H, s, OMe), 3.50 (1 H, m, CH_2), 3.55 (3 H, s, OMe), 4.70 (1 H, d, J_{PH} 10.7, PCH), 5.00 (1 H, d, J_{PH} 13.6, PCH), 6.43 (2 H, m, $m\text{-H}$), 6.60 (1 H, d, J_{HH} 2.2, $m\text{-H}$), 6.88 (1 H, d, J_{HH} 8.3, $m\text{-H}$), 6.95 (1 H, d, J_{HH} 8.3, $o\text{-H}$), 7.21 (1 H, d, J_{HH} 7.9, $o\text{-H}$) and 8.95 (1 H, d, J_{HH} 7.9, $o\text{-H}$); ^{13}C (150 MHz; C_6D_6 ; Me_4Si) 26.6 (3 C, d, J_{PC} 2.9, CMe_3), 36.2 (1 C, d, J_{PC} 29.5, CMe_3), 39.3 (2 C, s, NMe_2), 40.2 (2 C, s, NMe_2), 40.9 (1 C, d, J_{PC} 27.1, PCH), 44.3 (1 C, s, NMe), 48.9 (1 C, d, J_{PC} 33.5, PCH), 52.07 (1 C, s, OMe), 52.3 (1 C, s, OMe), 59.6 (1 C, s, CH_2), 59.9 (1 C, s, CH_2), 64.8 (1 C, d, J_{PC} 2.0, PCHC), 65.8 (1 C, d, J_{PC} 0.8, PCHC), 109.5 (2 C, s, $m\text{-C}_6\text{H}_4$), 111.5 (1 C, s, $m\text{-C}_6\text{H}_4$), 114.8 (1 C, s, $m\text{-C}_6\text{H}_4$), 122.6 (1 C, s, $o\text{-C}_6\text{H}_4$), 123.2 (1 C, d, J_{PC} 16.7, C_6H_4), 133.6 (1 C, d, J_{PC} 4.6, $o\text{-C}_6\text{H}_4$), 133.8 (1 C, d, J_{PC} 4.6, $o\text{-C}_6\text{H}_4$), 137.8 (1 C, d, J_{PC} 15.6, C_6H_4), 138.2 (1 C, d, J_{PC} 4.4, C_6H_4), 147.5 (1 C, s, $p\text{-C}_6\text{H}_4$), 149.6 (1 C, s, $p\text{-C}_6\text{H}_4$), 168.7 (1 C, d, J_{PC} 8.1, COO), 170.0 (1 C, d, J_{PC} 9.2, COO) and 205.3 (1 C, d, J_{PC} 4.7, CO); ^3P (121 MHz; C_6D_6 ; H_3PO_4) 47.8 (1 P, s, J_{PtP} 4874); ^{15}N (60 MHz; C_6D_6 ; MeNO_2) -339 (2 N, NMe_2) and -354 (1 N, NMe).

Reaction of PN ligand **66** with [PtMe₂(1,5-hexadiene)]

PN compound **66** (0.03 g, 0.082 mmol) and [PtMe₂(1,5-hexadiene)] (0.013 g, 0.041 mmol) were dissolved in either benzene-d₆ or toluene-d₈ (0.5 cm³) in a NMR tube at room temperature. Cooling the sample immediately to -20 °C allowed the observation of the complex *cis*-[PtMe₂(**66**)₂] (**102**). Leaving the sample at room temperature resulted in the conversion of complex **102** into a 2:1 *trans* complex in which one of the PN ligands was metallated.

Compound **102**:

³¹P (121 MHz; toluene-d₈; H₃PO₄; -20 °C) 33.9 (2 P, s, *J*_{PtP} 1830).

(*trans*-Metallated complex):

¹H (600 MHz; toluene-d₈; Me₄Si) -0.17 (1 H, t, *J*_{PH} 5.5, *J*_{PtH} 49, Me), 0.80 (9 H, d, *J*_{PH} 13.8, Bu^t) and 1.25 (9 H, d, *J*_{PH} 13.3, Bu^t); ¹³C (150 MHz; toluene-d₈; Me₄Si) -21.0 (1 C, br s, Me), 26.7 (3 C, d, *J*_{PC} 3, CMe₃) and 27.8 (3 C, m, CMe₃); ³¹P (121 MHz; toluene-d₈; H₃PO₄) 28.1 (1 P, d, *J*_{PP} 429, *J*_{PtP} 3061) and 59.6 (1 P, d, *J*_{PP} 429, *J*_{PtP} 3205).

Bibliography

1. van Leeuwen, P. W. N. M. *Homogeneous Catalysis*; Kluwer Academic Publishers, 2004.
2. Astruc, D. *Organometallic Chemistry and Catalysis*; Springer, 2007.
3. Peacock, A. F. A.; Sadler, P. J. *Chem. Asian J.* **2008**, *3*, 1890–1899.
4. van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741–2769.
5. Breslow, R.; Belvedere, S.; Gershell, L.; Leung, D. *Pure Appl. Chem.* **2000**, *72*, 333–342.
6. Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239–1272.
7. Togni, A.; Venanzi, L. M. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497–526.
8. Pettinari, C.; Masciocchi, N. *J. Organomet. Chem.* **2005**, *690*, 1871–1877.
9. Burrows, A. D. *Science Progress* **2002**, *85*, 199–217.
10. Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233–350.
11. Braunstein, P.; Naud, F. *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.
12. Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953–3967.
13. Guiry, P. J.; Saunders, C. P. *Adv. Synth. Catal.* **2004**, *346*, 497–537.
14. von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566–568.
15. Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769–1772.
16. Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149–3150.
17. Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658–2666.
18. Werner, H.; Hampp, A.; Windmüller, B. *J. Organomet. chem.* **1992**, *435*, 169–183.

19. Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 1401–1409.
20. Espino, G.; Jalón, F. A.; Maestro, M.; Manzano, B. R.; Pérez-Manrique, M.; Bacigalupe, A. C. *Eur. J. Inorg. Chem.* **2004**, 2542–2552.
21. Assmann, B.; Angermaier, K.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1994**, 941–942.
22. Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955–993.
23. Phillips, A. D.; Bolaño, S.; Bosquain, S. S.; Daran, J.; Malacea, R.; Peruzzini, M.; Poli, R.; Gonsalvi, L. *Organometallics* **2006**, *25*, 2189–2200.
24. Caporali, M.; Bianchini, C.; Bolaño, S.; Bosquain, S. S.; Gonsalvi, L.; Oberhauser, W.; Rossin, A.; Peruzzini, M. *Inorg. Chim. Acta* **2008**, *361*, 3017–3023.
25. Renfrew, A. K.; Phillips, A. D.; Egger, A. E.; Hartinger, C. G.; Bosquain, S. S.; Nazarov, A. A.; Keppler, B. K.; Gonsalvi, L.; Peruzzini, M.; Dyson, P. J. *Organometallics* **2009**, *28*, 1165–1172.
26. Mannich, C.; Mohs, P. *Chem. Ber.* **1930**, *B63*, 608–12.
27. Jeyaraman, R.; Avila, S. *Chem. Rev.* **1981**, *81*, 149–174.
28. Tramontini, M.; Angilini, L. *Tetrahedron* **1990**, *46*, 1791–1837.
29. Baliah, V.; Jeyaraman, R.; Chandrasekaran, L. *Chem. Rev.* **1983**, *83*, 379–423.
30. Arend, M.; Westermann, B.; Risch, N. *Angew. Chem. Int. Ed.* **1998**, *37*, 1044–1070.
31. Black, D. S.; Deacon, G. B.; Rose, M. *Tetrahedron* **1995**, *51*, 2055–2076.
32. Gogoll, A.; Grennberg, H.; Axén, A. *Organometallics* **1997**, *16*, 1167–1178.
33. Comba, P.; Kerscher, M.; Schiek, W. *Prog. Inorg. Chem.* **2007**, *55*, 613–704.
34. Breuning, M.; Steiner, M. *Synthesis* **2009**, *18*, 2841–2867.
35. Brandt, W.; Drosihn, S.; Haurand, M.; Holzgrabe, U.; Nachtsheim, C. *Arch. Pharm. Pharm. Med. Chem.* **1996**, *329*, 311–323.
36. Kögel, B.; Christoph, T.; Friderichs, E.; Hennies, H. H.; Matthiesen, T.; Schneider, J.; Holzgrabe, U. *CNS Drug Reviews* **1998**, *4*, 54–70.
37. Siener, T.; Cambareri, A.; Kuhl, U.; Englberger, W.; Haurand, M.; Kögel, B.; Holzgrabe, U. *J. Med. Chem.* **2000**, *43*, 3746–3751.

38. Brandt, W.; Holzgrabe, U. *J. Med. Chem.* **2003**, *46*, 1383–1389.
39. Bailey, B. R.; Berlin, K. D.; Holt, E. M.; Scherlag, B. J.; Lazzara, R.; Brachmann, J.; van der Helm, D.; Powell, D. R.; Pantaleo, N. S.; Ruenitz, P. C. *J. Med. Chem.* **1984**, *27*, 758–767.
40. Thompson, M. D.; Smith, G. S.; Berlin, K. D.; Holt, E. M.; Scherlag, B. J.; van der Helm, D.; Muchmore, S. W.; Fidelis, K. A. *J. Med. Chem.* **1987**, *30*, 780–788.
41. Comba, P.; Kerscher, M. *Cryst. Eng.* **2003**, *6*, 197–211.
42. Bukowski, M. R.; Comba, P.; Limberg, C.; Merz, M.; Que, Jr., L.; Wistuba, T. *Angew. Chem. Int. Ed.* **2004**, *43*, 1283–1287.
43. Comba, P.; Merz, M.; Pritzkow, H. *Eur. J. Inorg. Chem.* **2003**, 1711–1718.
44. Börzel, H.; Comba, P.; Hagen, K. S.; Kerscher, M.; Pritzkow, H.; Schatz, M.; Schindler, S.; Walter, O. *Inorg. Chem.* **2002**, *41*, 5440–5452.
45. Comba, P.; Kerscher, M.; Roodt, A. *Eur. J. Inorg. Chem.* **2004**, 4640–4645.
46. Bukowski, M. R.; Comba, P.; Lienke, A.; Limberg, C.; de Laorden, C. L.; Mas-Ballesté, R.; Merz, M.; Que, Jr., L. *Angew. Chem. Int. Ed.* **2006**, *45*, 3446–3449.
47. Bautz, J.; Comba, P.; Lopez de Laorden, C.; Menzel, M.; Rajaraman, G. *Angew. Chem.* **2007**, *119*, 8213–8216.
48. Vagana, R. *Novel Bicyclo[3.3.1]nonan-9-one Metal Complexes*, M.Sc. thesis, Victoria University of Wellington, 2005.
49. Gogoll, A.; Grennberg, H.; Axén, A. *Organometallics* **1998**, *17*, 5248–5253.
50. Wright, E. G.; Spencer, J. L. Unpublished Results.
51. Shen, C. *Electrophilic Metal Complexes*, Ph.D. thesis, Victoria University of Wellington, 2000.
52. Mulekar, S. V.; Berlin, K. D. *J. Org. Chem.* **1989**, *54*, 4758–4767.
53. Arjunan, P.; Berlin, K. D.; Barnes, C. L.; van der Helm, D. *J. Org. Chem.* **1981**, *46*, 3196–3204.
54. Yu, V. K.; Praliev, K. D.; Fomicheva, E. E.; Mukhasheva, R. D.; Klepikova, S. G. *Chem. Heterocycl. Compd.* **2006**, *42*, 512–519.
55. Welcher, R. P.; Johnson, G. A.; Wystrach, V. P. *J. Am. Chem. Soc.* **1960**, *82*, 4437–4438.
56. Welcher, R. P.; Day, N. E. *J. Org. Chem.* **1962**, *27*, 1824–1827.

57. Blackburne, I. D.; Katritzky, A. R.; Read, D. M. *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1155–1160.
58. Rampal, J. B.; Macdonell, G. D.; Edasery, J. P.; Berlin, K. D.; Rahman, A.; van der Helm, D.; Pietrusiewicz, K. M. *J. Org. Chem.* **1981**, *46*, 1156–1165.
59. Rampal, J. B.; Berlin, K. D.; Edasery, J. P.; Satyamurthy, N.; van der Helm, D. *J. Org. Chem.* **1981**, *46*, 1166–1172.
60. Rampal, J. B.; Satyamurthy, N.; Bowen, J. M.; Purdie, N.; Berlin, K. D. *J. Am. Chem. Soc.* **1981**, *103*, 7602–7609.
61. Doherty, R.; Haddow, M. F.; Harrison, Z. A.; Orpen, A. G.; Pringle, P. G.; Turner, A.; Wingad, R. L. *Dalton Trans.* **2006**, *36*, 4310–4320.
62. Lim, T. H.; Spencer, J. L.; Vagana, R.; Borrmann, T. Unpublished Results.
63. Jones, Jr., M. *Organic Chemistry*; W. W. Norton & company, Inc., 1997.
64. Enders, D.; Saint-Dizier, A.; Lannou, M.; Lenzen, A. *Eur. J. Org. Chem.* **2006**, 29–49.
65. Snider, T. E.; Morris, D. L.; Srivastava, K. C.; Berlin, K. D. *Org. Synth.* **1988**, *6*, 932–935.
66. Jones, N.; Taylor, H. T. *J. Chem. Soc.* **1961**, 1345–1347.
67. Reed, S. F. *J. Org. Chem.* **1962**, *27*, 4116–4117.
68. Japp, F. R.; Maitland, W. *J. Chem. Soc.* **1904**, *85*, 1473–1489.
69. Otto, H.; Ebner, U. *Archiv der Pharmazie* **1976**, *309*, 969–978.
70. Yates, P.; Yoda, N.; Brown, W.; Mann, B. *J. Am. Chem. Soc.* **1958**, *80*, 202–205.
71. Featherman, S. I.; Quin, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 4349–4356.
72. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley & Sons, Inc., 1998.
73. Simova, S. *Magn. Reson. Chem.* **1998**, *36*, 505–510.
74. Reynold, W. F.; McLean, S.; Tay, L.; Yu, M.; Enriquez, R. G.; Estwick, D. M.; Pascoe, K. O. *Magn. Reson. Chem.* **1997**, *35*, 455–462.
75. Leon, I.; Enriquez, R. G.; McLean, S.; Reynold, W. F.; Yu, M. *Magn. Reson. Chem.* **1998**, *36*, S111–S117.
76. Fernandez, M. J.; Casares, J. M.; Galvez, E.; Bellantato, J. *J. Heterocyclic Chem.* **1993**, *30*, 815–817.

77. Chen, C. H.; Reynolds, G. A.; Cossar, B. C. *J. Org. Chem.* **1981**, *46*, 2752–2757.
78. Azerbaev, N. I.; Omarov, T. T.; Gubasheva, A. S.; Al'Mukhanova, K. A.; Baisalbaeva, S. A. *Vestnik Akademii Nauk Kazakhskoi SSR* **1975**, *2*, 47–50.
79. Moss, J. R. *J. Mol. Catal. A: Chem.* **1996**, *107*, 169–174.
80. Hambley, T. W. *Coord. Chem. Rev.* **1997**, *166*, 181–223.
81. Comba, P.; Kerscher, M.; Merz, M.; Müller, V.; Pritzkow, H.; Remenyi, R.; Schiek, W.; Xiong, Y. *Chem. Eur. J.* **2002**, *8*, 5750–5760.
82. Comba, P.; de Laorden, C. L.; Pritzkow, H. *Helv. Chim. Acta* **2005**, *88*, 647–664.
83. Atanasov, M.; Comba, P.; Martin, B.; Müller, V.; Rajaraman, G.; Rohwer, H.; Wunderlich, S. *J. Comput. Chem.* **2006**, *27*, 1263–1277.
84. Knowles, W. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 1998–2007.
85. Zeise, W. C. *Mag. Pharm.* **1830**, *35*, 105.
86. Mingos, D. M. P. *J. Organomet. Chem.* **2001**, *635*, 1–8.
87. Amatore, C.; Fuxa, A.; Jutand, A. *Chem. Eur. J.* **2000**, *6*, 1474–1482.
88. Tsuji, J. *Pure Appl. Chem* **1989**, *61*, 1673–1680.
89. Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257–276.
90. Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422.
91. Carturan, G.; Belluco, U.; Del PRA, A.; Zanotti, G. *Inorg. Chim. Acta* **1979**, *33*, 155–160.
92. Kollmar, M.; Helmchen, G. *Organometallics* **2002**, *21*, 4771–4775.
93. Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M.; DeCian, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966–2981.
94. Braunstein, P.; Zhang, J.; Welter, R. *Dalton Trans.* **2003**, 507–509.
95. Zhang, J.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2004**, *43*, 4172–4177.
96. Rosenfeld, S. *J. Am. Chem. Soc.* **1997**, *119*, 8395–8396.
97. Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–352.
98. Bruce, M. I. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 73–86.
99. Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.
100. Brookhart, M.; Green, M. L. H.; Parkin, G. *PNAS* **2007**, *104*, 6908–6914.

101. Scherer, W.; McGrady, G. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1782–1806.
102. Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358–3363.
103. Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 1510–1511.
104. Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767–773.
105. Siedle, A. R.; Newmark, R. A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 3412–3418.
106. Anderson, B. G.; Hoyte, S. A.; Spencer, J. L. *Inorg. Chem.* **2009**, *48*, 7977–7983.
107. Green, M.; Grove, D. M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2228–2234.
108. Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49–52.
109. Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653–2662.
110. Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326–328.
111. Carr, N.; Dunne, B. J.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1991**, 863–871.
112. Jain, V. K. *Curr. Sci.* **1990**, *59*, 143–151.
113. Michelin, R. A.; Pizzo, E.; Scarso, A.; Sgarbossa, P.; Strukul, G.; Tassan, A. *Organometallics* **2005**, *24*, 1012–1017.
114. Sgarbossa, P.; Scarso, A.; Pizzo, E.; Sbovata, S. M.; Tassan, A.; Michelin, R. A.; Strukul, G. *J. Mol. Catal. A: Chem.* **2007**, *261*, 202–206.
115. Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S. *Chem. Eur. J.* **1999**, *5*, 1391–1410.
116. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.
117. Skapski, A. C.; Troughton, P. G. H. *J. Chem. Soc. (A)* **1969**, 2772–2781.
118. Mintcheva, N.; Tanabe, M.; Osakada, K. *Organometallics* **2006**, *25*, 3776–3783.
119. Vicente, J.; Arcas, A.; Gálvez-López, M.; Juliá-Hernández, F. *Organometallics* **2008**, *27*, 1582–1590.
120. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

121. Marek, R.; Lyčka, A. *Curr. Org. Chem.* **2002**, *6*, 35–66.
122. Mason, J.; Larkworthy, L. F.; Moore, E. A. *Chem. Rev.* **2002**, *102*, 913–934.
123. Ryan, J. M. *Novel Secondary Metabolites from New Zealand Marine Sponges*, Ph.D. thesis, Victoria University of Wellington, 2007.
124. Toom, L.; Kutt, A.; Kaljurand, I.; Leito, I.; Ottosson, H.; Grennberg, H.; Gogoll, A. *J. Org. Chem.* **2006**, *71*, 7155–7164.
125. Buchanan, G. W. *Tetrahedron* **1989**, *45*, 581–604.
126. Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 4685–4693.
127. Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Szłyk, E. *Magn. Reson. Chem.* **2007**, *45*, 1045–1058.
128. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.
129. Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Magn. Reson. Chem.* **2002**, *40*, 489–505.
130. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
131. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.