

Iminophosphine Complexes of Palladium and Platinum: Catalysis and Metallacycloalkanes Synthesis

Tebello Mahamo



University of Cape Town

2012

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

Iminophosphine Complexes of Palladium and Platinum: Catalysis and Metallacycloalkanes Synthesis

A thesis submitted to the University of Cape Town in partial fulfilment of
the requirements for the degree of Doctor of Philosophy

By
Tebello Mahamo

Supervisors: **Dr. Gregory S. Smith**
Prof. Koop Lammertsma

Co-supervisors: **Prof. Selwyn F. Mapolie**
Dr. J. Chris Slootweg
Dr. Andreas W. Ehlers

Department of Chemistry
University of Cape Town
Rondebosch, 7701
Cape Town

September 2012

DECLARATION

I declare that “Iminophosphine Complexes of Palladium and Platinum: Catalysis and Metallacycloalkanes Synthesis” is my own work and to the best of my knowledge has never been reported or submitted for any degree or examination in any university. All sources of information used are cited, acknowledged and completely referenced at the end of each chapter.

Tebello Mahamo

DEDICATION

To my mother, who always encourages, supports, hopes and prays.

To Professor John R. Moss.

University of Cape Town

ACKNOWLEDGEMENTS

Praise and glory go to my creator, God Almighty for all His neverending goodness, mercy, protection and abundant blessings.

I would like to take this opportunity to extend my heartfelt gratitude to the following people, without whom I would not have been able to make to this point:

To my supervisors and co-supervisors, Dr. Gregory Smith, Dr. Chris Slootweg, Dr. Andreas Ehlers, Prof. dr. Koop Lammertsma, and Prof. Selwyn Mapolie: thank you all very much for the guidance, encouragement, motivation and and for the invaluable advice and knowledge that contributed so greatly to this project.

My sincere gratitude goes to the technical and support staff at the University of Cape Town and Vrije Universiteit Amsterdam for all their help and assistance. Thanks to Mr Noel Hendricks and Mr Pete Roberts (UCT) and Dr Frans de Kanter (VU Amsterdam) for help with NMR experiments; Mr Pierro Benincasa (UCT) for all the elemental analyses. To Dr Hong Su (UCT) for collecting X-ray crystallographic data. To Dr Maritjie Stander (University of Stellenbosch) and Elwin Janssen (VU Amsterdam) for collecting the mass spectral data.

I would also like to extend my sincere thanks to Ms Deidre Brooks in the Chemistry Department's central office at the University of Cape Town and Mrs Miep Smits at Vrije Universiteit Amsterdam for their administrative support and encouragement.

Special thanks to Frank Hoffmann who was an invaluable source of help and encouragement with the calculations. To Dr. Emma Hager, Dr. Setshaba Khanye, Denis Ongarora and Feng Zheng, thank you for taking the time to read through different parts of this thesis.

To family: my mother, 'Matebello, you truly are the best. My sister, Aus' Ma and My brother, Ab'ti Kamoho, you guys are simply awesome. My sister, Ausi M'lebo, words can not express what a great blessing you are. Thank you guys so much for your unwavering love, support, confidence and prayers.

To my dear friends on and off campus: thank you guys for your friendship and encouragement. I am truely blessed to have you all in my life. To my colleagues, both past and present, thanks for making the labs at the University of Cape Town and Vrije Universiteit Amsterdam a wonderful environment to work in, and for the useful and informative discussions and your input into this project.

Acknowledgements

I wish to express gratitude to the Royal Netherlands Academy of Arts and Sciences (KNAW) for the Carolina MacGillavry PhD Fellowship, which provided financial support for me throughout this project.

Finally, I would like to acknowledge my late supervisor, Professor John Moss, whose enthusiasm for and love of organometallic and transition metal chemistry was nothing if not contagious.



ABSTRACT

A series of N-functionalized 2-diphenylphosphinobenzaldimino ligands (**3.1** – **3.6**) bearing pendant groups on the imine moiety were prepared by the Schiff-base condensation reaction of 2-diphenylphosphinobenzaldehyde and appropriate primary amines. The ligands were subsequently used to synthesize a range of palladium complexes of the types $[\text{Pd}(\text{P}^{\wedge}\text{N})\text{Cl}_2]$ (**3.7** – **3.12**) and $[\text{Pd}(\text{P}^{\wedge}\text{N})(\text{Me})\text{Cl}]$ (**3.13** – **3.18**) from precursor complexes $[\text{Pd}(\text{COD})\text{Cl}_2]$ and $[\text{Pd}(\text{COD})(\text{Me})\text{Cl}]$, respectively. Platinum complexes of the type $[\text{Pt}(\text{P}^{\wedge}\text{N})\text{Cl}_2]$ (**3.19** – **3.24**) were synthesized by the ligand displacement reaction between $[\text{Pt}(\text{COD})\text{Cl}_2]$ and ligands **3.1** – **3.6**. All compounds were characterized by multinuclear NMR and infrared spectroscopies as well as elemental analysis. In addition, the structure of complex **3.14** was determined by x-ray crystallography.

Palladium complexes **3.8** – **3.10** and **3.16** were evaluated as pre-catalysts in the Suzuki-Miyaura coupling reaction. These complexes were found to be highly active and tolerant of a wide range of reaction conditions and functional groups on substrates. Low catalyst loadings (0.1 mol% Pd) were required, while high conversions and short reaction times were maintained. Having a substituent bearing a donor atom on the imine moiety of the ligand (ligands **3.3** and **3.4**) was found to enhance catalytic activity. Palladium methyl chloride complexes were found to show slightly more activity than their palladium dichloride counterparts.

Reaction of $[\text{Pt}(\text{P}^{\wedge}\text{N})\text{Cl}_2]$ complexes with $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$ in an attempt to synthesize platinacycloalkane complexes resulted in the formation of bromobutyl complexes $[\text{Pt}(\text{P}^{\wedge}\text{N})(\text{C}_4\text{H}_9)\text{Br}]$ (**3.25** and **3.26**) instead. Successful synthesis of platinacyclopentane complexes, **5.1** – **5.6**, and platinacycloheptane complexes, **5.7** – **5.12**, was achieved by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ with appropriate di-Grignard reagents, followed by ligand displacement with the iminophosphine ligands. All complexes were fully characterized using various NMR spectroscopies, mass spectrometry and elemental analysis. Crystal structures of the bromobutyl and platinacyclopentane complexes **3.25** and **5.1** were determined.

Studies on the thermal decomposition of the platinacycloalkane complexes were carried out. Platinacyclopentane complexes **5.1** – **5.6** were found to be markedly stable, with the decomposition reaction requiring temperatures higher than 100 °C. Reaction temperature and duration were found to have a significant influence on the organic product distribution obtained. These reactions gave 1-butene (for the platinacyclopentane complexes) and 1-hexene (for the platinacycloheptane complexes) as major products. Kinetic data obtained for

the decomposition of **5.1** and **5.7** shows that the decomposition reaction follows first order kinetics for the initial 30% of the decomposition reaction. Thereafter, reaction order deviates from first order behaviour, indicating increasing involvement of products in the reaction mechanism.

The generally accepted β -hydride elimination/reductive elimination reaction mechanism for the decomposition of metallacycloalkanes was investigated using DFT methods. The simplified complex, **5.13B**, was used as a model for platinacyclopentane complexes. Results from these calculations show that intramolecular β -hydride elimination from the carbocyclic ring of platinacyclopentane complexes is unlikely to occur as this process requires an extremely high energy barrier ($>64 \text{ kcal}\cdot\text{mol}^{-1}$). Furthermore, these calculations reveal that ligand hemilability is energetically disfavoured in the β -elimination reaction while it is favoured in the reductive elimination reaction.

Table of Contents

DEDICATION.....	I
ACKNOWLEDGEMENTS.....	II
ABSTRACT	IV
LIST OF ABBREVIATIONS	XI
PUBLICATIONS AND CONFERENCE PARTICIPATION.....	XIII
CHAPTER 1	1
IMINOPHOSPHINE LIGANDS AND THEIR COMPLEXES IN SYNTHESIS AND CATALYSIS.....	1
1.1 INTRODUCTION.....	1
1.2 SCOPE	2
1.3 CYCLIC IMINE N-DONOR LIGANDS	3
1.3.1 Pyridine-Based Ligands.....	3
1.3.2 Quinazoline-Based Ligands.....	7
1.3.3 Pyrazole-Based Ligands.....	8
1.3.4 Imidazoline-Based Ligands	8
1.3.5 Oxazoline- and Thiazoline-Based Ligands.....	9
1.3.6 Oxazine-Based ligands.....	11
1.4 ACYCLIC IMINE N-DONOR LIGANDS.....	12
1.5 PHOSPHOLANE-BASED LIGANDS	15
1.6 SUMMARY.....	16
1.7 REFERENCES.....	17
CHAPTER 2	21
REVIEW OF THE SYNTHESIS AND REACTIVITY OF PLATINACYCLOALKANES	21
2.1 INTRODUCTION.....	21
2.2 SCOPE	21
2.3 SYTHESIS OF SMALL AND MEDIUM PLATINACYCLES.....	22
2.3.1 Transmetallation.....	22
2.3.2 Cyclometallation	28
2.3.3 Insertion into C-C Bonds	31
2.3.4 Cycloaddition of Unsaturated Molecules.....	34
2.3.5 Nucleophilic Attack on Coordinated Ligands.....	36

2.4	REACTIVITY OF PLATINACYCLOALKANES	37
2.4.1	Decomposition Reactions	37
2.4.1.1	β -Hydride Elimination	38
2.4.1.2	Reductive Elimination	40
2.4.1.3	α -Hydride Elimination	42
2.4.1.4	C-C-Bond Cleavage (Retro-cycloaddition).....	43
2.4.1.5	Other Decomposition Pathways	43
2.4.2	Insertion Reactions.....	44
2.4.2.1	Insertion of Carbon Monoxide, Isocyanides and Sulfur	44
2.4.2.2	Insertion of Alkenes, Alkynes and Allenes	46
2.5	METALLACYCLOALKANES IN ETHYLENE OLIGOMERIZATION	47
2.6	SUMMARY.....	51
2.7	AIMS AND OBJECTIVES	51
2.7.1	Specific Aims.....	51
2.8	REFERENCES.....	52
CHAPTER 3	59	
	IMINOPHOSPHINE LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II)	
	COMPLEXES.....	59
3.1	INTRODUCTION.....	59
3.2	RESULTS AND DISCUSSION.....	60
3.2.1	Synthesis and Characterization of Iminophosphine Ligands (3.1 – 3.6).....	60
3.2.1.1	NMR Spectroscopy for 3.1 – 3.6.....	61
3.2.1.2	FTIR Spectroscopy for 3.1 – 3.6.....	63
3.2.1.3	Mass Spectrometry and Microanalysis for 3.1 – 3.6	63
3.2.2	Synthesis and Characterization of Palladium Dichloride Complexes (3.7 – 3.12) ..	
	65
3.2.2.1	NMR Spectroscopy for complexes 3.7 – 3.12.....	65
3.2.2.2	FTIR Spectroscopy for 3.7 – 3.12.....	66
3.2.2.3	Mass Spectrometry and Microanalysis for 3.7 – 3.12	66
3.2.3	Synthesis and Characterization of Palladium Methyl Chloride Complexes (3.13 –	
	3.18).....	68
3.2.3.1	NMR Spectroscopy for complexes 3.13 – 3.18.....	69
3.2.3.2	FTIR Spectroscopy for 3.13 – 3.18.....	70
3.2.3.3	Mass Spectrometry and Microanalysis for 3.13 – 3.18.....	70
3.2.3.4	X-ray Structure Determination for Complex 3.14	70

3.2.4	Synthesis and Characterization of Platinum Dichloride Complexes (3.19 – 3.24) ..	73
3.2.4.1	NMR Spectroscopy for complexes 3.19 – 3.24	74
3.2.4.2	FTIR Spectroscopy for 3.19 – 3.24	77
3.2.4.3	Mass Spectrometry and Microanalysis for 3.19 – 3.24	77
3.2.5	Synthesis and Characterization of Platinum Butyl Bromide Complexes (3.25 – 3.26)	77
3.2.5.1	NMR Spectroscopy for complexes 3.25 – 3.26	78
3.2.5.2	Mass Spectrometry and Microanalysis for 3.25 – 3.26	81
3.2.5.3	X-ray Structural Determination for Complex 3.26	81
3.3	SUMMARY AND CONCLUSION	84
3.4	REFERENCES	85
CHAPTER 4		89
PALLADIUM-CATALYZED SUZUKI-MIYaura COUPLING REACTIONS		89
4.1	INTRODUCTION	89
4.2	RESULTS AND DISCUSSION	92
4.2.1	Optimization of Reaction Conditions	93
4.2.1.1	Effect of Temperature	93
4.2.1.2	Catalyst Loading	93
4.2.1.3	Effect of Base	94
4.2.1.4	Choice of Solvent	95
4.2.1.5	Mercury Poisoning Test	96
4.2.2	Choice of Arylhalides and Phenylboronic Acids	97
4.2.3	Catalytic Activity of Complexes 3.8, 3.9, 3.10 and 3.16	102
4.3	SUMMARY AND CONCLUSIONS	103
4.4	REFERENCES	105
CHAPTER 5		108
SYNTHESIS, DECOMPOSITION AND DFT STUDIES OF PLATINACYCLOALKANES		108
5.1	INTRODUCTION	108
5.2	RESULTS AND DISCUSSION	110
5.2.1	Synthesis and Characterization of Platinacycloalkanes (5.1 – 5.12)	110
5.2.1.1	NMR Spectroscopy for Platinacycloalkanes 5.1 – 5.12	111
5.2.1.2	FTIR Spectroscopy for 5.1 – 5.12	119
5.2.1.3	Mass Spectrometry and Microanalysis for 5.1 – 5.12	119

Table of Contents

5.2.1.4	X-ray Structure Determination for Complex 5.1	119
5.2.2	Thermal Decomposition of Platinacycloalkanes 5.1 – 5.12	122
5.2.2.1	Effect of Temperature on Product Distribution	122
5.2.2.2	Effect of Time on Product Distribution for 5.1	125
5.2.2.3	Thermal Decomposition of Complexes 5.2 – 5.12	128
5.3	DFT INVESTIGATION INTO THE MECHANISM THERMAL DECOMPOSITION OF PLATINACYCLOPENTANES	129
5.3.1	Selection of Method.....	130
5.3.2	β -Hydride Elimination	131
5.3.3	Reductive Elimination	140
5.4	SUMMARY	146
5.5	REFERENCES	148
CHAPTER 6	153	
CONCLUSIONS	153	
CHAPTER 7	155	
EXPERIMENTAL PROCEDURES	155	
7.1	CHEMICALS AND PURIFICATION OF SOLVENTS	155
7.2	PHYSICAL AND SPECTROSCOPIC INFORMATION (CHAPTERS 3 & 5)....	155
7.3	CATALYTIC SUZUKI-MIYaura COUPLING REACTIONS (CHAPTER 4) ...	156
7.4	THERMAL DECOMPOSITION REACTIONS (CHAPTER 5).....	156
7.5	COMPUTATIONAL DETAILS (CHAPTER 5).....	157
7.6	EXPERIMENTAL DETAILS FOR CHAPTERS 3 & 5.....	158
7.6.1	General Procedure for the Synthesis of Primary imine ligands 3.1 – 3.6 (Chapter 3)	158
7.6.2	General Procedure for the Synthesis of Palladium Dichloride Complexes 3.7 – 3.12 (Chapter 3)	161
7.6.3	General Procedure for the Synthesis of Methyl Chloride Palladium Complexes 3.13 – 3.18 (Chapter 3)	163
7.6.4	General Procedure for the Synthesis of Platinum Dichloride Complexes 3.19 – 3.24 (Chapter 3)	166
7.6.5	General Procedure for the Synthesis of Platinum Alkyl Bromide Complexes 3.25 – 3.26 (Chapter 3)	168
7.6.6	General Procedure for the Synthesis of Platinacycloalkanes 5.1 – 5.12 (Chapter 5)	170
7.6.6.1	Preparation of Platinacyclopentanes (5.1 – 5.12) (Chapter 5).....	170

Table of Contents

7.6.6.2	Preparation of Platinacycloheptanes 5.7 – 5.12 (Chapter 5).....	174
7.7	CRYSTALLOGRAPHIC DATA FOR 3.14, 3.25 and 5.1	177
7.8	REFERENCES	181

University of Cape Town

LIST OF ABBREVIATIONS

Ar	Aromatic/Aryl
CDCl ₃	Deuteriochloroform
DMSO- <i>d</i> ₆	Deuterodimethylsulfoxide
Toluene- <i>d</i> ₆	Deuterotoluene
EtOAc	Ethyl acetate
EtOH	Ethanol
Et	Ethyl
Ph	Phenyl
THT	Tetrahydrothiophene
Cy	Cyclohexyl
Tol	Tolyl
Mes	Mesityl
Bn	Benzyl
Pr	Propyl
OTf	Triflate
OAc	Acetoxy
NEt ₃	Triethyl amine
DMF	N,N-dimethylformamide
THF	Tetrahydrofuran
TMEDA	N,N,N',N'-tetramethylethylenediamine
HMPA	Hexamethylphosphoramide
P(<i>o</i> -Tol) ₃	Tri(<i>o</i> -tolyl)phosphine
OMe	Methoxy
Ph	Phenyl
MeCN	Acetonitrile
Et ₂ O	Diethyl ether
DCM	Dichloromethane
EtOH	Ethanol
MeOH	Methanol
Me	Methyl
Et	Ethyl
Bu	Butyl

List of Abbreviations

COD	1,5-cyclooctadiene
PPh ₃	Triphenylphosphine
dppe	1,2-bis(diphenylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	Dimethylsulfoxide, (CH ₃) ₂ S=O
L	Ligand
R	Alkyl
Ar	Aryl
Nu	Nucleophile
<i>o</i>	ortho
<i>m</i>	meta
<i>p</i>	para
¹ H NMR	Proton Nuclear Magnetic Resonance
¹³ C NMR	Carbon Nuclear Magnetic Resonance
³¹ P NMR	Phosphorus Nuclear Magnetic Resonance
s	singlet
d	doublet
t	triplet
m	multiplet
br m	broad multiplet
J	coupling constant
MS	Mass spectrometry
ESI	Electrospray ionization
<i>m/z</i>	mass to charge ratio
FT-IR	Fourier Transform Infrared
°C	degrees Celsius
mmol	millimoles
ml	milliliters
g	grams
mg	milligrams
ppm	parts per million
min	minutes
h	hours

PUBLICATIONS AND CONFERENCE PARTICIPATION

PUBLICATIONS

T. Mahamo, F. Zheng, A. Sivaramakrishna, J. R. Moss, G. Smith, **New synthesis and thermal studies of palladacycloalkanes and their precursors.** *Journal of Organometallic Chemistry*, 2008, **693**, 103.

M. M. Mogorosi, T. Mahamo, J. R. Moss, S. F. Mapolie, J. C. Sloopweg, K. Lammertsma, G. S. Smith, **Neutral palladium(II) complexes with P,N Schiff-base ligands: Synthesis, characterization and catalytic oligomerization of ethylene.** *Journal of Organometallic Chemistry*, 2011, **696**, 3585.

T. Mahamo, M. M. Mogorosi, J. R. Moss, S. F. Mapolie, J. C. Sloopweg, K. Lammertsma, G. S. Smith, **Neutral palladium(II) complexes with P,N Schiff-base ligands: Synthesis, characterization and application as Suzuki-Miyaura coupling catalysts.** *Journal of Organometallic Chemistry*, 2012, **703**, 34.

CONFERENCE ATTENDANCE

T. Mahamo, F. Zheng, A. Sivaramakrishna, G. Smith, J. R. Moss, C. Sloopweg, K. Lammertsma, **Synthesis, Characterization and Thermal Decomposition Studies of New Palladacycloalkanes.** July, 2008, 16th International Symposium on Homogeneous Catalysis, Florence, Italy. Poster Presentation.

T. Mahamo, G. S. Smith, S. F. Mapolie, J. C. Sloopweg, K. Lammertsma, **Neutral Pd(II) Complexes with Schiff-Base P^N Ligands as Suzuki-Miyaura Catalysts.** November, 2011, Chemistry As Innovating Science, Maarssen, The Netherlands. Poster Presentation.

CHAPTER 1

IMINOPHOSPHINE LIGANDS AND THEIR COMPLEXES IN SYNTHESIS AND CATALYSIS

1.1 INTRODUCTION

Ligand design is becoming an increasingly important part of synthetic organometallic and coordination chemistry.¹ This is because the properties of metal complexes in synthesis and catalysis are a direct result of the interactions between the metal centre and its supporting ligands.² Ligands composed of significantly different chemical functionalities such as hard and soft donor moieties, often called hybrid ligands, find increasing use in molecular chemistry. A special class of these ligands is that of hemilabile ligands. The concept of hemilability was introduced in 1979 by Rauchfuss^{3,4} to describe multidentate ligands that 'would bind well enough to the metal centre to allow isolation of the complex, but would readily dissociate the hard end component thus generating a vacant site for substrate binding'⁵ (Figure 1.1).⁶

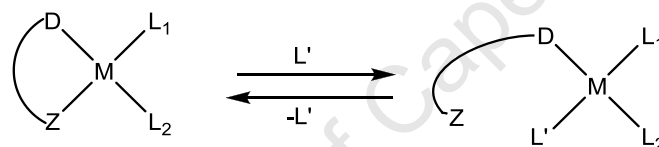


Figure 1.1: Generalized description of adaptive coordination of hemilabile ligands (M = metal centre, D = strong donor, Z = weak donor and L' = substrate).

This is a particularly desirable characteristic for complexes which might have application in catalysis, and since the majority of metals used in such systems are middle or late transition metals, it is usually the soft donor atom which is continually bound to the metal centre.⁷ An important property of these ligands is that they can stabilize metal ions in a variety of oxidation states and geometries, which form during the catalytic cycle.⁴ In addition, the hard ends are weakly coordinated to the soft metal centre, and can be easily dissociated in solution, affording a vacant site whenever demanded, whereas the chelate effect confers stability to the catalyst precursor in the absence of substrate⁴ thereby preventing catalyst decomposition/deactivation.

Over the past few decades, interest in metal complexes of this type of ligands, which are essentially functionalized phosphine ligands, and their role in catalysis has been steadily growing as the different features associated with each donor atom confer unique properties to their metal complexes.⁷⁻¹⁰ Unlike homo-donor chelate ligands, hetero-donor ligands have a distinct *trans* effect which can play a role in controlling the selectivity/activity, especially in co- and/or polymerization processes.¹¹ The syntheses and reactivity/catalytic activity of

complexes bearing hemilabile ligands of the type P^δN^δ^{4,12} and P^δO^δ,¹³ have been widely reported.

Of the reported hemilabile ligands, those bearing phosphorus and nitrogen atoms as their donors form the most commonly used class. These ligands can display quite different coordination modes compared to the homo-donor P^δP^δ and N^δN^δ ligands. The π-acceptor character of the phosphorus ligand can stabilize a metal centre in a low oxidation state, while the σ-donor ability of the nitrogen donor makes the metal centre more susceptible to oxidative addition reactions. This combination can help to stabilize intermediate oxidation states and geometries which form during the catalytic cycle.^{4,11}

This electronic asymmetry can also be used to optimize a ligand for a particular reaction by appropriate choice of the nature of the donor atoms. For example, binding the phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen^{12,14} will reduce its electron donating capability while also enhancing its π-acceptor capacity. On the other hand, the presence of an imino rather than amino group will result in a nitrogen donor atom of greater δ-donating capabilities.^{12,15} Moreover, this type of ligand allows modulation of the steric crowding around the metal centre through the simple variation of the substituents on the imine and phosphine groups.¹⁶

Finally, the past decade or so has witnessed an unprecedented increase in the number of reports on chiral iminophosphine ligands. Complexes based on these ligands have been successfully used in asymmetric catalytic reactions such as hydrosilylation,¹⁷ hydroboration of olefins,¹⁸ transfer hydrogenation of ketones¹⁹ to name but a few. Their success is based not only on steric factors, but also on electronic asymmetry on the metal centre generated by the presence of very different donor atoms on the metal,^{4,5} a concept that was called electronic differentiation by Faller.⁷

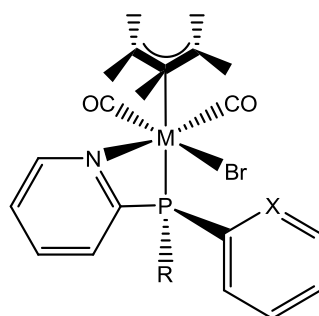
1.2 SCOPE

This brief review covers a specific subset of bidentate, heterodonor ligands: the iminophosphine ligands. The diverse structural motifs found in this ligand class are highlighted. In addition, because these ligands are usually used as supporting ligands in coordination chemistry and catalysis, the broad range of synthetic and catalytic reactions in which the ligands and their complexes are applied will also be mentioned. The main aim of this exercise is to give a brief overview of the structural diversity found in this class of ligands as well as the diversity in their application in organic synthesis and homogeneous catalysis.

1.3 CYCLIC IMINE N-DONOR LIGANDS

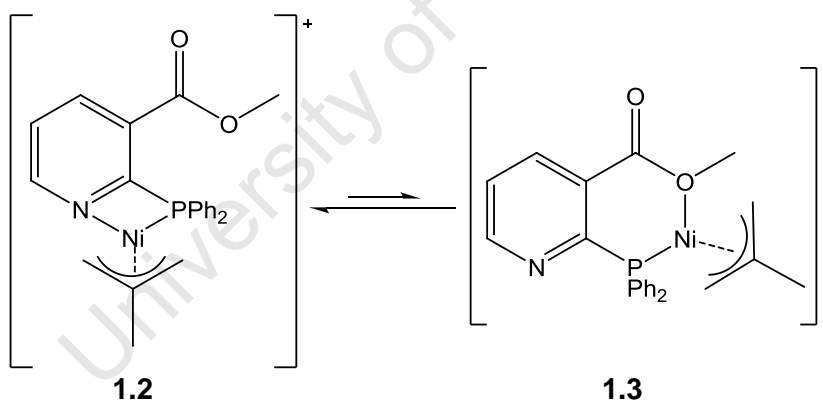
1.3.1 Pyridine-Based Ligands

Pyridylphosphines represent one of the most widely used class of iminophosphine ligands. The simplest of these is 2-(diphenylphosphino)pyridine. Although this ligand is better suited to bridge two metal centres, there are examples of complexes where it acts as a bidentate hemilabile ligand (complex **1.1**), forming a 4-membered chelate ring with the metal centre.²⁰

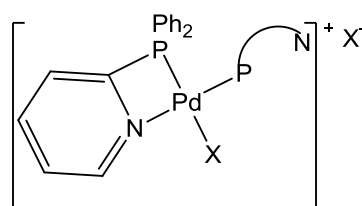


1.1: M = Ru, Mo; X = N

Cationic complexes **1.2** and **1.3** were prepared from the reaction of methyl 2-(diphenylphosphino)nicotinate with a nickel precursor. X-ray crystallographic data revealed that, although this ligand is potentially a tridentate P,N,O ligand, the preferred structures are the bidentate P^N or P^O complexes **1.2** and **1.3** respectively.^{21a,21b}



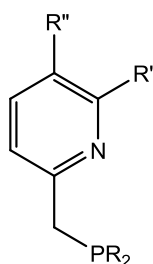
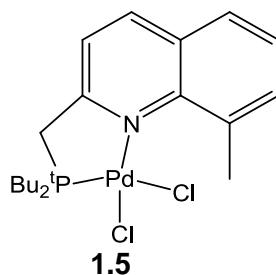
Drent and co-workers^{21c,21d} developed a highly efficient class of homogeneous palladium cationic catalysts, **1.4**, for the carbonylation of alkynes. These catalysts allowed the development of cost-effective, large scale production of methyl methacrylate (MMA), a large-scale chemical intermediate for the production of homopolymers and copolymers.



1.4

Due to the unprecedented high selectivities shown by these catalysts, this process has the benefit of exerting minimal negative environmental impact.

5-membered chelate rings can be formed with a metal centre when ligands derived from 8-phosphinoquinoline or phosphines linked to the pyridyl moiety by a methylene linker are used. These complexes are more stable than those that have 4-membered chelate ring structures due to reduced ring strain. Examples of such complexes include the palladium complex **1.5** reported by Deeming and co-workers²² as well as rhodium complexes of ligands **1.6 – 1.9** reported by Lavigne, Lugan and co-workers.²³



1.6: R = Ph; R' = Me; R'' = H

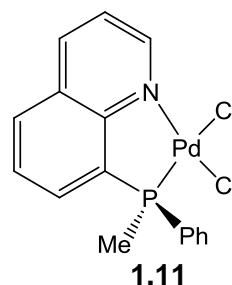
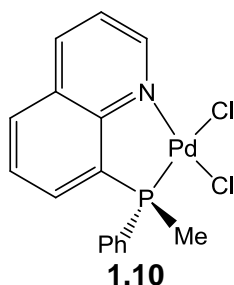
1.7: R = Ph; R' = C₄H₄; R'' = C₄H₄

1.8: R = Cy; R' = Me; R'' = H

1.9: R = Cy; R' = C₄H₄; R'' = C₄H₄

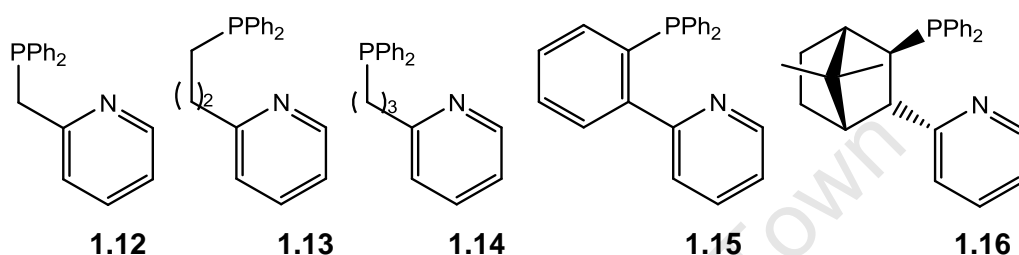
Rhodium complexes of ligands **1.6 – 1.9** were tested for activity in transfer hydrogenation using a wide range of ketones as substrates. The complexes showed good activities, with high turnover frequencies and high enantioselectivities.

The chiral ligand 1-(2-diphenylphosphino-3,6-dimethoxyphenyl)-isoquinoline reacts with palladium precursors to give a racemic mixture of the complex [Pd(P[^]N)Cl₂], **1.10** and **1.11**.²⁴

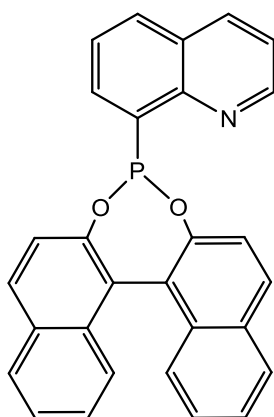


Kamer and co-workers reported the synthesis of ligands **1.12 – 1.16** and their corresponding neutral nickel and palladium complexes as well as cationic palladium complexes.²⁵ These complexes were tested for activity in ethylene oligomerization. Upon activation with MAO,

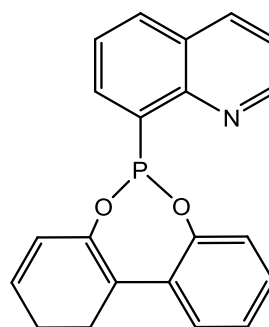
the nickel complexes were found to be highly active while both the neutral and cationic palladium complexes showed very low activities. Butenes were the major products in all cases. The ligands all consist of a diphenylphosphine moiety and a 2-pyridyl group and differ in the backbone connecting these functionalities. Ligands **1.12** – **1.14** have respectively one, two and three methylene units as the backbone. Ligand **1.15** has a two-carbon bridge integrated in a phenylene ring between the 2-pyridyl and the phosphine moiety. As in **1.12** – **1.14**, the two-carbon bridge in **1.16** is aliphatic. However, due to this spacer being part of a substituted ring system, the backbone in these ligands is more rigid than in ligands **1.12** – **1.14**.²⁵



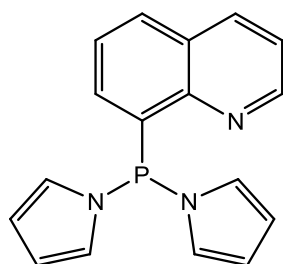
Electronic asymmetry can be used to optimize ligands for use in a particular reaction by appropriate choice of the nature of the donor atoms. For example, bonding a phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen will reduce its electron-donating capability while enhancing its π -acceptor capacity.¹¹ Consiglio and co-workers reported the synthesis and complexation, to palladium and nickel, of ligands **1.17** – **1.20**. The palladium complexes were tested for activity in the copolymerization of styrene and ethylene with carbon monoxide while the nickel complexes were tested for activity in ethylene oligomerization. The nickel complexes were found to be highly active at ambient temperature and low ethylene pressure (1 – 2 bar) and the major products were found to be C_4 and C_6 oligomers.²⁶



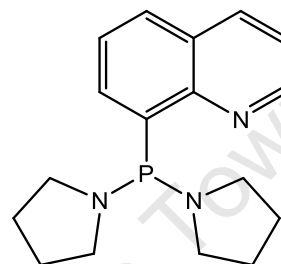
1.17



1.18

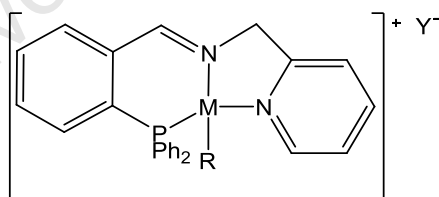


1.19



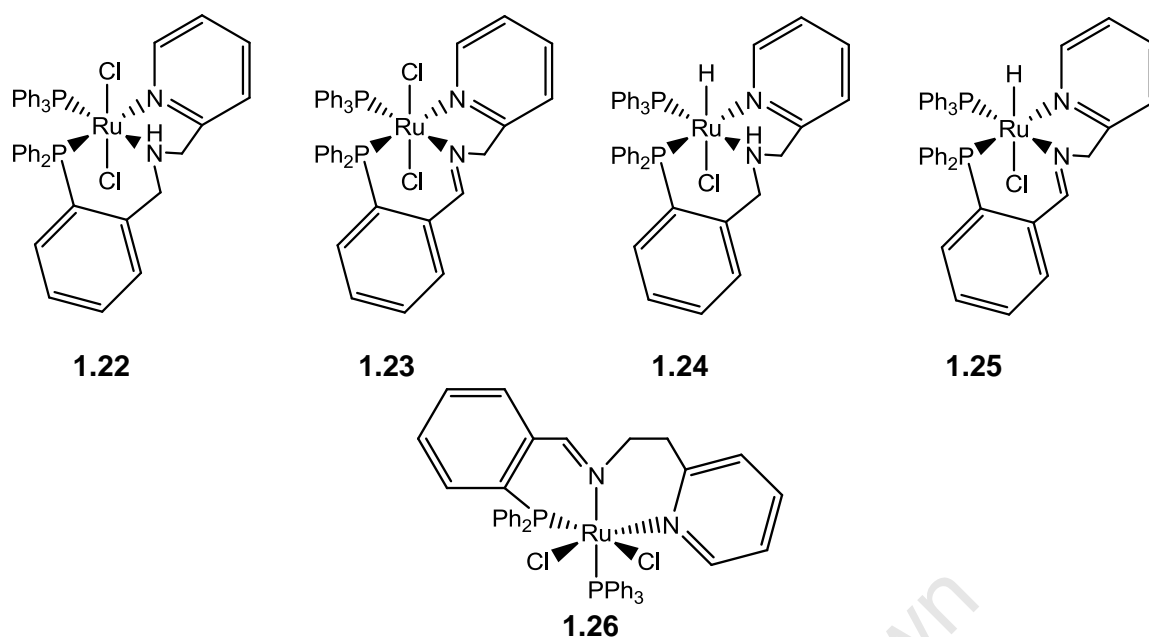
1.20

Vrieze and co-workers prepared palladium and platinum complexes of the type **1.21**, based on a multifunctional and hemilabile phosphorus-bis(nitrogen) ligand, which combined both imine and pyridyl moieties.²⁷ The ligand was found to coordinate in a terdentate fashion to group 10 metals, resulting in the formation of cationic complexes of the type $[M^{II}(PNN)(R)]Y$, where $M = Pd, Pt$; $R = \text{alkyl, acetyl or } \eta^1\text{-allyl}$ and $Y = Cl, CF_3SO_3$. Catalytic studies showed that the palladium complexes were highly active in allylic alkylation reactions.

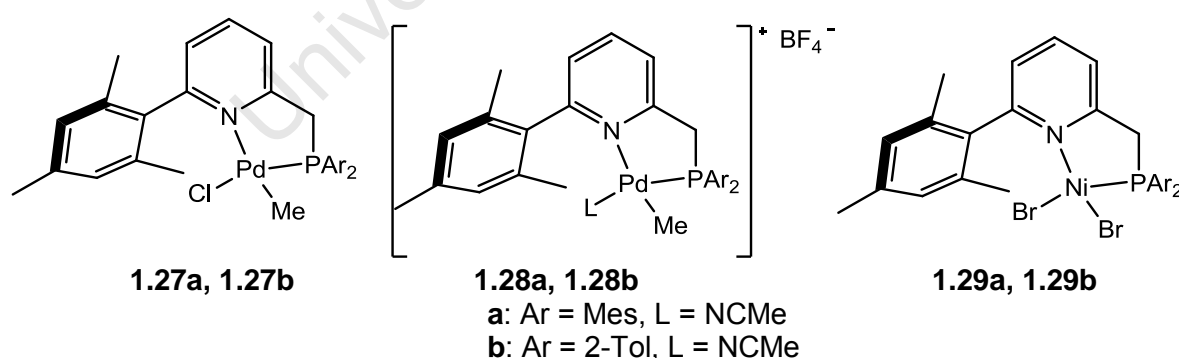


1.21

Del Zotto, Baratta and co-workers prepared similar ligands and tested their rhodium complexes **1.22** – **1.26** for activity in the transfer hydrogenation of ketones.^{15a} They reported that complex **1.26** catalyzes the quantitative reduction of acetophenone to 1-phenylethanol with high turnover frequencies. Replacing the amino complex with amino derivatives **1.23** and **1.24** resulted in slightly lower turnover frequencies, but these complexes still showed comparable activities to those reported by other groups.^{14a,28}



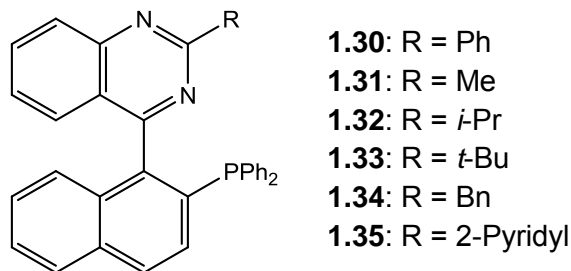
Liu and co-workers prepared bulky pyridylphosphine ligands (6-mesityl-2-((diaryl)methyl)pyridine) by the Suzuki coupling of mesitylboronic acid with 6-bromo-2-picoline followed by phosphinylation.²⁹ Palladium (**1.27**, **1.28**) and nickel (**1.29**) complexes were prepared by reaction of these ligands with $[\text{Pd}(\text{COD})(\text{Me})\text{Cl}]$ and $[\text{Ni}(\text{DME})\text{Br}]$. The cationic methylpalladium(II) complexes, **1.28**, performed poorly in catalytic ethylene polymerization and could only catalyze ethylene dimerization and trimerization.³⁰ The nickel complexes, on the other hand, were found to be efficient catalysts upon activation by MAO. The nickel complexes catalyzed the polymerization of ethylene when an Al/Ni ratio of 150 was used whereas dimerization and trimerization were observed when the Al/Ni ratio was increased to 500.²⁹



1.3.2 Quinazoline-Based Ligands

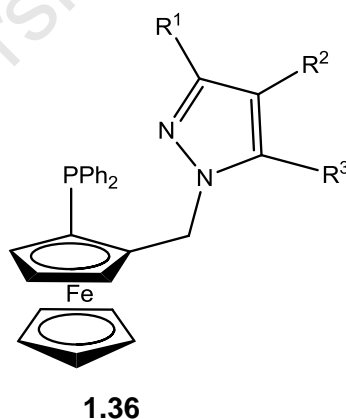
Guiry and co-workers prepared a series of quinazoline-based ligands, **1.30** – **1.35** and found them to be efficient ligands in palladium-catalyzed allylic alkylation reactions. Ligand **1.31**, in particular, showed excellent enantioselectivities, while more bulky ligands gave poorer results, indicating that the steric properties of substituents on the 2' position have a

significant influence on asymmetric induction conferred by the ligand on the reaction outcome.³¹



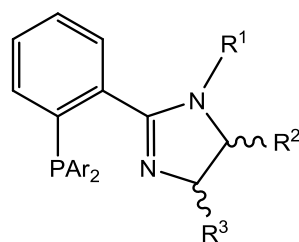
1.3.3 Pyrazole-Based Ligands

Pyrazole-containing ligands such as **1.36**, in which substituents on the phosphorus and the pyrazole ring can be easily varied allow for optimization of both steric and electronic properties of their metal complexes. This, in turn, influences their activity and selectivity in catalytic reactions. Rhodium complexes of ligand **1.36** have been used as catalysts in a number of asymmetric metal-catalyzed reactions such as hydrosilation of norbornene,³² and hydroboration of styrene.³³ In addition to the advantages brought on by the presence of different donor groups on the metal centre, having a ferrocenyl core, which plays the important role of a spectator, on the ligand backbone gives the ligand the coordinative mobility and serves as an electron reservoir needed for pendant/donating switches.^{34a} Hor and co-workers have also used this ligand backbone in their iminophosphine palladium complexes used in Suzuki-Miyaura coupling reactions.³⁴



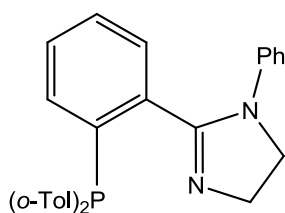
1.3.4 Imidazoline-Based Ligands

The synthesis of phosphinoimidazoline ligands such as **1.37** and their metal complexes has been reported by several groups.

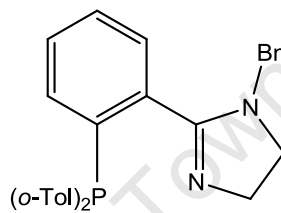


1.37

These ligands are analogous to phosphinooxazolines (see 1.3.4 below), but possess an additional nitrogen atom, which provides a further point for electronic tuning of the ligand. Pfaltz and co-workers prepared a number of these ligands and applied **1.38** and **1.39** in iridium-catalyzed hydrogenation of several alkenes.³⁵

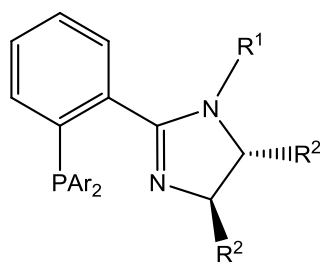


1.38



1.39

Busacca and co-workers reported the application of ligands such as **1.40** in the asymmetric intermolecular Heck reaction and made several interesting observations.³⁶ They observed that, 1) under the same reaction conditions, basic ligand ($R^1 = \text{Me}, \text{Bn}$) gave the opposite enantiomer to non-basic ligands (N-acylated); 2) ligands with alkyl substituents on the imidazolidine ring gave the enantiomer opposite to that obtained with aryl-substituted ligands; and 3) there was a direct correlation between phosphine electron density and enantioselectivity.¹¹

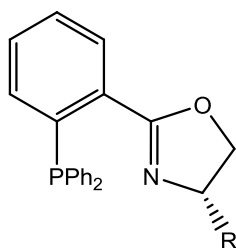


1.40: $R^1 = 2\text{-naphthyl}$
 $R^2 = \text{Ar} = 3,5\text{-F}_2\text{C}_6\text{H}_3$

1.3.5 Oxazoline- and Thiazoline-Based Ligands

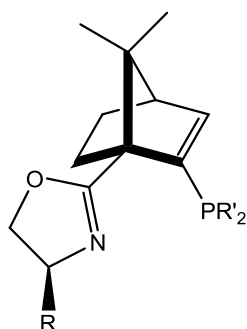
One of the most successful ligand classes is that of diphenylphosphinoaryloxazolines such as ligands **1.41** – **1.45**, which were independently reported by the groups of Pfaltz,³⁷ Helmchem,³⁸ and Williams³⁹ in 1993. Their palladium complexes were found to be highly efficient catalysts for allylic substitution of 1,3-diphenyl-2-propenyl acetate with a number of different nucleophiles. The ligands have also been successful in many other asymmetric

reactions with the best results coming from enantioselective Diel-Alder reactions, asymmetric intermolecular Heck reactions and the iridium-catalyzed hydrogenation of alkenes.⁴⁰



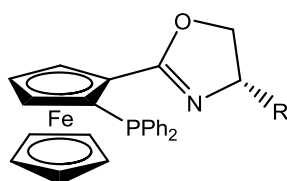
- 1.41:** R = Me
1.42: R = *i*-Pr
1.43: R = *t*-Bu
1.44: R = Ph
1.45: R = Bn

Gilbertson and co-workers developed a series of oxazoline-containing bicyclic phosphine ligands **1.46** – **1.49**, based on ketopinic acid. These ligands have been used in palladium-catalyzed processes such as the intermolecular Heck reaction, where ligand **1.46** gave excellent enantioselectivities with a number of substrates.⁴¹

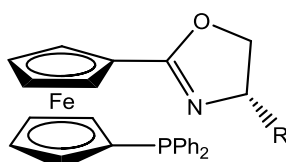


- 1.46:** R = *t*-Bu; R' = Ph
1.47: R = *i*-Pr; R' = Ph
1.48: R = Ph; R' = Ph
1.49: *t*-Bu; R' = Cy

The ferrocenyl backbone structural motif has also been used by several groups in the preparation of oxazoline-based iminophosphine ligands such as ligands **1.50** – **1.55** and **1.56** - **1.58**.



- 1.50:** R = Me
1.51: R = *i*-Pr
1.52: R = *t*-Bu
1.53: R = Ph
1.54: R = Bn
1.55: R = *s*-Bu

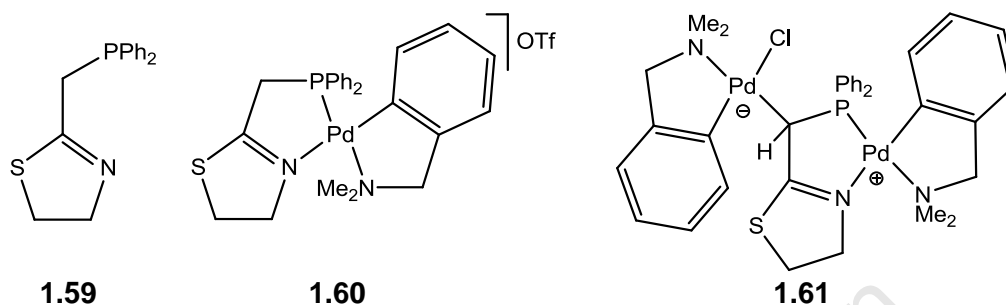


- 1.56:** R = Ph
1.57: R = *i*-Pr
1.58: R = *t*-Bu

Metal complexes formed with these ligands have been applied as catalysts in a wide range of metal-catalyzed reactions, including allylic substitutions, transfer hydrogenation of

ketones, hydrosilylation of acetophenone and intermolecular Heck reaction, among others.^{42,43}

Unlike oxazoline-based iminophosphine ligands, thiazoline derivatives are not as widely reported. Braunstein and co-workers reported the synthesis and structural characterization of diphenylphosphinothiazoline **1.59** and its palladium complexes **1.60** and **1.61**.⁴⁴



1.3.6 Oxazine-Based ligands

Oxazines are six-membered ring ligands related to the oxazolines. A two-dimensional schematic of these ligands (Figure 1.2) shows that the substituent on the 4-position of both rings should be closer to the metal centre in the oxazines than it is in the oxazoline ligands.¹¹

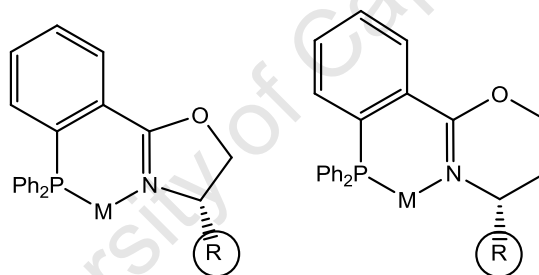
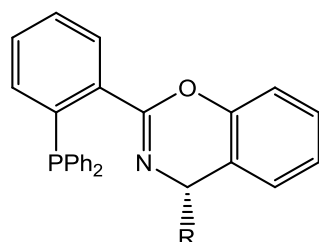


Figure 1.2: A two-dimensional schematic of oxazoline and oxazine ligands complexed to a metal centre, M.

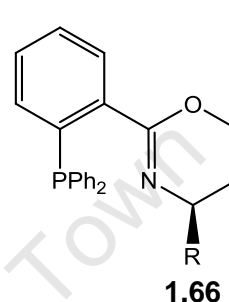
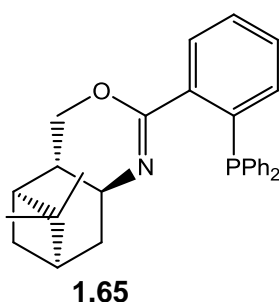
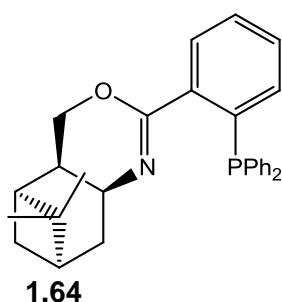
This substituent should, therefore, exert a larger steric influence on the outcome of the reaction for metal complexes bearing oxazine ligands than for those bearing oxazoline ligands. However, while the oxazoline ring is relatively flat, the oxazine ring can exist in both the chair- and boat- conformations, which may interfere with the efficient transfer of chirality to products. One strategy to reduce the number of possible conformations in the oxazine ring is fusing the oxazine ring to another ring. Kündig and co-workers used an aromatic ring to restrain the oxazine ring in ligands **1.62** and **1.63**. Complexes of these ligands were found to be good catalysts in a wide variety of reactions.^{11,45}



1.62: R = *t*-Bu

1.63: R = *i*-Pr

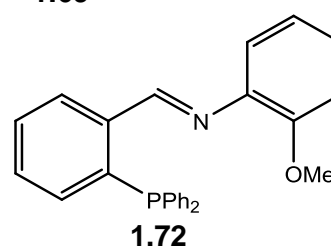
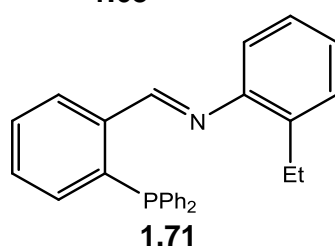
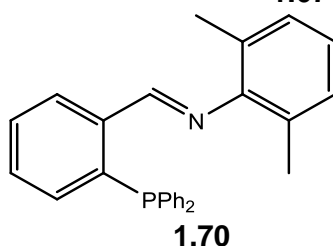
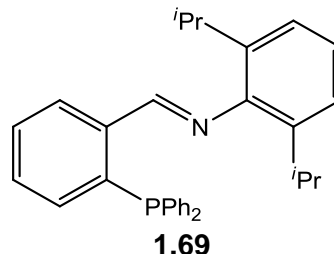
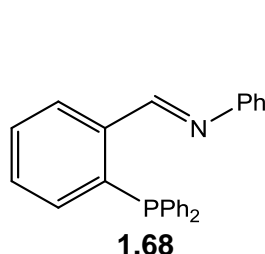
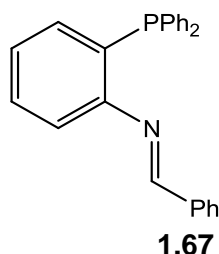
Ligands **1.64** and **1.65** reported by Evans and Brandt comprised of a β -pinene ring fused to the oxazine ring.⁴⁶

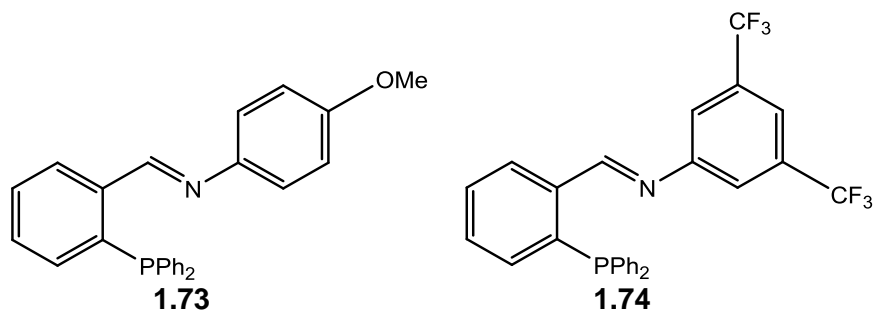


Their complexes were tested for activity in palladium-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate, where ligand **1.64** gave high yields and enantioselectivities over a wide range of reaction conditions.^{11,47} It was also observed that under similar reactions, ligand **1.64** performed better than phosphinooxazolines.⁴⁷ The palladium complex of the unfused oxazine **1.66** gave excellent enantioselectivity in the allylic alkylation of 1,3-diphenyl-2-propenyl acetate.⁴⁷

1.4 ACYCLIC IMINE N-DONOR LIGANDS

Most iminophosphine ligands in which the imine moiety is not included in a cyclic system are prepared by a condensation reaction between phosphine-bearing aldehydes/ketones such as diphenylphosphinobenzaldehyde and amines.



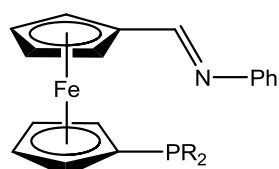


Neutral and cationic palladium methyl complexes of ligands **1.67** – **1.69** were reported by Liu and co-workers.⁴⁸ The complexes were used as catalysts for the copolymerization of ethylene and carbon monoxide. They observed that ligand **1.67**, which forms five-membered chelate rings with metal centres confers better activity toward carbonylation and copolymerization than ligands **1.68** and **1.69** which form six-membered chelate structures. Shirakawa and co-workers tested a palladium complex of ligand **1.68** for activity in the homocoupling of organostannanes using allyl acetate or air as an oxidant. Good to excellent conversions as well as isolated yields were obtained.^{15b}

Haynes and co-workers explored the reactivity of rhodium(I) carbonyl complexes of ligands **1.67** – **1.74** with methyl iodide.⁴⁹ They observed that all complexes react with methyl iodide to give rhodium(III) methyl or acetyl complexes. Results from this study indicate that migratory CO insertion is favoured for systems in which the N-aryl group of the ligand is bulky or contains an *o*-methoxy group. For reactions involving complexes with ortho-substituted ligands **1.69**, **1.71** and **1.72**, only the acetyl complexes were obtained as products. In contrast, reactions involving ligands with no ortho-substituents on the N-aryl group, equilibrium between methyl and acetyl complexes was obtained.

Hor and co-workers prepared ligands **1.75** – **1.82** and tested their palladium complexes as catalysts in the Suzuki-Miyaura coupling reactions.³⁴ The ligand system was chosen because the strong (phosphine) and weak (imine) donor sites are separated by the conformationally flexible ferrocenyl moiety. This motif would enable the weak donor group to undergo facile reversible coordination to the metal centre. Both donor sites also have variable substituents, allowing the introduction of different substituents (R, and R').

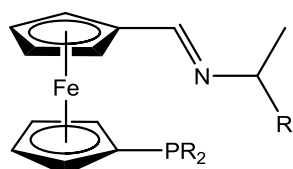
In addition, the redox-active Fe(II) in the ferrocenyl backbone provides an additional electronic buffer that allows the catalytic metal to maintain its catalytic activity at different redox stages. Therefore it is possible to systematically and independently alter the electronic and steric properties of both donor sites. The complexes were found to be effective with good to excellent conversions being obtained even when aryl chlorides were used as substrates, with complex **1.82** giving the best results.^{34b}



1.75: R = *t*-Bu

1.76: R = Cy

1.77: R = Ph



1.78: R = *t*-Bu; R' = Ph

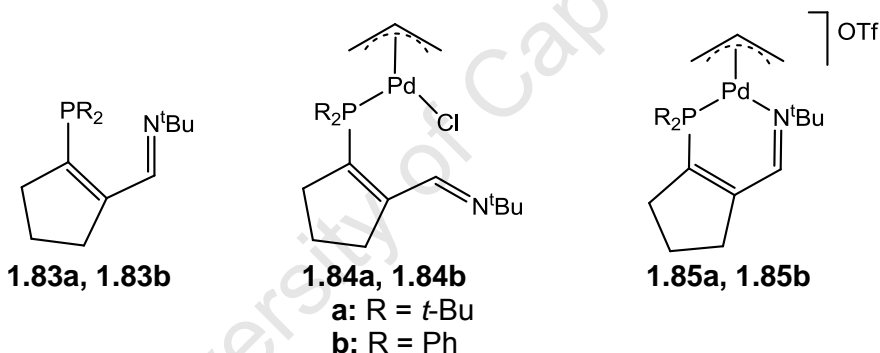
1.79: R = *t*-Bu; R' = *p*-Tolyl

1.80: R = *t*-Bu; R' = *p*-Fluorophenyl

1.81: R = *t*-Bu; R' = *m*-methoxyphenyl

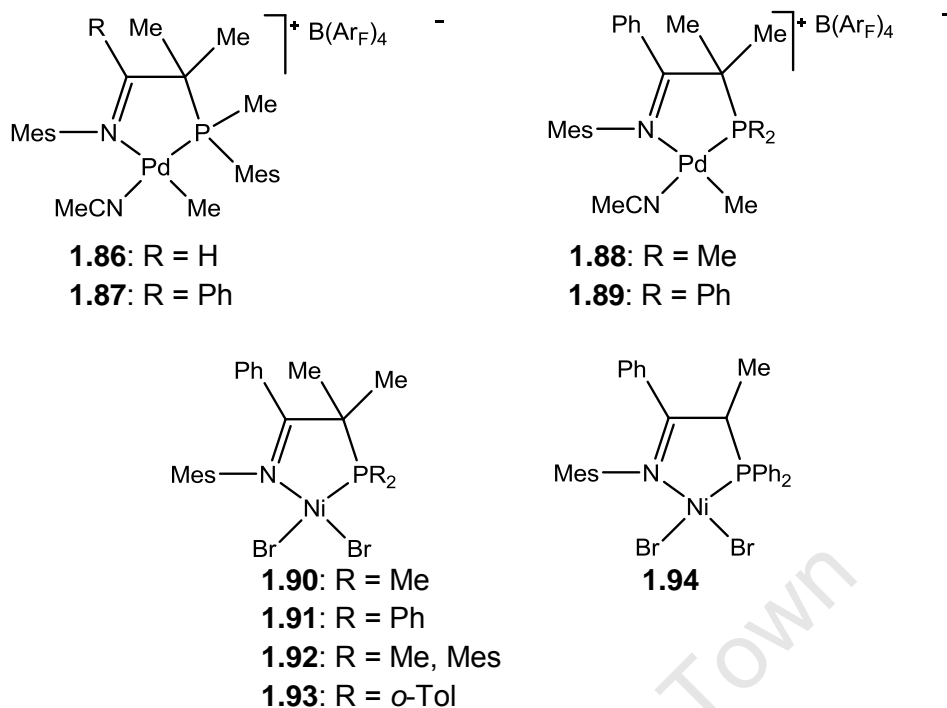
1.82: R = *t*-Bu; R' = naphthyl

The iminophosphine ligand **1.83**, incorporating a cyclopentenyl backbone was prepared by Schmidt and co-workers, who reported the use of its palladium complexes **1.84** and **1.85**.^{10,50} The cationic complexes, **1.85a** and **1.85b** showed excellent catalytic activity in the hydroamination of 3-methyl-1,2-butadiene with anilines. For complex **1.85a**, the reaction was found to be 100% atom-efficient and selective for the branched allylic amine products in high conversion at ambient temperature for non-halogenated substrates. For halogenated substrates, the hydroamination reaction was found to be efficient at 70 °C, with moderate yields. The reaction was also found to be selective for the branched product.



Complex **1.85a** was also found to catalyze the coupled hydroamination and aryl amino Claisen rearrangement reaction to produce substituted 2-allyl-anilines in a one-pot reaction. This two-step, one-pot reaction was found to work well for a wide range of substrates originally screened for the hydroamination reaction.

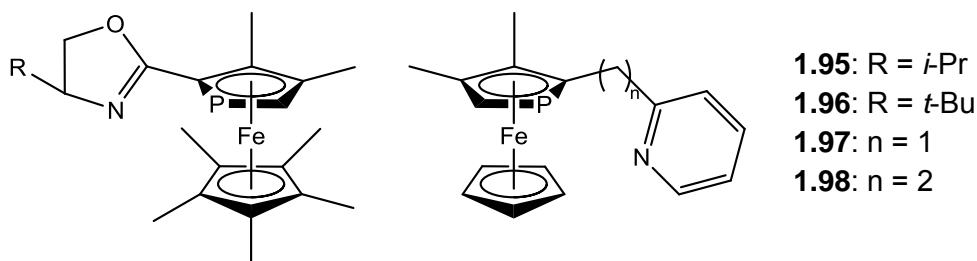
A number of palladium(II) (**1.86** – **1.89**) and nickel(II) (**1.90** – **1.94**) complexes based on bulky, non-enolizable iminophosphine ligands were reported by Daugulis and Brookhart.⁵¹ These complexes were tested for activity as ethylene polymerization catalysts and their activity was compared to that of corresponding α -diimine complexes previously reported by the same authors. The iminophosphine complexes showed better activity and improved temperature tolerance. The nickel complexes **1.90** – **1.93**, with *gem*-dimethyl substituent adjacent to the phosphine moiety displayed moderate activity and were found to produce substantially higher molecular weight polymers than analogous enolizable complexes.



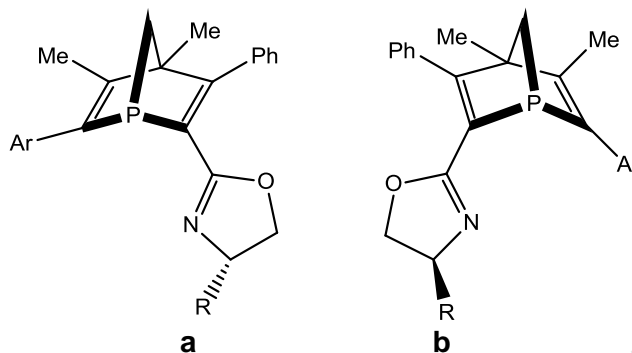
1.5 PHOSPHOLANE-BASED LIGANDS

There have been a number of reports on iminophosphine ligands bearing a stereogenic phosphorus atom incorporated in a cyclic structure. A class of these is the phosphoferrocenyl ligands, in which the phosphorus atom is part of the Cp ring. The ligands coordinate in a bidentate fashion, via the phosphorus and nitrogen atoms, to their metal centres. The rationale behind the design of this type of ligand is that once the metal centre coordinates, it will be in close proximity to the element of planar chirality of the ligand, allowing the transfer of chirality in asymmetric reactions. The phosphorus atom in these systems has the electronic character of an sp^2 -centre and is strongly π -accepting.¹¹

Fu *et al.*⁵² and Ganter *et al.*⁵³ reported the preparation of ligands **1.95** - **1.96**, and their application in palladium-catalyzed allylic alkylation of 1,3-diphenyl-2-propenyl acetate. While all the ligands tested showed activity, the best results were obtained when ligands **1.95** and **1.96**, bearing the oxazoline functionality were used. Excellent yields and better enantioselectivities were obtained with these ligands than with **1.97** and **1.98**.



Ligands **1.99** – **1.102** were synthesized and used in the palladium-catalyzed allylic alkylation and Heck cross coupling reactions by Gilbertson and co-workers.⁵⁴ Ligand **1.100a** was found to be an efficient ligand in the Heck reaction between 2,3-dihydrofuran and cyclohexenyl triflate. **1.99a** and **1.100a** gave excellent conversions and high enantioselectivities in the allylic alkylation of 1,3-diphenylallyl acetate.



1.99a, 1.99b: Ar = Ph, R = *i*-Pr

1.100a, 1.100b: Ar = Ph, R = *t*-Bu

1.101a, 1.101b: Ar = Phenanthryl, R = *i*-Pr

1.102a, 1.102b: Ar = Anthracyl, R = *i*-Pr

1.6 SUMMARY

The use of heterodonor, hemilabile ligands in synthesis and catalysis continues to be a rapidly growing area of research. Of the commonly used heterodonor ligands, those bearing phosphorus and nitrogen as their donor atoms have attracted a lot of attention due to the unique steric and electronic properties they confer to their metal complexes. In particular, iminophosphine ligands have found wide applicability in organometallic synthesis and homogenous catalysis. This brief review has highlighted the wide variety of structural motifs found in the design of iminophosphine ligands. In addition, attention has been paid to the broad range of catalytic processes in which metal complexes bearing iminophosphine ligands have been used as catalysts.

1.7 REFERENCES

1. Braunstein, P. and Naud, F., *Angew. Chem. Int. Ed.*, 2001, **40**, 680.
2. Grützmacher, H., *Angew. Chem. Int. Ed.*, 2008, **47**, 1814.
3. Jeffrey, J. C. and Rauchfuss, T. B., *Inorg. Chem.*, 1979, **18**, 2658.
4. Espinet, P. and Soulantica, K., *Coord. Chem. Rev.*, 1999, **193 – 195**, 499.
5. Bhattacharyya, P., Parr, P. B. J. and Slawin, A. M., *J. Chem. Soc., Dalton Trans.*, 1998, 3609.
6. Lindner, R., van den Bosch, B., Lutz, M., Reek, J. N. H. and van der Vlugt, *Organometallics*, 2011, **30**, 499.
7. Ni Dhubhnaill, O. M., Lennon, J. and Drew, M. G. B., *Dalton Trans.*, 2005, 3213.
8. (a) Davies, J. A. and Hartley, F. R., *Chem. Rev.*, 1979, **81**, 2658. (b) Lindner, E., Hausteiner, M., Mayer, H. A., Gierling, K., Fawzi, R., and Steinman, M., *Organometallics*, 1995, **14**, 2246. (c) Higgins, T. B. and Mirkin, C. A., *Inorg. Chim. Acta*, 1995, **240**, 347.
9. Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *J. Chem. Soc., Dalton, Trans.*, 2002, 1776.
10. (a) Shaffer, A. R. and Schmidt, J. A. R., *Organometallics*, 2008, **27**, 1259. (b) Shaffer, A. R. and Schmidt, A. R., *Organometallics*, 2009, **28**, 2494.
11. Guiry, P. J. and Saunders, C. P., *Adv. Synth. Catal.*, 2004, **346**, 497.
12. (a) Slawin, A. M. Z., Smith M. B. and Woollins J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 4575. (b) Bhattacharyya, P., Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Inorg. Chem.*, 1996, **35**, 3675. (c) Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 1283. (d) Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Polyhedron*, 1996, **15**, 1579.
13. Polosukhin, A. I., Bondarev, O. G., Korostylev, A. V., Hilgraf, R., Davankov, V. A. and Gavrillov, K. N., *Inorg. Chim. Acta.*, 2001, **323**, 55.
14. Crociani, L., Bandoli, G., Dolmella, A., Basato, M. and Corain, B., *Eur. J. Chem.*, 1998, 1811.
15. (a) Del Zotto, A., Baratta, W., Ballico M., Herdtweck, E. and Rigo, P., *Organometallics*, 2007, **26**, 5636. (b) Shirakawa, E., Nakao, Y., Murota, Y. and Hiyama, T., *J. Organomet. Chem.*, 2003, **670**, 132. (c) Crossetti, G. L., Filgueiras, C. A., Howie, R. A., Wardell, J. L. and Ziglo, C. M., *Acta Cryst.*, 2001, **C57**, 1279. (d) del Campo, O., Carbayo, A., Cuevas, J. V., Garcia-Herbaso, G. and Munoz, A., *Eur. J. Inorg. Chem.*, 2009, 2254. (e) Thibault, M-H., Lucier, B. E. G., Schurko, R. W. and Fontaine, F-G., *Dalton Trans.*, 2009, 7701.
16. Ghilardi, C.A., Midollini, S., Moneti, S., Orlandini, A. and Scapacci, G., *J. Chem. Soc., Dalton Trans.*, 1992, 3371.

17. Doherty, S., Knight, J. G., Scanlan, T. H., Elsegood, M. R. J. and Clegg, W., *J. Organomet. Chem.*, 2002, 650, 231.
18. Maclsaac, D. I., Geier, S. J., Vogel, C. M., Decken, A. and Westcott, S. A., *Inorg. Chim. Acta*, 2006, 359, 2771.
19. a) Christ, L. M., Zablocka, M., Spencer, S., Lavender, R., Lemaire, M. and Majoral, J. P., *J. Mol. Catal. A: Chem.*, 2006, 245, 210. b) Durry, W. J. III, Zimmermann, N., Keenan, M., Hayashi, M., Kaiser, S., Goddard, R. and Pfaltz, A., *Angew. Chem. Int. Ed.*, 2004, 43, 70. c) Crochet, P., Gimeno, J., Borge, J. and Garcia-Granda, S., *New J. Chem.*, 2003, 27, 414.
20. Casares, J. A., Espinet, P., Hernando, R., Iturbe, G., Villafane, F., Ellis, D. D. and Orpen, A. G., *Inorg. Chem.*, 1997, **36**, 44.
21. (a) Bonnet, M. C., Dahan, F., Ecke, A., Keim, W., Shulz, R. P. and Tkatchenko, I., *J. Chem. Soc. Chem. Commun.*, 1994, 615. (b) Ecke, A., Keim, W., Bonnet, M. C., Tkachenko, I. and Dahan, F., *Organometallics*, 1995, **15**, 5032. (c) Drent, E., Arnoldy, P. and Budzelaar, P. H. M., *J. Organomet. Chem.*, 1994, **475**, 57. (d) Drent, E., Arnoldy, P. and Budzelaar, P. H. M., *J. Organomet. Chem.*, 1993, **455**, 247.
22. Deeming, A. J., Rothwell, I. P., Hursthouse, M. B. and Malik, K. M. A., *J. Chem. Soc. Dalton Trans.*, 1980, 1974.
23. Mothes, E., Sentets, S., Luquin, M. A., Mathieu, R., Lugan, N. and Lavigne, G., *Organometallics*, 2008, **27**, 1193.
24. Alcock, N. W., Brown, J. M., Pearsons, M. and Woodward, S., *Tetrahedron: Asymmetry*, 1992, **3**, 17.
25. Flapper, J., Kooijman, H., Lutz, M., Spek, A. L., van Leeuwen, P. W. N. M., Elsevier, C. J. and Kamer, P. C. J., *Organometallics*, 2009, **28**, 1180.
26. Sirbu, D., Consiglio, G. and Gischig, S., *J. Organomet. Chem.*, 2006, **691**, 1143.
27. Rülke, R. E., Kaasjager, V. E., Wehman, P., Elsevier, C. J., van Leeuwen, P. V. N. M., Fraanje, J., Goubitz, K. and Spek, A. L., *Organometallics*, 1996, **15**, 3022.
28. Crochet, P., Gimeno, J., Garcia-Granda, S. and Borge, J., *Organometallics*, 2001, **20**, 4369.
29. Chen, H.-P., Liu, Y.-H., Peng, S.-M. and Liu, S.-T., *Organometallics*, 2003, **22**, 4839.
30. Chen, J. T., Liu, S.-T. and Zhao, K.-Q., *J. Chin. Chem. Soc.*, 2000, **47**, 279.
31. (a) Lacey, P. M., McDonell, C.M. and Guiry, P. J., *Tetrahedron Lett.*, 2000, **41**, 2475. (b) McCarthy, M., Goddard, R. and Guiry, P. J., *Tetrahedron: Asymmetry*, 1999, **10**, 2797.
32. Pioda, G. and Togni, A., *Tetrahedron: Asymmetry*, 1998, **9**, 3903.
33. (a) Schnyder, A., Hintermann, L. and Togni, A., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 391. (b) Schnyder, A., Tongi, A. and Wiesli, U., *Organometallics*, 1997, **16**, 225.

34. (a) Weng, Z., Teo, S. and Hor, T. S. A., *Acc. Chem. Res.*, 2007, **40**, 676. (b) Teo, S., Weng, Z. and Hor, T. S. A., *J. Organomet. Chem.*, 2011, **696**, 2928.
35. Menges, F., Neuburger, M. and Pfaltz, A., *Org. Lett.*, 2002, **4**, 4713.
36. Busacca, C. A., Grossbach, D., So, R. C., O'Brien, E. M and Spinelli, E. M., *Org. Lett.*, 2003, **5**, 595.
37. von Matt, P. and Pfaltz, A., *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 566.
38. Sprinz, J. and Helmchen, G., *Tetrahedron Lett.*, 1993, **34**, 1769.
39. Dawson, G. J., Frodt, C. G., Williams, J. M. J. and Coote, S. J., *Tetrahedron Lett.*, 1993, **34**, 3149.
40. (a) Helmchen, G. and Pfaltz, A., *Acc. Chem. Res.*, 2000, **33**, 336. (b) Pfaltz, A. *Chimia*, 2001, **55**, 708. (c) Hiroi, K. and Watanabe, K., *Tetrahedron: Asymmetry*, 2002, **13**, 1841.
41. Gilbertson, S. R. and Fu, Z., *Org. Lett.*, 2001, **3**, 161.
42. (a) Sammakia, T. and Latham, H. A., *J. Org. Chem.*, 1995, **60**, 6002. (b) Richards, C. J. and Locke, A. J., *Tetrahedron: Asymmetry*, 1998, **9**, 2377. (c) Zhang, W., Hirao, T. and Ikeda, I., *Tetrahedron Lett.*, 1996, **37**, 4545. (d) Malone, Y. M. and Guiry, P. J., *J. Organomet. Chem.*, 2000, **603**, 110. (e) Hennessy, A. J., Malone, Y. M. and Guiry, P. J., *Tetrahedron Lett.*, 1999, **40**, 9163. (f) Hennessy, A. J., Malone, Y. M. and Guiry, P. J., *Tetrahedron Lett.*, 1999, **41**, 2261. (g) Sammakia, T. and Strangeland, E. L., *J. Org. Chem.*, 1997, **62**, 6104.
43. (a) Nishibayashi, Y., Takei, I., Uemura, S. and Hidai, M., *Organometallics*, 1999, **18**, 2291. (b) Nishibayashi, Y., Segawa, K., Ohe, K. and Uemura, S., *Organometallics*, 1995, **14**, 5486. (c) Nishibayashi, Y., Segawa, K., Takada, H., Ohe, K. and Uemura, S., *Chem. Commun.*, 1996, **14**, 847. (d) Nishibayashi, Y., Takei, I., Uemura, S. and Hidai, M., *Organometallics*, 1998, **17**, 3420. (e) Takei, I., Nishibayashi, Y., Ishii, Y., Mizobe, I., Uemura, S. and Hidai, M., *Chem. Commun.*, 2001, 2360. (f) Zhang, W., Yoneda, Y., Kida, T., Nakatsuji, Y. and Ikeda, I., *Tetrahedron: Asymmetry*, 1998, **9**, 3373. (g) Park, J., Quan, Z., Lee, S., Ahn, K. H. and Cho, C. W., *J. Organomet. Chem.*, 1999, **584**, 140. (h) Deng, W. P., Hou, X. L., Dai, L. X., Yu, Y. H. and Xia, W., *Chem. Commun.*, 2000, 285. (i) Deng, W. P., You, S. L., Hou, X. L., Dai, L. X., Yu, Y. H., Xia, W. and Sun, J., *J. Am. Chem. Soc.*, 2001, **123**, 6508. (j) You, S. L., Hou, X. L., Dai, L. X., Yu, Y. H. and Xia, W., *J. Org. Chem.*, 2002, **67**, 4684. (k) Manoury, E., Fossey, J. S., Aït-Haddou, H., Daran, J. C. and Balavoine, G. G. A., *Organometallics*, 2000, **19**, 3736. (l) Deng, W. P., Hou, X. L., Dai, L. X. and Dong, X. W., *Chem. Commun.*, 2000, 1483.
44. Pattacini, R., Margraf, G., Messaoudi, A., Oberbeckmann-Winter, N. and Braunstein, P., *Inorg. Chem.*, 2008, **47**, 9886.
45. (a) Kündig, E. P. and Meier, P., *Helv. Chim. Acta*, 1999, **82**, 1360. (b) Pfaltz, A., Radkowski, A., Zimmermann, N. and Zehnder, M., *Helv. Chim. Acta*, 2000, **84**, 3233.

46. Evans, P. A. and Brandt, T. A., *Tetrahedron Lett.*, 1996, **37**, 9143.
47. Liu, S., Muller, J. F. K., Neuburger, M., Schaffner, S. and Zehnder, M., *Helv. Chim. Acta*, 2000, **83**, 1256.
48. Reddy, K. R., Tsai, W.-W., Surekha, K., Lee, G.-H., Peng, S.-M., Chen, J.-T. and Liu, S.-T., *J. Chem. Soc., Dalton Trans.*, 2002, 1776.
49. Best, J., Wilson, J. M., Adams, H., Gonsalvi, L., Peruzzini, M. and Hayes, A., *Organometallics*, 2007, **26**, 1960.
50. Beck, J. F. and Schmidt, J. A. R., *RSC Adv.*, 2012, **2**, 128.
51. Daugulis, O. and Brookhart, M., *Organometallics*, 2002, **21**, 5926.
52. Shintani, R., Lo, M. M. C. and Fu, G. C., *Org. Lett.*, 2000, **2**, 3695.
53. Ganter, C., Glinsbockel, C. and Ganter, B., *Eur. J. Chem.*, 1998, 1163.
54. Gilbertson, S. R., Genov, D. G. and Rheingold, A. L., *Org. Lett.*, 2000, **2**, 2885.

CHAPTER 2

REVIEW OF THE SYNTHESIS AND REACTIVITY OF PLATINACYCLOALKANES

2.1 INTRODUCTION

Metallacyclic compounds of the transition metals can be defined as ‘carbocyclic systems in which one or more carbon atoms have been substituted by a transition metal’.^{1,2} This class of compounds has become a subject of considerable research interest due to the important role they play in catalytic reactions³ such as alkene metathesis, isomerization of strained carbocyclic rings as well as oligomerization and polymerization of olefins.⁴ These compounds have been shown to be key intermediates in various catalytic reactions and their subsequent thermolysis or substitution reactions have been used to model catalytic cycles.⁵

The chromium-based catalyst systems developed by Sasol in recent years for the selective trimerization and tetramerization of ethylene to 1-hexene and 1-octene, respectively, is a prime example of reactions that involve metallacycloalkanes as key intermediates. Their high selectivity for α -olefins has led to increased interest in the mechanism of these systems. Ethylene labeling experiments have revealed that these reactions, often catalyzed by chromium catalysts, proceed *via* metallacycloalkanes as key intermediates.^{5,6} A similar metallacyclic pathway, supported by computational studies, has also been proposed for some homogeneous titanium and tantalum catalysts for ethylene oligomerization.^{7,8}

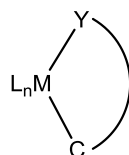
Many other transition metal catalyzed processes such as the palladium-catalyzed intramolecular Stille reaction, coupling reactions that proceed via C-H activation,⁹ as well as dimerization and telomerization reactions of 1,3-butadienes¹⁰ involve metallacycloalkanes as key intermediates. One of the interesting classes of reactions that proceed via palladacyclic intermediates is the “Heck-type” reactions, where the final step in the reaction, the *syn*- β -hydrogen elimination step is inhibited due to lack of suitable β -hydrogen atoms.⁹

2.2 SCOPE

This review focuses on three main areas of interest. The first is the different synthetic methods used for the preparation of platinacyclic complexes of small to medium ring sizes. The merits and drawbacks of each method are presented. The second area deals with the reactivity of platinacycloalkanes, with specific focus on decomposition and insertion reactions of these complexes. The final section deals with the subject of ethylene

oligomerization reactions that involve metallacycloalkanes as key intermediates. This section is not restricted to processes that involve platinacycles. Early transition metal-based catalysts that are proposed to employ metallacycloalkanes as key intermediates are covered in this section as well.

For the purposes of this review, the definition of metallacycloalkanes is limited to those complexes in which the metal centre is bonded to two carbon atoms with σ M-C bonds in a cyclic system, and therefore excludes complexes formed by chelating ligands such as diphosphines and diimines in which the metal centre is bonded to heteroatoms.¹¹ Furthermore, this review only covers complexes in which the metallacyclic ring consists of the metal centre and carbon atoms. Therefore complexes of the type shown in Figure 2.1, where heteroatoms are incorporated into the metallacyclic ring are not discussed.



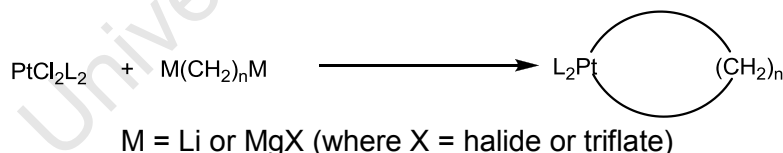
Y = Heteroatom

Figure 2.1: Metallacyclic complexes incorporating a heteroatom.

2.3 SYNTHESIS OF SMALL AND MEDIUM PLATINACYCLES

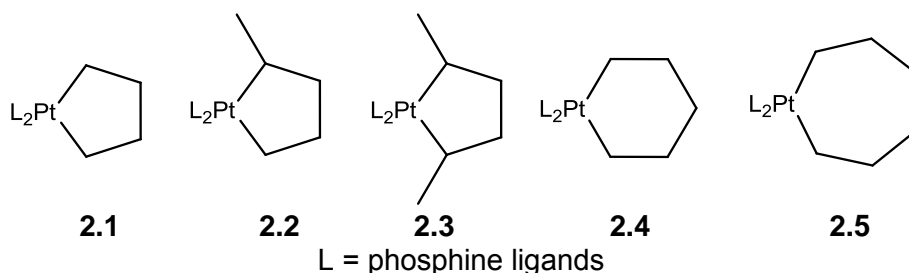
Several methods have been reported for the preparation of platinacycles. The main synthetic routes include transmetallation, cyclometallation, insertion into C-C bonds and the oxidative coupling of unsaturated molecules.^{2,4a,11}

2.3.1 Transmetallation



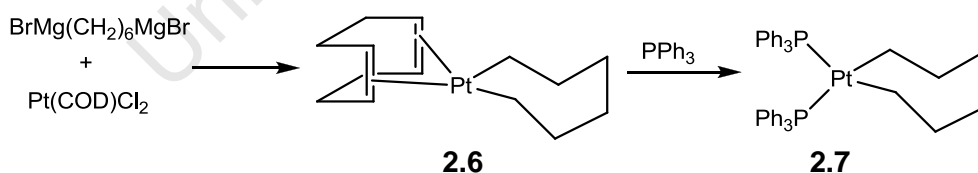
Scheme 2.1: Preparation of platinacycloalkanes *via* transmetallation.

The use of dilithio and di-Grignard reagents (Scheme 2.1) offers a convenient route to metallacycloalkanes for metals throughout the transition series.^{4a} Although in principle this procedure can be used for the preparation of metallacycles of any ring size, it is most often used in the preparation of metallacyclopentanes.^{2,11} One of the earliest examples of such a reaction for platinum complexes was reported in 1958 by Chatt and Shaw, who reported the preparation of the platinacyclohexane $[\text{Pt}(\text{PPh}_3)_2(\text{C}_5\text{H}_{10})]$ *via* the treatment of $[\text{cis-Pt}(\text{PPh}_3)_2\text{Cl}_2]$ with 1,5-dilithiopentane.¹² In a series of mechanistic studies on the decomposition of platinacycloalkanes in the 1970s, Whitesides^{13,14} and Grubbs¹⁵ reported the synthesis of a series of platinacycloalkanes **2.1 – 2.5**.



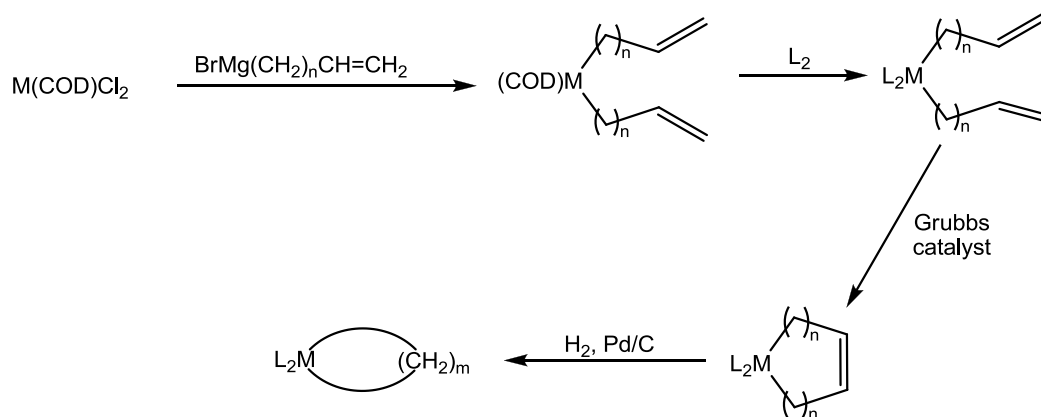
Whitesides prepared the complexes by reaction of (1,5-cyclooctadiene)dichloroplatinum(II) with the appropriate di-Grignard reagents followed by the displacement of the labile cyclooctadienyl ligand by tertiary phosphine ligands. Grubbs prepared the complexes by treatment of *cis*-bis(triphenylphosphine)dichloroplatinum(II) with one equivalent of the appropriate dilithio reagents. Platinacyclopentanes such as **2.2** and **2.3**, bearing methyl groups on the β -carbons were also prepared using this synthetic method.^{14,16}

The use of di-Grignard alkylating reagents in the synthesis of platinacycloalkanes has two major drawbacks. Firstly, the direct reaction of *cis*-dichlorobis(triphenylphosphine)platinum(II) with the di-Grignard reagents is reported to be an unsatisfactory method for the preparation of platinacycloalkanes as it yields a mixture of products containing large quantities of monoalkylated Pt(II) complexes.¹⁴ Secondly, for medium and large ring platinacycloalkanes, the yields obtained using this route are poor. The platinacycloheptane **2.7** was synthesized in 3% yield by the reaction of the appropriate di-Grignard with [Pt(COD)Cl₂] followed by ligand displacement with triphenylphosphine.¹³ The low yields observed could be due to the lower thermal stability of medium to large metallacycles compared to their small ring size counterparts,² leading to rapid decomposition as well as formation of side products such as monoalkylated and oligomeric species.



Due to the low yields obtained for the preparation of medium and large ring platinacycloalkanes *via* the dilithio and di-Grignard routes, alternative methods for the synthesis of these complexes have had to be devised. Moss and co-workers reported a synthetic route that involves the treatment of [M(COD)Cl₂] with two equivalents of 1-alkenyl Grignard reagents to form bisalkenyl metal complexes. Displacement of the labile COD ligand with phosphine ligands gave bisalkenyl metal complexes stable enough to undergo the ring closing metathesis reaction. Ring closing metathesis of the *bis*-alkenyl complexes using Grubbs catalysts yields metallacycloalkenes which can then be hydrogenated with

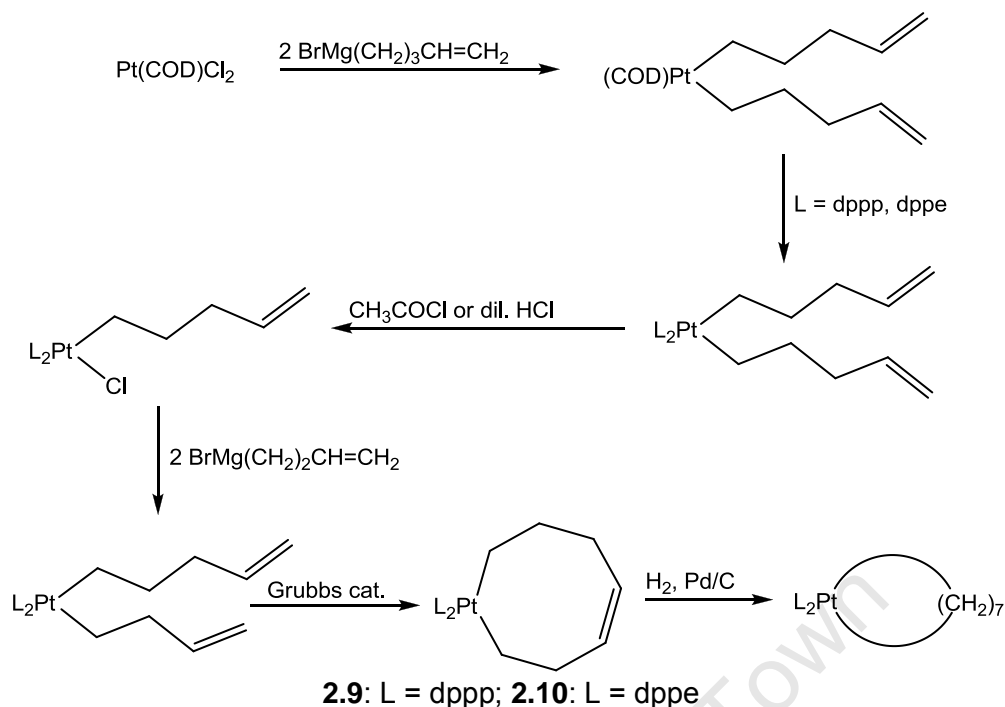
molecular hydrogen using Pd/C as the catalyst. This route proved successful for the preparation of medium and large ring metallacycles of both platinum^{17,18} and palladium¹⁹ (Scheme 2.2).



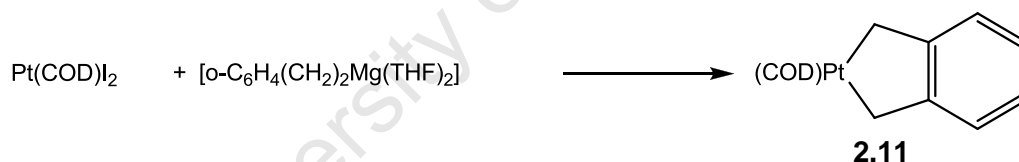
Scheme 2.2: Preparation of metallacycloalkanes via bis(alkenyl) intermediates.

Using this route, Moss and co-workers prepared platinacycloalkanes ranging in size from 7-membered to 13-membered rings in moderate to good yields.^{17,18,20} A slight modification of this bisalkenyl route provides access to even larger metallacycloalkanes. In this method, cross metathesis of the bisalkenyl complexes with dienes such as 1,7-octadiene and 1,5-hexadiene, followed by hydrogenation, yields platinacycloalkanes with up to 21-membered rings.²⁰ Preparation of substituted platinacycloalkanes was also achieved by the cross metathesis of the bisalkenyl platinum complexes with unsaturated molecules such as diphenylacetylene, followed by hydrogenation.²⁰

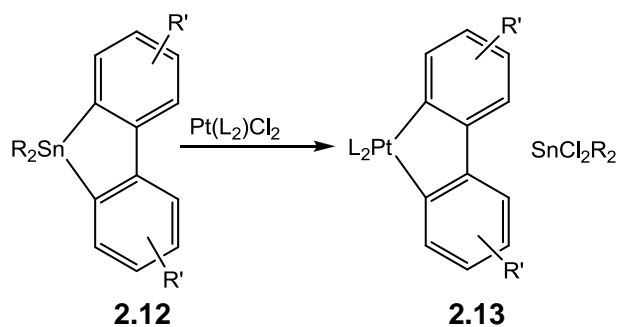
However, because the platinacycloalkanes prepared by the bisalkenyl route are derived from complexes with two equal length alkenyl groups, only metallacycloalkanes with odd-numbered rings can be prepared. To circumvent this, a modified metal bisalkenyl route was reported by Moss and co-workers.²¹ In this route, a bis-1-pentenyl platinum complex was prepared as previously reported. Careful reaction of this complex with acetyl chloride or a dilute solution of HCl in diethyl ether yielded a monopentenyl platinum complex that was then reacted with one equivalent of 1-butenyl Grignard, giving a bisalkenyl complex with alkenyl chains of different lengths. Ring closing metathesis of this complex yielded platinacyclooctenes, which, upon hydrogenation yielded the first reported platinacyclooctanes **2.9** and **2.10**.²¹



Other platinacycles that have been prepared using the transmetalation reaction include some unsaturated platinacycles such as benzo[c]metallacyclopentenes (*o*-xylene complexes), platinacyclopentadienes and dibenzoplatinacyclopentadienes.¹¹ Lappert and co-workers reported the synthesis of several *o*-xylene complexes of different transition metals including the platinacyclic complex **2.11**.²²

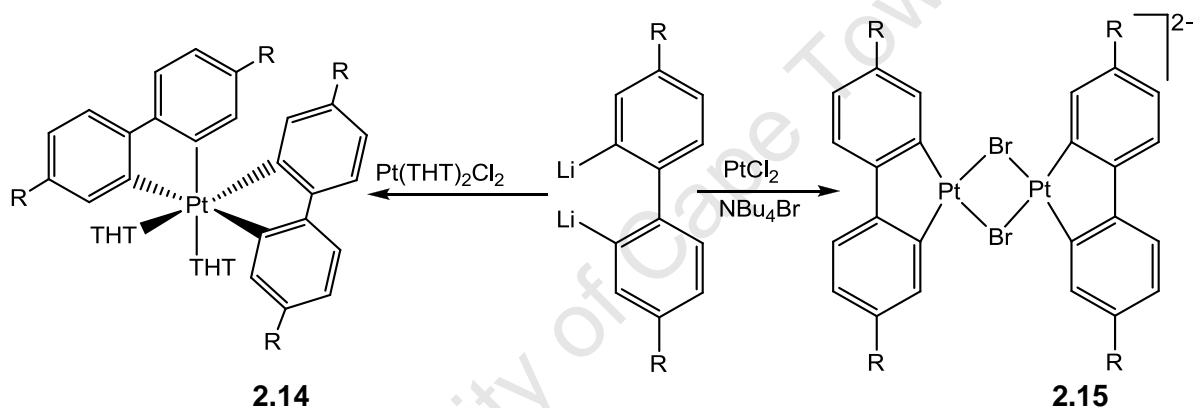


While synthesis of tetraphenyl substituted nickel metallacyclopentadiene using 1,2-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene has been reported by several researchers,²³ the use of di-Grignard and dilithio reagents for the preparation of similar mononuclear platinum complexes as well as biphenyl substituted platinum complexes has only met with limited success.²⁴ The research groups of Vicente²⁵ and Brune²⁶ prepared these biphenyl platinacyclic complexes by employing the use of the stannole reagent **2.12** and this route has allowed the synthesis of substituted dibenzoplatinacyclopentadiene **2.13** in yields of up to 60%.

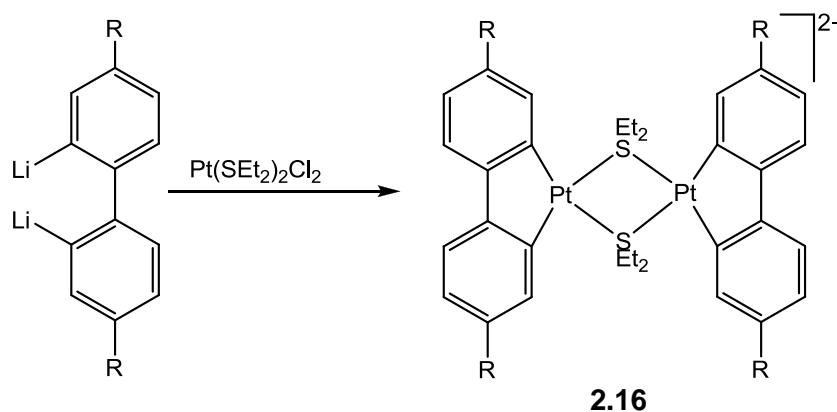


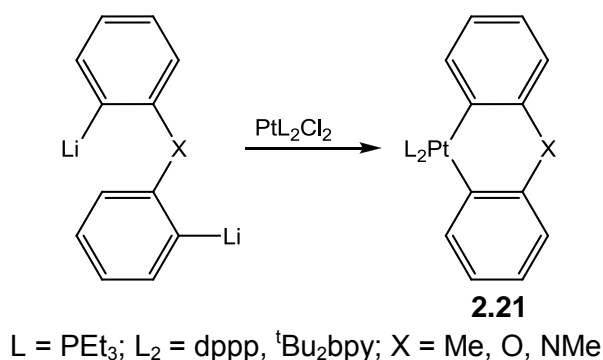
$\text{L}_2 = \text{COD}, \text{ nbd}; \text{ R} = \text{Pr}, \text{ Bu}; \text{ R}' = \text{CF}_3, \text{ MeO}, \text{ }^t\text{Bu}$ (substitution pattern 3,3' or 4,4')

Displacement of the olefin ligands in these complexes with other donor ligands such as bipy, bipym or PPh_3 offered easy access to other derivatives of these complexes.^{25,27} Interestingly, the reaction of $\text{Pt}(\text{THT})_2\text{Cl}_2$ with 2,2'-dilithiobiphenyl gave the Pt(IV) metallacyclic complex **2.14**,²⁸ while a similar reaction using PtCl_2 with excess 2,2'-dilithiobiphenyl gave the bromide-bridged binuclear complex **2.15**.²⁹



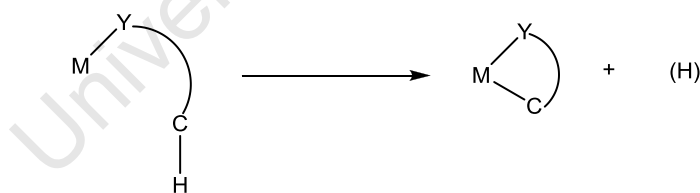
A complex similar to **2.15** was prepared by the reaction of 2,2'-dilithiobiphenyl with *cis*- $[\text{PtCl}_2(\text{SEt}_2)_2]$ at -10°C in diethyl ether to give complex **2.16** with bridging sulphur ligands.³⁰ Rillema³¹ and von Zelewsky³² also reported the preparation of other sulphur-bridged binuclear platinacycles using 2,2'-dilithiobiphenyl in their studies of photophysical properties of inorganic materials that can potentially behave as energy- or electron-transfer photocatalysts.





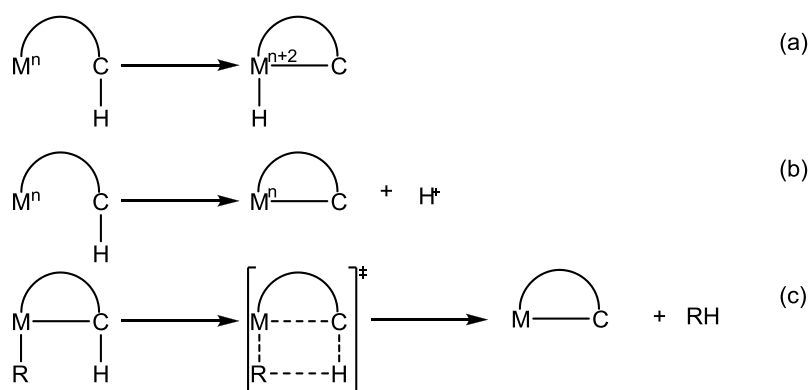
2.3.2 Cyclometallation

Since the first report of a cyclopalladation reaction by Cope and Siekman,⁴² there has been growing interest in the chemistry of cyclometallated compounds of Pd(II) and Pt(II).^{43,44} These complexes find numerous applications in organic synthesis,⁴⁵ metallomesogens,⁴⁶ as well as exhibiting remarkable photophysical properties.⁴⁷ The chemistry of cyclometallated complexes has thus become one of the most advanced areas of modern organometallic chemistry and several reviews have been written on the subject.⁴⁸ The complexes are formed by the intramolecular C-H activation, or cyclometallation reaction as shown in Equation 2.1. The development of methods to selectively activate and functionalize hydrocarbon C-H bonds is considered one of the ultimate goals in organometallic chemistry. Since the initial discovery by Shilov and co-workers of the catalytic functionalization of methane by aqueous Pt(II) chloride salts, efforts to develop alternative Pt-based systems for the activation and functionalization of C-H bonds have been widely pursued.⁴⁹

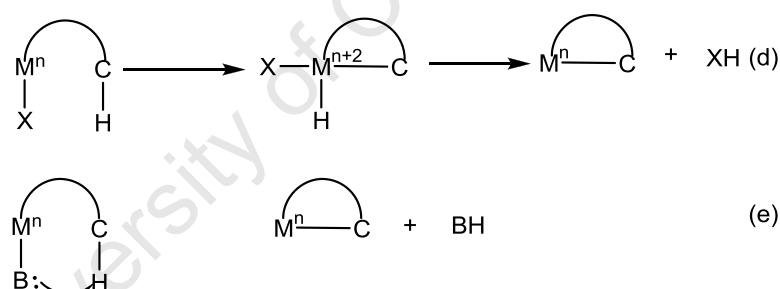


Equation 2.1: Metallacycloalkane formation via C-H activation.

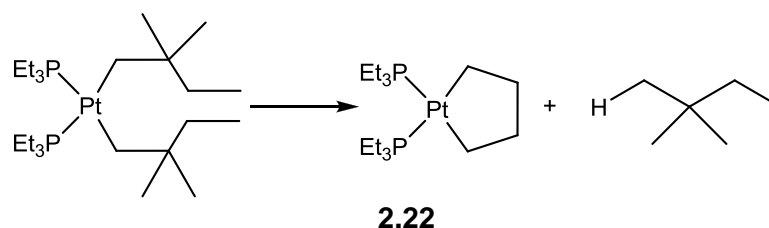
For most of the compounds prepared by this method, Y is a two electron donor heteroatom.^{48,50,51} However, for metal alkyl complexes, where Y is a -CR₂- group, this route provides access to metallacycloalkanes.¹¹ From a mechanistic point of view, the cyclometallation reaction can be classified into three categories: (a) oxidative addition, (b) electrophilic substitution, and (c) concerted or multicentered pathway as shown in Equation 2.2.

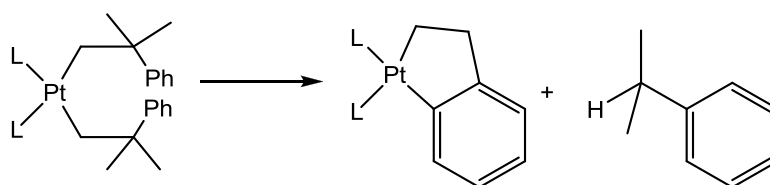

Equation 2.2: Cyclometallation reaction.

For group 10 transition metals, there is very little experimental evidence reported in the literature supporting the concerted pathway.⁵² However, considerable effort has been put into studies trying to distinguish between the oxidative addition and electrophilic substitution pathways. Although this distinction may appear to be straightforward, for the group 10 M(II) systems, both pathways give the same products. The metal hydrides of the type shown in pathway d readily undergo reductive elimination and pathway e needs the assistance of a base that may enter the coordination sphere of the metal centre. Consequently, the overall results of the two mechanisms end up being very similar (Equation 2.3).¹¹

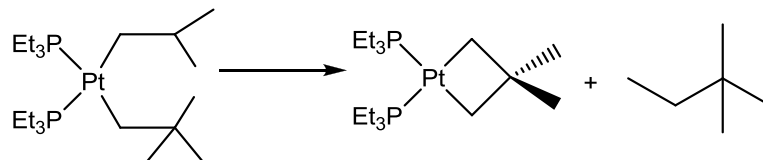

Equation 2.3: Base-assisted cyclometallation.

Cyclometallation has provided a synthetic route for the preparation of several platinacycles. The thermal rearrangement of platinum dialkyl complexes that lack β -hydrogen atoms leads to the formation of platinacycles **2.22** – **2.24** with accompanying hydrocarbons.⁵³⁻⁵⁵ This route mostly produces platinacyclobutanes and platinacyclopentanes, although the formation of platinacyclohexanes has been reported.⁵³ Whitesides and Young carried out mechanistic studies on the formation of the platinacyclobutane **2.24**⁵³ and the platinacyclopentane **2.23**.⁵⁴



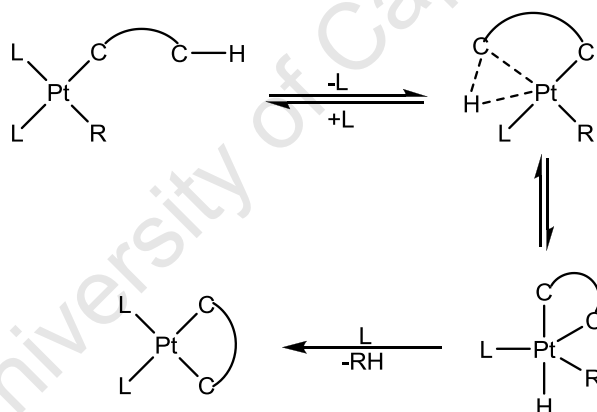


2.23



2.24

These kinetic studies revealed that the C-H activation reaction follows first order kinetics and the experimental evidence obtained is in agreement with the mechanism depicted in Equation 2.4.¹¹ Measurement of the rate of thermolysis for the complexes containing deuterated alkyl (neopentyl and neophenyl) chains indicated that either oxidative addition at the C-H bond or reductive elimination of R-H takes place as the rate determining step. Interestingly, the photochemical cyclometallation of the complex $[\text{Pt}(\text{dppe})(\text{CH}_2\text{CMe}_2\text{Ph})_2]$ takes place *via* a radical pathway involving Pt-C homolysis and H-abstraction by the resulting neophyl radical.⁵⁶

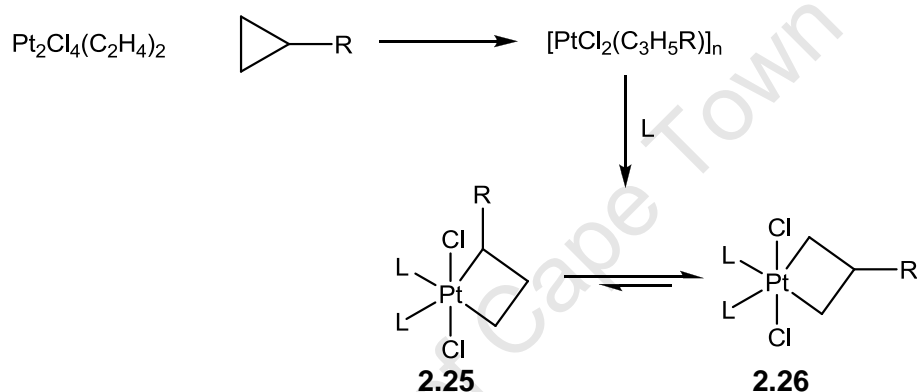


Equation 2.4: Mechanism of cycloplatination via C-H activation.

The thermolysis of bis(2,2-dimethyl)-alkyl complexes of platinum with alkyl chains of differing lengths seems to proceed via the mechanism outlined in Equation 2.4 and yields mixtures of platinacycles of varying ring sizes.⁵³ From the experimental evidence obtained from isotopic labeling experiments, the following conclusions can be drawn: (1) as expected, ring strain increases in the order 5-membered > 6-membered > 4-membered ring, and (2) the strain energy difference between platinacyclobutanes and platinacyclopentanes is considerably smaller than that between cyclobutanes and cyclopentanes.¹¹

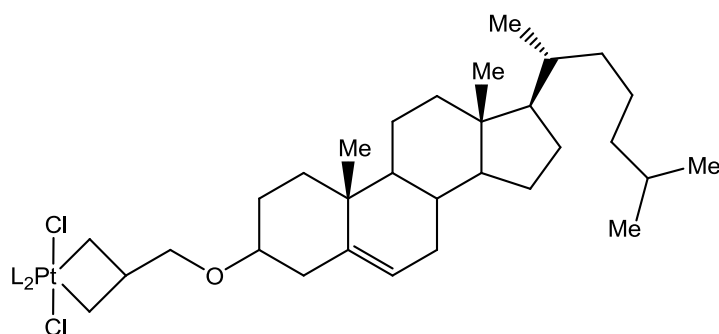
2.3.3 Insertion into C-C Bonds

Carbocyclic compounds can oxidatively add to transition metal centres to form metallacycles. The first metallacyclic compound reported is an oligomeric complex which was prepared by the treatment of hexachloroplatinic acid with cyclopropane in acetic anhydride to give a compound of formula $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_n$.⁵⁷ The structure was later shown to be a chloride bridged tetramer, with the structure analogous to Pt(IV) alkyls, in which the metal centre had inserted into the cyclopropane ring. Subsequent research has shown that this synthetic method is useful for a small number of transition metals and many platinacycles have been prepared by the reaction of platinum compounds with cyclopropanes. A more general route employs the treatment of Zeise's dimer with the relevant substituted cyclopropane.^{4a,11}

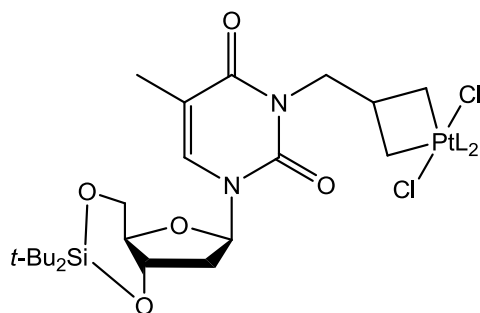


Both mono- and dialkylated cyclopropane derivatives react with Zeise's dimer to produce substituted polymeric platinacyclobutanes, which can then be reacted with various donor ligands to give soluble mononuclear species.¹¹ Although 2-substituted metallacycles are usually obtained from monoalkylated cyclopropanes, a mixture of the 1- and 2- isomers may form from acylcyclopropanes, due to the so-called Pudephatt rearrangement.^{11,58,59} The platinum centre acts as an electrophile in the process, and therefore electron withdrawing substituents deactivate the cyclopropane ring.^{11,60} Pt(0) compounds react with cyclopropane derivatives bearing electron withdrawing groups like 1,2,2,2-tetracyanopropane to give divalent platinacyclobutanes.¹¹ In these reactions, the metal centre inserts into the C-C bond bearing the electron withdrawing substituents.^{4a}

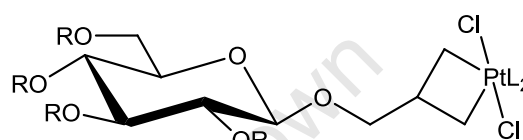
Hoberg and Stocker recently used this strategy to synthesize platinacyclobutanes **2.27** – **2.29**, bearing biomolecules such as cholesterol, nucleosides and carbohydrates as cis-platin prodrugs.⁶¹



2.27

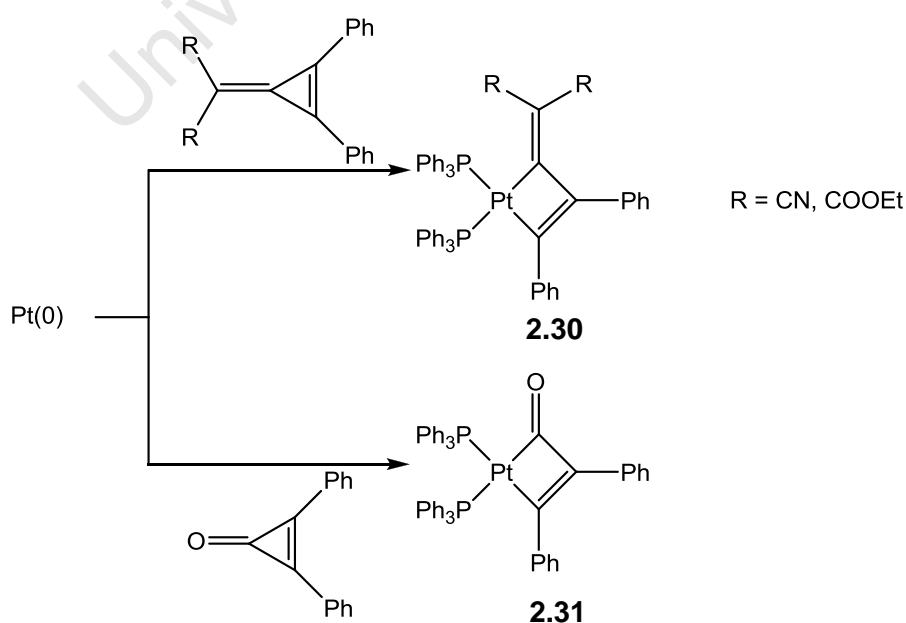


2.28

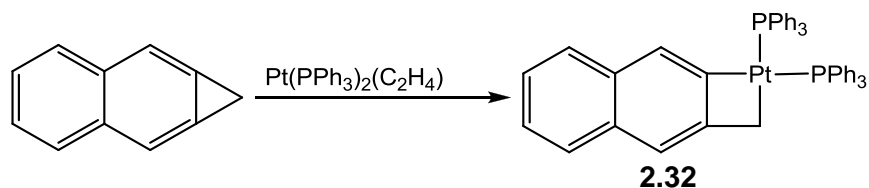


2.29

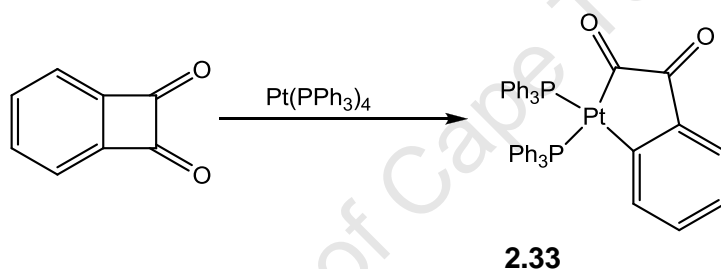
Complexes **30** and **31** were prepared by the reaction of substituted cyclopropenes with Pt(0) precursors such as $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ and $[\text{Pt}(\text{PPh}_3)_4]$.^{62,63} The driving force in these formal insertion reactions seems to be the presence of a partial positive charge on the carbon atoms rather than the drive to relieve strain in the small ring.⁶² Platinum (0) complexes react in a similar fashion with diphenylcyclopropenone⁶⁴ and cyclobutenedione⁶⁵ derivatives. For the reaction of the cyclobutenedione, a stable metal olefin intermediate was isolated and characterized.⁶⁶ A similar platinacyclobutene complex was recently prepared by Kakiuchi and co-workers by the reaction of $[\text{Pt}(\text{PPh}_3)_4]$ with polyalkynes.⁶⁷



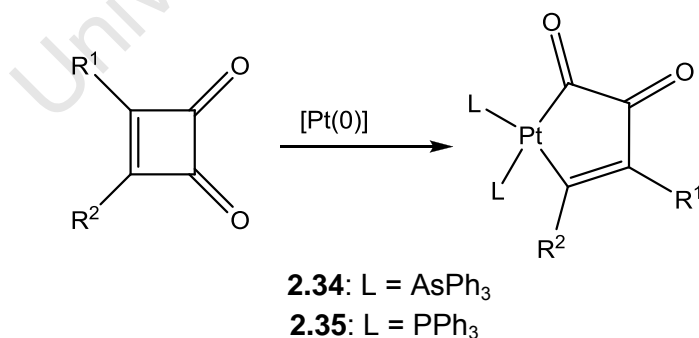
Cyclopropabenzene and cyclopropa[b]naphthalene also react with M(0) compounds of the Ni group to give M(II) metallacycles. Synthesis of the platinacyclobutane **2.32** from the reaction of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ and cyclopropa[b]naphthalene was reported by Stang.⁶⁸



Although the C-C bond cleavage of carbocyclic rings larger than cyclopropanes and cyclopropenes is less common, a number of examples of insertion into C-C bonds of cyclobutene derivatives have been reported. The reaction of $[\text{Pt}(\text{PPh}_3)_4]$ and 1,2-benzocyclobutadienequinone, in which the $\text{Pt}(\text{PPh}_3)_2$ unit inserts into the phenyl-carbon bond of the cyclic dione to give 1,2-platinacyclopentenediones was reported by Kemmitt and co-workers.⁶⁹

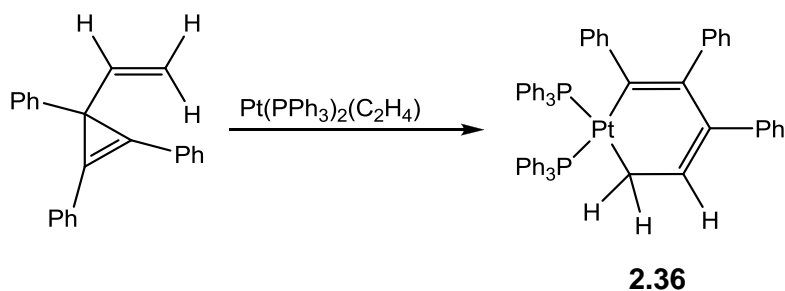


They also reported a similar reaction in which substituted cyclobutenediones and $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ react to give 1,2-platinacyclopentenediones **2.34** and **2.35**.⁷⁰ An interesting feature of this reaction is its regioselectivity. The formation of the 1,2-platinacyclopentenedione is preferred over the formation of other possible products.

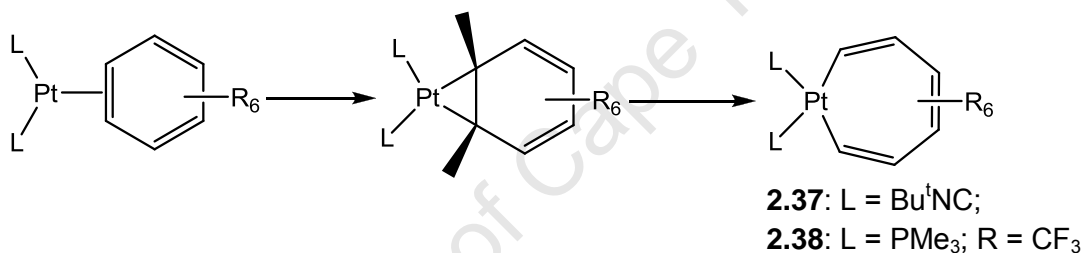


Rheingold and co-workers reported the synthesis of the platinacyclohexa-1,2-diene **2.36**, which they prepared by the reaction of 1,2,3-triphenyl-3-vinylcycloprop-1-ene and $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$. The X-ray crystal structure of the complex shows that the metallacycle contains localized single and double bonds between the carbon atoms, and shows no evidence of interaction between the olefinic bonds and the metal centre. The complex is formed, presumably, by the initial coordination of the olefinic vinylcyclopropene to the low

valent metal centre, followed by the rapid cleavage of the cyclopropene C-C bond, to give the platinacyclohexadiene in a net oxidative addition reaction.⁷¹



Stone and co-workers reported the synthesis of platinacycloheptatrienes **2.37** and **2.38** from the reaction of hexakis(trifluoromethyl)benzene.⁷² The complexes are presumed to form *via* the formation of an initial η^2 -complex, which rearranges with C-C bond cleavage to form the observed product. The ring opening reaction is highly dependent on the nature of the ligands used on the platinum precursor, as the reaction does not proceed when PEt_3 is the coordinating ligand.

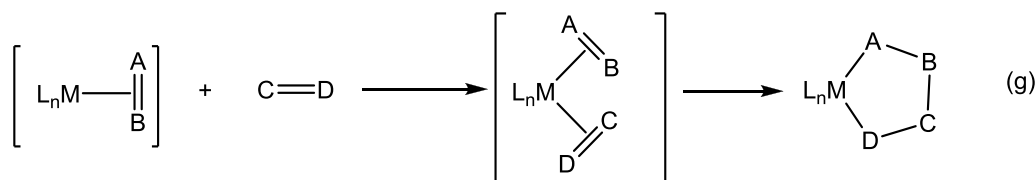
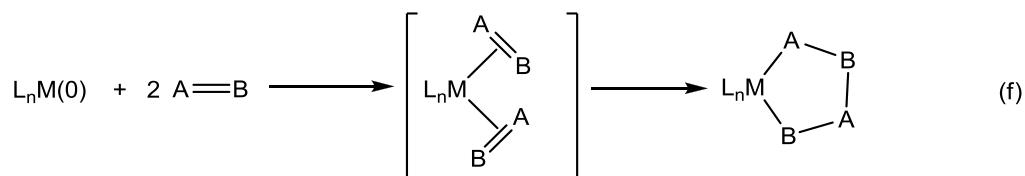


2.3.4 Cycloaddition of Unsaturated Molecules

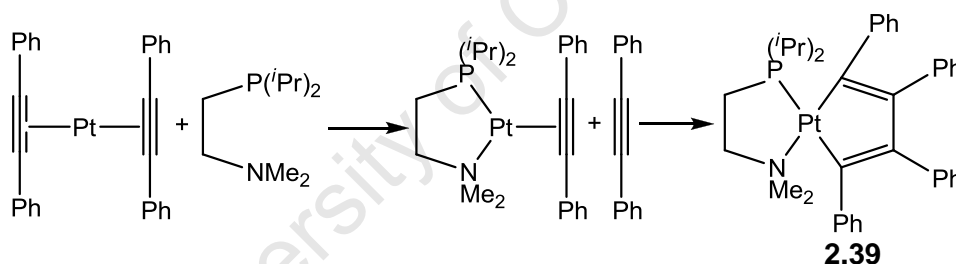
One of the most common synthetic methods for the preparation of metallacycles is the oxidative coupling (cycloaddition) of unsaturated molecules. Alkenes and alkynes react with metal centres to give metallacycloalkanes and metallacycloalkadienes, respectively. This method is highly useful as it provides access to relatively complex molecules from simple unsaturated organic starting materials.^{4a,11} The cycloaddition reaction is also important in the ethylene oligomerization reactions catalyzed by early transition metals such as Cr, Ti and Ta, where metallacycloalkanes have been shown to be key intermediates^{4,7a,7r,8a} as well as in the palladium catalyzed telomerization of conjugated dienes.⁷³

For group 10 metals, the reaction can take place on $\text{M}(0)$ and $\text{M}(\text{II})$ metal centres to give $\text{M}(\text{II})$ and $\text{M}(\text{IV})$ metallacycles respectively. The oxidative coupling reaction can be classified into two categories: (1) homocoupling, where coupling occurs between two identical molecules and (2) heterocoupling, where coupling occurs between two different unsaturated molecules (equations f and g). In addition, the unsaturated units themselves can be further categorized into two groups: the 'activated' and 'unactivated' unsaturated molecules.¹¹

Attaching electron donating groups on unsaturated molecules ‘activates’ them towards oxidative addition to $M(0)$ metal centres. For instance, ethylene would be considered an unactivated unsaturated molecule while methylvinyl ketone is considered to be activated.

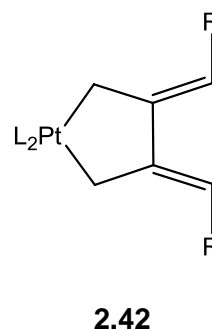
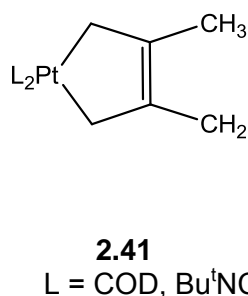
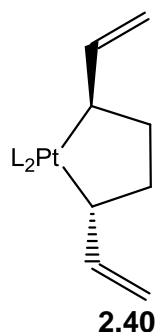


A large amount of work has been carried out on alkyne reactions as many transition metals mediate the cyclotrimerization of these molecules to give benzene derivatives.^{4a} Generally, the insertion of an alkyne into the $M-\eta^2$ -acetylene bond initially leads to a metallacyclopentane-2,4-diene such as complex **2.39**. Insertion of another acetylene molecule into this metallacyclopentadiene and subsequent decomposition yields the desired benzene derivatives.⁷⁴

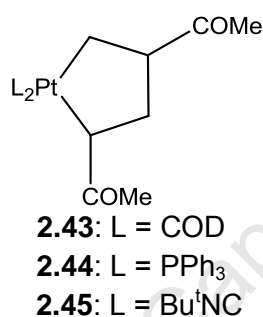


Although the formal cycloaddition of more than two unsaturated molecules is possible, this process frequently consists of a true cycloaddition of two unsaturated molecules and a subsequent insertion into the resultant platinapentacycle.¹⁰ Thus, this synthetic method yields, almost exclusively, metallacyclopentanes and metallacyclopentadienes.^{4a,74}

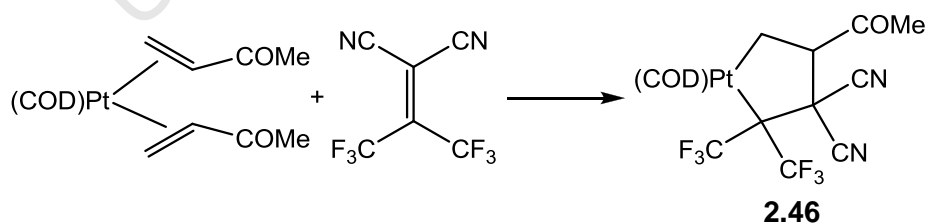
The cycloaddition of unactivated unsaturated molecules to platinum is relatively unusual and literature reports indicate that reactivity follows the trend: alkenes < dienes < alkyne < allenes. The reaction of 1,3-butadienes with $[Pt(COD)_2]$ gives stable metallacycles. The double bonds on the butadiene can react independently to give vinyl substituted metallacycles **2.40** or they can both react with the platinum centre to give platinacycles of the type **2.41**.⁷⁵ Phosphine derivatives of these complexes can be obtained by the substitution of the labile cyclooctadienyl ligand with appropriate phosphine ligands. Allenes react with platinum to give complexes of the type **2.42**.⁷⁶



The reaction between Pt(0) and activated alkenes and alkynes to give substituted platinacyclopentanes and platinacyclopentenes is facile. Cyclodimerization of methylvinyl ketone by Pt(COD)₂ gives the stable platinacyclopentanes **2.43 – 2.45**.⁷⁶

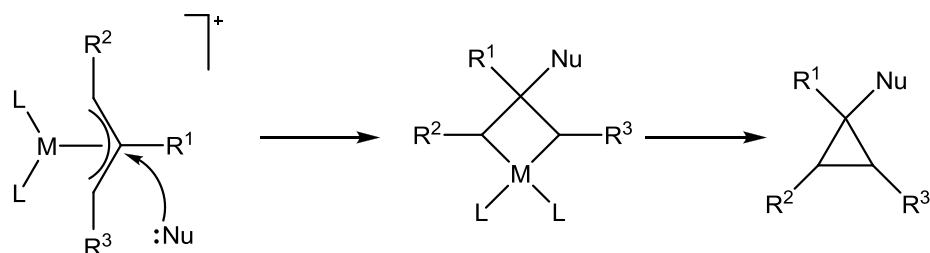


The reaction of a mixture of two different unsaturated molecules can lead to the formation of unsymmetrical metallacycles. The drawback of this synthetic method is that formation of a mixture of products is highly likely. However, this route is still an effective way of preparing substituted metallacycles that would otherwise be inaccessible. The selectivity problem can be circumvented by reacting a π -complex that contains one of the unsaturated substrates with the second unsaturated substrate.^{11,76}



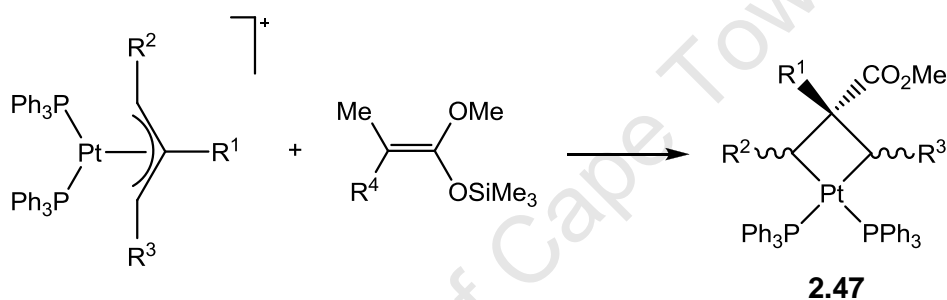
2.3.5 Nucleophilic Attack on Coordinated Ligands

Metallacyclobutanes of group 10 transition metals are often presumed to be key intermediates in nucleophilic addition reactions involving π -allyl complexes (Scheme 2.3).

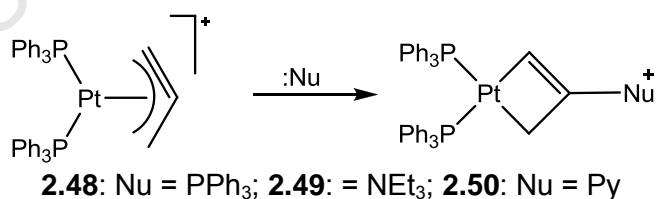


Scheme 2.3: Metallacycloalkane formation by nucleophilic attack on a π -allyl complex.

In these reactions the nature of the ligands bonded to the metal complex as well as the nucleophile play an important role in both the rate and the regioselectivity of the reaction.⁷⁷ When attack of a nucleophile on a π -allyl complex occurs on the central carbon atom, the result is the formation of a metallacyclobutane, and this process is kinetically favoured by sterically hindered and basic nucleophiles as well as by good σ -donor ligands on the metal centre.⁷⁸



Metallacyclobutenes can be formed by the nucleophilic attack on the central atom of η^3 -propargyl complexes. However, for platinacycles this process is often complicated by subsequent proton transfer reactions that lead to π -oxatrimethylene, π -azatrimethylene or π -trimethylene complexes. Platinacyclobutenes can, therefore, be obtained if the attacking nucleophile lacks exchangeable hydrogens as demonstrated by the preparation of complexes **2.48** – **2.50**.⁷⁹



2.4 REACTIVITY OF PLATINACYCLOALKANES

2.4.1 Decomposition Reactions

The final step in the mechanism of any synthetically useful catalytic reaction in which metallacycles are involved is the decomposition of the metallacycle to give the desired organic products. Understanding this process is therefore of great importance in the design of new applications of metallacycles.^{11,36} Metallacycloalkanes have two metal–carbon single

bonds and can therefore be regarded as metal complexes with two alkyl ligands; however, their thermal chemistry can be quite different from that of acyclic dialkyl complexes.¹ Thermal decomposition studies have shown that metallacyclobutanes, -pentanes and -hexanes, which have quite rigid rings are found to be much more thermally stable than their acyclic analogues. However, as ring size increases, the decomposition pathways of metallacycloalkanes becomes increasingly similar to those of acyclic metal-alkyl complexes.⁸⁰

The thermal chemistry of metallacycloalkanes involves several processes reported for the decomposition of dialkyl complexes such as β -hydride elimination, reductive elimination, α -hydride elimination and carbon-carbon bond cleavage (retro-cycloaddition) (Figure 2.2), as well as certain processes which have only been proposed in metallacyclic systems.^{11,80} The decomposition process is an aspect of the chemistry of metallacycles which sometimes differs considerably from that of metal dialkyl complexes.

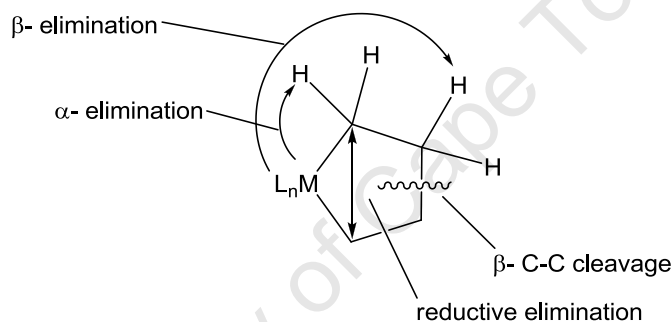


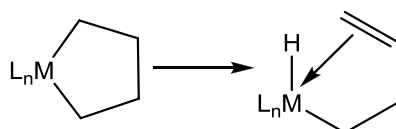
Figure 2.2: Decomposition pathways for metallacycloalkanes.

The decomposition pathways of metallacycles are dependent on the nature of the ligand on the metal centre as well as reaction conditions. Most decomposition studies are carried out in solvent, in which the reaction can easily take place and reported temperatures are usually low. Decompositions in the solid state or gas phase are less common due to instrumental and other limitations. Decomposition reaction under solvent-less conditions would, however, be very interesting since no solvent molecules are present to influence the decomposition pathways.⁸⁰

2.4.1.1 β -Hydride Elimination

β -Hydride elimination requires a transition state in which the dihedral angle $M-C-C-H$ is nearly 0° . This transition state is not readily attained in 4-, 5-, 6-membered platinacycles, therefore β -elimination is relatively hindered in these complexes. As the ring size of the metallacycle increases, this transition state is more readily achieved, thereby making these complexes more prone to decomposition via this route. In fact, no metallacyclobutane has ever been directly observed to form an allyl hydride complex by β -hydride elimination.¹

However, there is evidence to suggest that β -hydride elimination reactions of 5-membered metallacyclic complexes, to give hydridometal alkene complexes is possible (Scheme 2.4).^{8,81} Reductive elimination of R-H from these hydridometal alkene complexes would then yield α -olefins, the target products in ethylene oligomerization reactions.



Scheme 2.4: β -Hydride elimination of metallacyclopentanes.

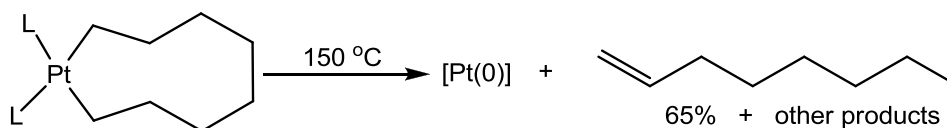
Theoretical studies have been carried out to explore β -hydride elimination in several ruthenium and platinum metallacycloalkanes by Huang and co-workers. These studies revealed that, while structural arrangements in which the transferring hydrogen is in close proximity with the metal centre for facile β -hydride elimination exist for ruthenacycloalkanes, these arrangements were less favourable for platinacycles, making the process more difficult for 4-, 5- and 6-membered platinacycloalkanes.⁸² In 7-membered and larger platinacycloalkanes, β -hydride elimination is expected to be less hindered.¹⁴ Table 2.1 summarizes experimental conditions as well as the product distribution for the decomposition of selected platinacycloalkanes. The initial step in the formation of the major products is generally accepted to be β -hydride elimination followed by reductive elimination from the resultant hydrido-metal alkene intermediates.^{13,14,82,83a}

Table 2.1: Thermal decomposition products of platinacycloalkanes

Complex	Ligand	Solvent	Temp (°C)	Products (%)
	PPh ₃ , dppe	DCM	120	(78) (20)
	PPh ₃ , dppe	DCM	120	(75) (17)
	PPh ₃ , dppe	DCM	120	(83) (17)
	PCy ₃	Cyclohexane	99	& isomers (60 – 93)

Moss and co-workers carried out decomposition studies on medium ring platinacycloalkanes, which revealed that the primary decomposition pathway for these complexes is β -hydride elimination followed by reductive elimination, giving 1-alkenes as

major products (Scheme 2.5).^{17,18-20} The decomposition reactions were carried out under solvent free conditions.



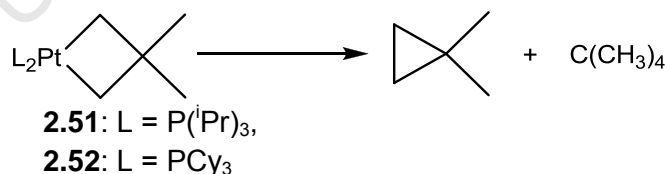
Scheme 2.5: Thermal decomposition of platinacyclononanes.

These results suggest that the compounds can be useful models for intermediates in ethylene oligomerization reactions to give α -olefins.

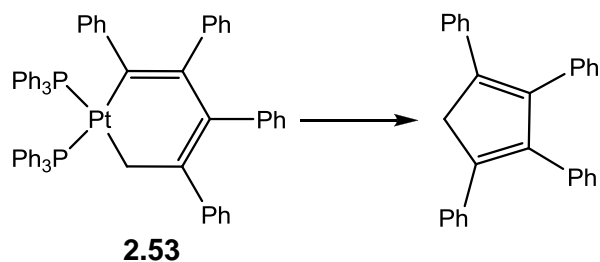
2.4.1.2 Reductive Elimination

Carbon–carbon bond formation by reductive elimination from transition metal alkyl complexes is an important product forming reaction in organometallic synthesis and catalysis^{83b} and is frequently observed in dialkyl complexes. Thus in complexes such as PtR_2L_2 ($\text{L} = \text{PPh}_3$, $\text{R} = \text{alkyl}$), reductive elimination of a C–H bond to form alkanes through the intermediacy of hydridoalkylplatinum(II) compounds is the key step in the decomposition process.⁸⁰ Thermal decomposition studies of platinum and palladium dialkyl complexes show that platinum complexes preferably decompose *via* reductive elimination of C–H bonds, while analogous palladium complexes preferably decompose *via* C–C reductive elimination.

Like β -hydride elimination, reductive elimination is also thermally less favourable in small and medium-sized metallacycles than it is in open chain metal dialkyls as it leads to strained organic products such as cyclopropanes and cyclobutanes.¹¹ However for platinum complexes such as **2.51** and **2.52**, where β -hydride elimination is prevented by the absence of β -hydrogens, C–C reductive elimination occurs.⁸⁴ The 1,2-dimethylcyclopropane produced in this reaction was obtained in 94 – 98% yield.

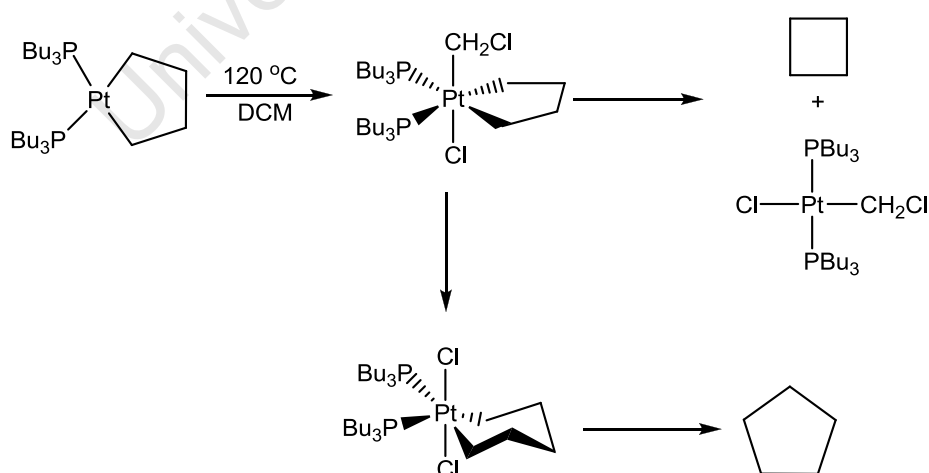


C–C reductive elimination is extremely facile for platinacyclic complexes that both lack β -hydrogen atoms and one of the carbon atoms attached to the metal centre is sp^2 hybridized. A rare type of this complex is the platinahexacycle **2.53**, which readily decomposed in hot C_6D_6 giving tetraphenylcyclopentadiene.⁷¹



The reductive elimination in M(II) metallacycles of the Ni group metals can be efficiently induced by π -acceptor ligands such as maleic anhydride.³³ The effect of electron acceptor ligands may be understood on the basis of the destabilization of the proposed pentacoordinated species that results from the interaction of the metallacyclic complex due to the partial electron transfer from the metal to the ligand. In line with this reasoning, the reductive elimination of Ni and Pd complexes can be induced by oxidizing agents such as molecular oxygen. Alkyl halides can also play a similar role, inducing the reductive elimination of pallada- and platinacycles although a closer look at the reductive elimination of the pallada- and platina-cycles reveals that the species that actually decomposes is a M(IV) metallacycle.¹¹

Metallacycloalkanes of divalent Ni group metals are known to undergo oxidative addition with alkyl halides to form M(IV) metallacycles. These M(IV) metallacycles, therefore, readily undergo reductive elimination to give cyclic organic product as well as M(II) complexes as the main organometallic products of the reaction as shown in the example in Scheme 2.6.^{83b} The formation of C₅ hydrocarbons can be explained by a ring expansion to give a platina(IV)cyclopentane, which then reductively eliminates cyclopentane.



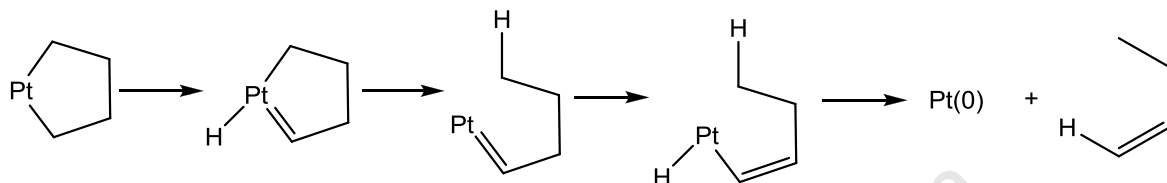
Scheme 2.6: Reductive elimination of platinacyclopentanes and -hexanes.

The presence of π -acceptor ligands or ligands with a strong *trans* effect favours the reductive elimination of metallacycloalkanes. Thus the addition of phosphines, arsines, stilbines or anionic ligands such as I⁻, SCN⁻ and CN⁻ to otherwise stable

platina(IV)cyclobutane complexes can induce their decomposition *via* reductive elimination.^{58,61}

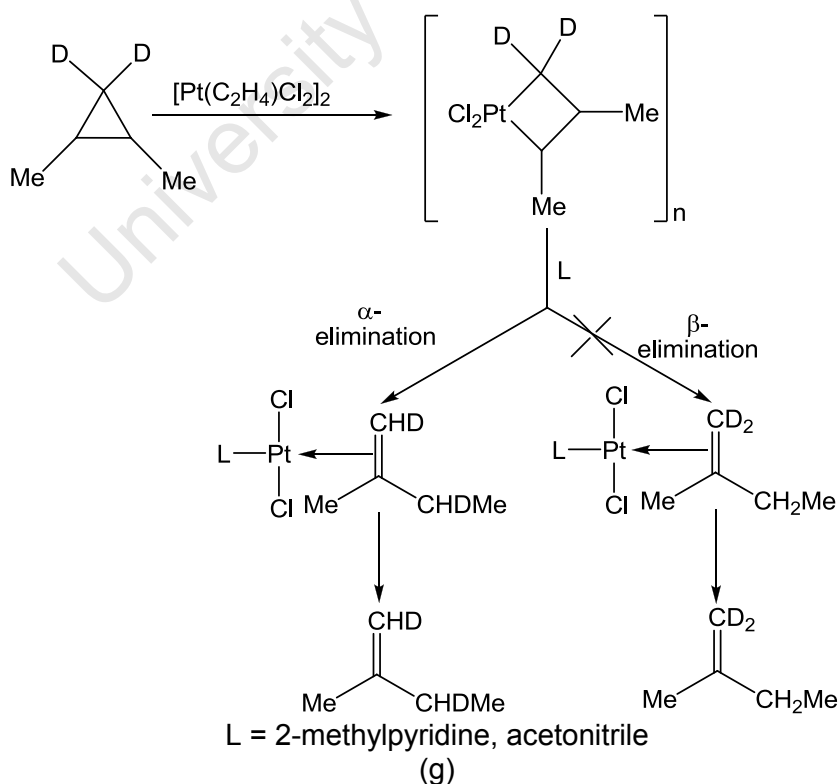
2.4.1.3 α -Hydride Elimination

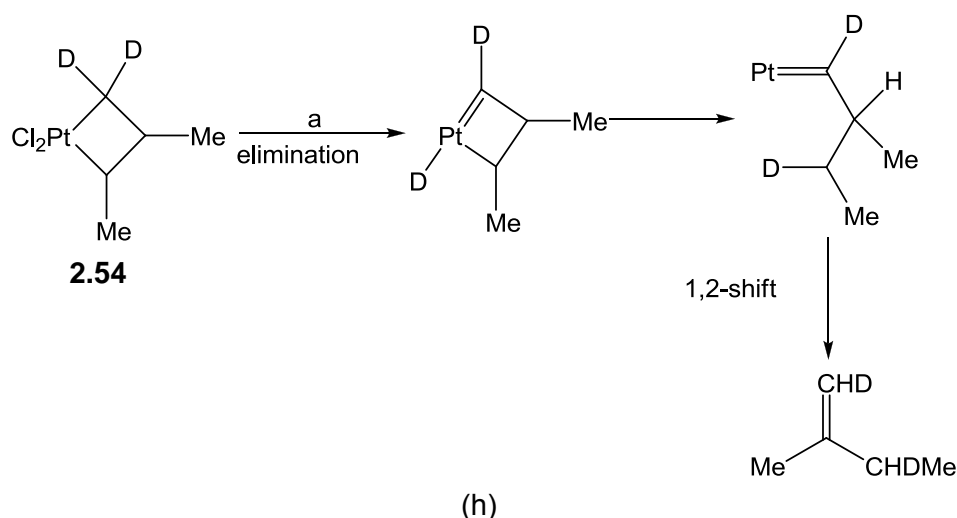
Hydrogen elimination from the carbon directly bonded to the metal centre is much less favourable than that from the β carbon. However, Whitesides and co-workers suggested the possibility of an olefin extrusion step starting with α -hydride elimination (Scheme 2.7) in the decomposition mechanism of the platinacyclopentane, $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_2)_4]$.¹⁴



Scheme 2.7: α -Hydride elimination from platinacycloalkanes.

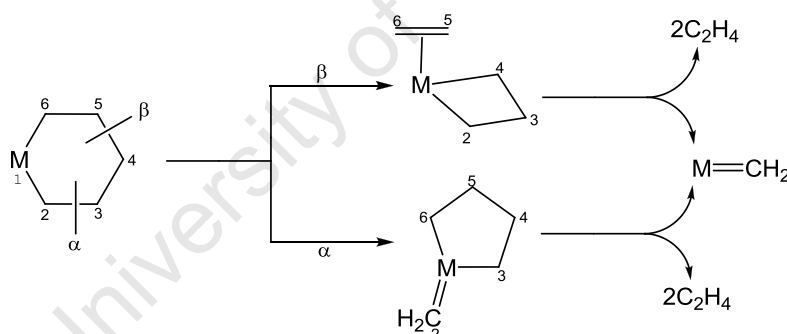
For platinacycloalkanes, α -hydride elimination is observed more commonly in the decomposition of M(IV) complexes. The rearrangement of platinacyclobutanes **2.54** was initially studied by Puddephatt and coworkers.⁸⁵ Although the decomposition of the complex *via* β -hydride elimination is possible, deuterium-labeling experiments by Puddephatt as well as studies by Fischer and co-workers revealed that the decomposition of **2.54** leads to an isotopic distribution which is consistent with an α -elimination process followed by a 1,2-hydrogen shift.^{86,87}





2.4.1.4 C-C-Bond Cleavage (Retro-cycloaddition)

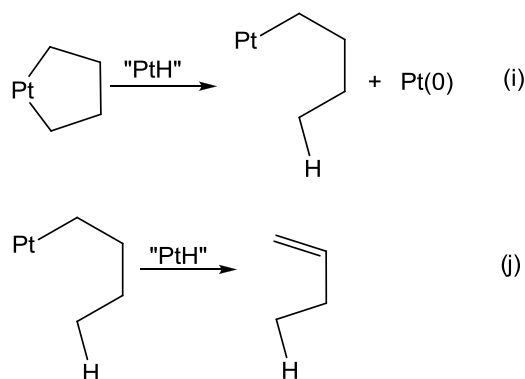
α - or β -C-C bond cleavage can be a facile process in some metallacycles of group 10 transition metals (Scheme 2.8). β -C-C bond cleavage takes place in metallacyclopentane systems that have symmetrical β,β -carbon atoms. Although the organic product distribution in decomposition reactions of some Ni complexes is in agreement with this pathway,⁸⁸ this distribution has not been reported for Pd and Pt metallacycles. The decomposition of nickellacyclopentanes via this pathway gives ethylene as the major product.



Scheme 2.8: Metallacycloalkane decomposition via C-C bond cleavage.

2.4.1.5 Other Decomposition Pathways

Other less common decomposition pathways postulated for the decomposition of metallacycloalkanes include intermolecular chain reactions as well as concerted transition metal assisted β -hydride transfer (Scheme 2.9).^{13,14} The latter pathway was postulated by Whitesides and co-workers in their decomposition studies of platinacycloalkanes. The most unsatisfactory aspect of the metal β -hydride elimination mechanism as a rationalization for the thermal decomposition of the platinacycles is that it is not clear that the platinum atom and a β -hydrogen atom can be brought close enough together for a concerted elimination to take place, without introducing energetically unacceptable bond angle distortions.¹⁴



Scheme 2.9: Metal-assisted β -hydride elimination.

The intermolecular chain reaction was first proposed by Whitesides for the decomposition of $[\text{Pt}(\text{PCy}_3)_2(\text{C}_4\text{H}_8)]$. In this work, they suggested that the decomposition pathway is an intermolecular hydride chain transfer process, and not the simple β -hydride elimination/reductive elimination pathway, due to the high thermal stability of the platinacyclopentane ring.^{83a}

2.4.2 Insertion Reactions

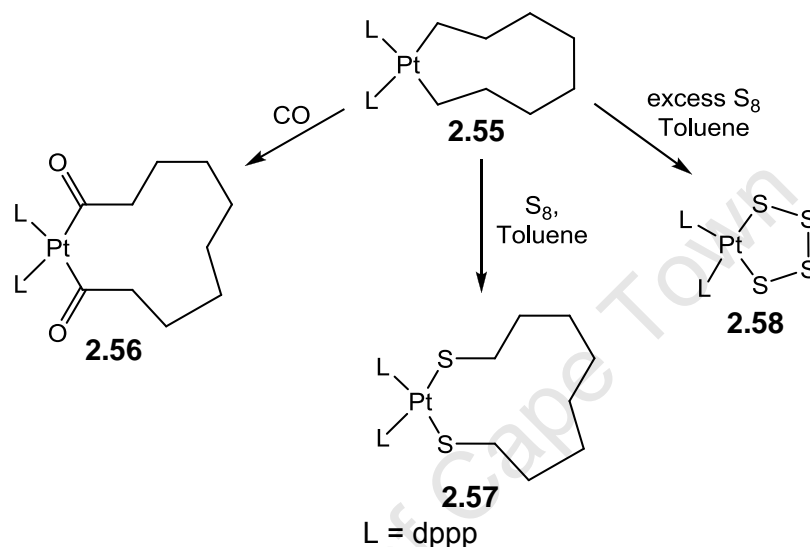
The interest in reactions of metallacycloalkanes resides in the scope they offer for functionalizing hydrocarbons to give valuable organic products such as aldehydes, acids, ethers and thiolates.⁸⁰ The reaction of group 10 metallacycles with small, unsaturated molecules may lead to their insertion into the M-C bonds and expansion of the ring. Often, a decomposition reaction follows, yielding desirable organic products.¹¹ The majority of the insertion reactions effected at Ni, Pd and Pt can be regarded as migratory insertion reactions, in which the unsaturated molecule first coordinates to the metal centre followed by an intramolecular attack of the coordinated molecule on the M-C bond. Square planar Ni(II) complexes easily coordinate a fifth ligand and undergo migratory insertion while such a process for Pd(II) and Pt(II) complexes has seldom been reported.¹¹

2.4.2.1 Insertion of Carbon Monoxide, Isocyanides and Sulfur

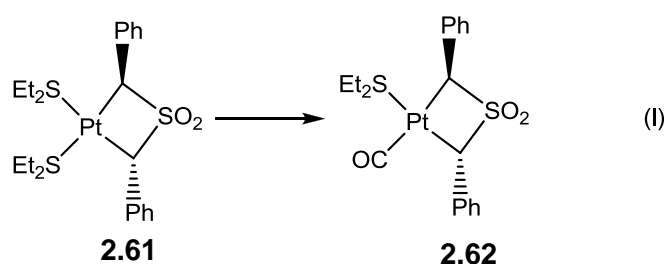
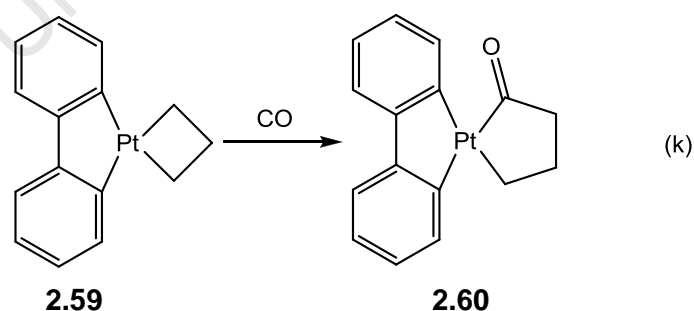
The carbonylation of metallacycles allows their transformation to cyclic ketones. In general, the insertion of one equivalent of CO is followed by the reductive elimination of a cyclic ketone.¹¹ Extensive work has been published on the insertion of CO into transition metal-carbon bonds. Generally all the metals have been shown to undergo CO insertion, except for Nb, Ta, Tc, Cu, Ag, and Au.⁸⁹

For complexes of the Ni group metals, the reaction seems to be sensitive to the co-ligands on the metal complex.¹¹ Only a small number of investigations of CO insertion into Pt-alkyl complexes have been undertaken.^{89f} Moss and coworkers carried out carbonylation

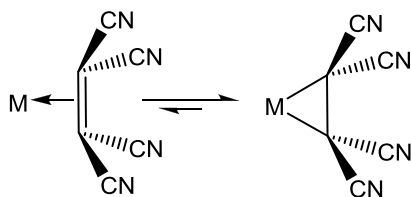
reactions on the platinacyclononane **2.55** and observed that two equivalents of CO inserted into the Pt-C bonds and the diacyl complex **2.56** was obtained in reasonable yield. This reaction proved to be relatively slow, and this could primarily be due to the strong metal-carbon bond seen in most 5d transition metal complexes.²⁰ A mechanism leading to this product may proceed via an intermediate 5-coordinate platinum species.⁹⁰ Reaction of **2.55** with elemental sulfur (S_8) gave the di-inserted complex **2.57**, whereas reaction with excess sulfur gave the platinacyclosulphide **2.58**. Similar products have been observed in the reaction of S_8 with platinum bisalkyl complexes.²⁰



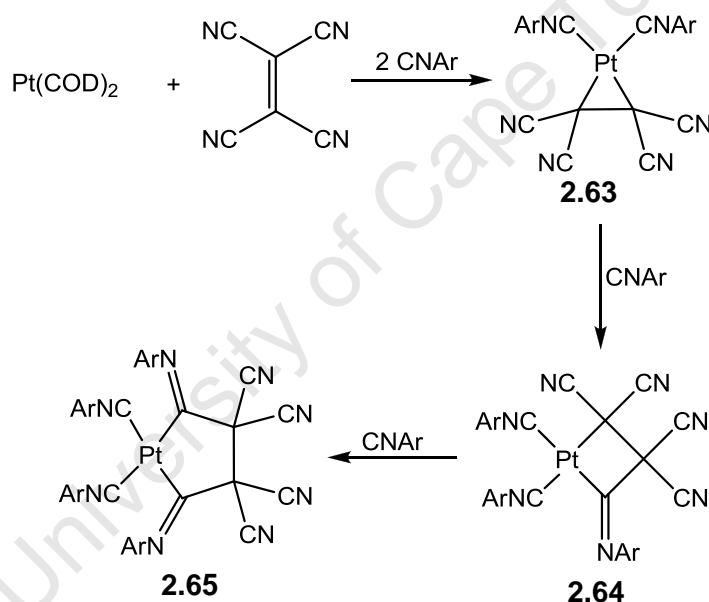
Although the insertion of one equivalent of CO into Pt-C bonds of platinacyclobutanes (k) has been reported,⁹¹ it has also been found that for certain platinacyclobutanes, CO can displace a neutral ligand on platinacycles (l).⁹² The high kinetic barrier to insertion in these complexes could be due to the restrictions imposed by the metallacycle for the migration of one of the CH_2 termini to the coordinated CO ligand.¹¹



The insertion of isocyanides into platinacyclopropane **2.63** was studied by Nagashima and co-workers.⁹³ Since TCNE is a strong electron acceptor, **2.63** is a platinacyclopropane as opposed to a π -complex (Scheme 2.10). This complex undergoes a double insertion of CNR to give the platinacyclopentane **2.65**. Although the platinacyclobutane intermediate **2.64** was not isolated, an analogous metallacyclobutane intermediate was isolated in the insertion of isocyanides to a η^2 -alkyne-cobalt complex that was reported by Yamazaki and Wakatsuki.⁹⁴ DFT calculations by Hsiao and Su provide further support for the mechanism of the reaction via a platinacyclobutane intermediate.⁹⁵



Scheme 2.10: Equilibrium between a metallacyclopropane and an η^2 -alkene complex.



2.4.2.2 Insertion of Alkenes, Alkynes and Allenes

A survey of the literature reveals that the insertion of unsaturated organic molecules into platinacycloalkanes is very rare. Although allenes are promising candidates to undergo insertion reactions, their reactivity towards group 10 metallacycles has been studied only sparsely. Tom Dieck carried out investigations into the catalytic transformations of allenes using Pd and Pt metallacycles, and found that platinacyclopentadienes supported by diazabutadiene co-ligands react with allenes.⁹⁶ Insertion of alkenes and alkynes into platinacycles has not been reported.

2.5 METALLACYCLOALKANES IN ETHYLENE OLIGOMERIZATION

Olefins, particularly ethylene, propylene and butenes are the basic building blocks of the petrochemical industry. They are readily available, cheap, reactive, and can be easily transformed into a range of useful products. The past half century or so has witnessed increasing importance of higher linear α -olefins, which today are a source of biodegradable detergents, new kinds of polymers, lubricants, and many other industrially useful chemicals.⁹⁷ Of the linear α -olefins (LAOs), 1-hexene and 1-octene are the most valuable. The conventional method of producing these is by catalytic oligomerization of ethylene, which yields a wide spectrum of LAOs that follow a Schulz-Flory type of distribution and consequently require tedious product separation processes. From an industrial point of view, processes that are selective for the production of higher value LAOs such as 1-hexene and 1-octene are desirable.^{5,6} As a result, there is ongoing effort both in industry and academic communities to develop more efficient catalysts that will produce 1-hexene and 1-octene selectively.^{8b}

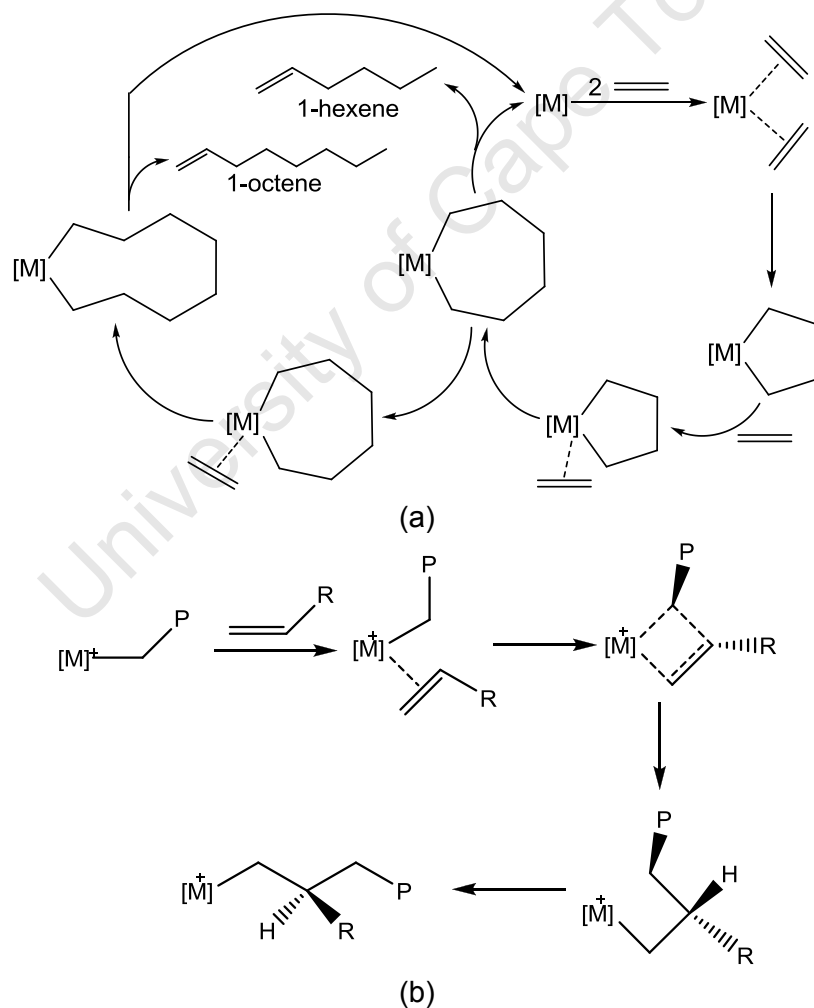
The selective trimerization of ethylene to 1-hexene is a well known technology. Most of the catalyst systems for this process are based on chromium,⁶ although catalyst systems based on tantalum⁸ and titanium⁷ have been reported. Of these systems, the Cr catalysts show the best activity and selectivity.^{6c} The observed selectivity in ethylene trimerization reactions is a consequence of the unusual metallacyclic mechanism proposed to be operative (Scheme 2.11).^{6c,6p,6q}

The initial step in the catalytic cycle is the oxidative coupling of two ethylene molecules with the active catalytic metal to give a metallacyclopentane intermediate. The geometrical constraints of this species limit the interaction needed between the β -hydrogen atoms and the metal centre for the complex to decompose *via* β -hydride elimination of 1-butene. Coordination and subsequent migratory insertion of a third ethylene molecule is thus facilitated, and the resultant metallacycloheptane is flexible enough for β -hydride transfer to occur and reductive elimination of 1-hexene from this intermediate is facile.⁵

Until recently, a corresponding selective tetramerization reaction of ethylene to give 1-octene was thought to be improbable. This is due to the fact that if ethylene tetramerization were to proceed *via* a metallacyclic mechanism similar to that of ethylene trimerization, it would imply expansion of a seven-membered to a nine-membered metallacyclic intermediate. It has been argued that this is unlikely to occur as the nine-membered ring is the least favoured medium-sized ring and should thus be disfavoured relative to the seven-membered ring.^{7g,8b} It was thought that coordination and migratory insertion of a fourth ethylene molecule to give a

metallacyclononane or selective elimination of 1-octene from such an intermediate was improbable.^{5,6a} However, a catalyst system capable of ethylene tetramerization with selectivities of up to 70% was recently reported by the group at Sasol.^{6a} Considerable effort has been made to modify the catalyst system to improve its performance, but so far this system is still by far the most active and selective for 1-octene.^{6b}

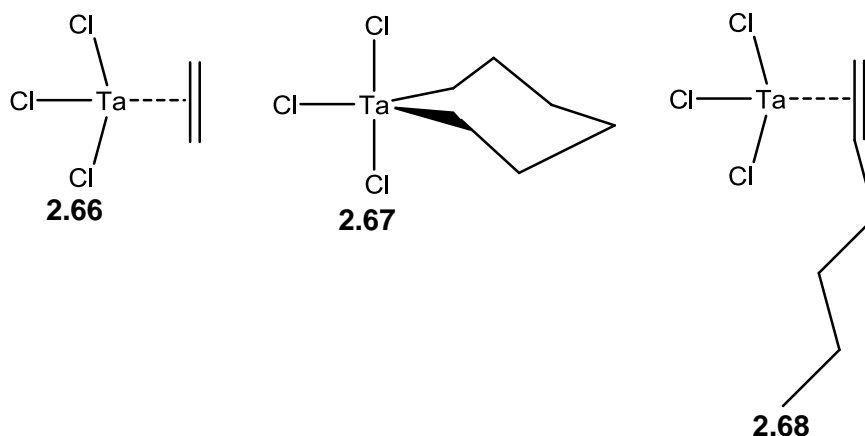
The high selectivity for 1-hexene and 1-octene displayed by these catalysts has been explained by the involvement of metallacycloalkanes as key intermediates in the oligomerization reactions (Scheme 2.11(a)). The metallacyclic mechanism has been favoured over the Cossee-Arlman mechanism (Scheme 2.11(b))^{6s} used to explain the product distribution observed for the late transition metal catalysts such as those based on nickel and palladium as a Cossee-type mechanism offers no reasonable explanation for the high selectivity for the C₆ and/or C₈ α-olefins. Production of higher linear α-olefins (up to C₃₀) has also been proposed to proceed *via* an extended metallacycloalkane mechanism.^{6r}



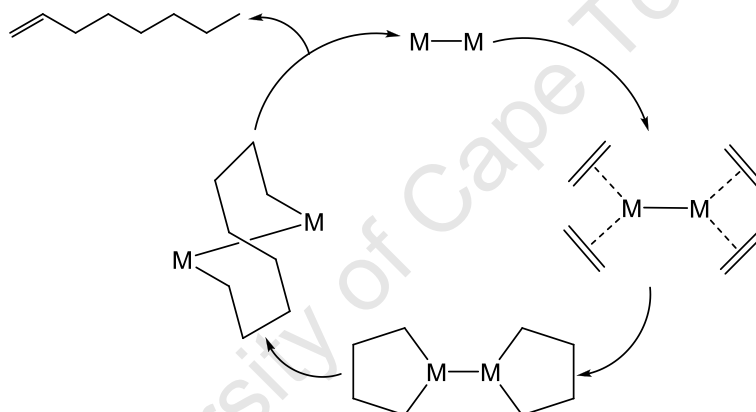
Scheme 2.11: (a) Proposed metallacyclic mechanism of ethylene tri- and tetramerization, (b) modified, Cossee-Arlman mechanism for olefin oligomerization and /or polymerization.

In support of the metallacyclic mechanism, Jolly and co-workers reported well-defined chromacyclopentane and chromacycloheptane complexes, and the latter readily decomposes to give 1-hexene.^{6c,6p} In addition, the group at Sasol as well as Bercaw and co-workers carried out deuterium labeling studies in an effort to conclusively determine the reaction mechanism for the production of 1-octene.^{5,6c} A 50:50 mixture of C₂H₄ and C₂D₄ was used. The ratio of C₂H₄ to C₂D₄ incorporated into the products can be calculated, independent of the mechanism, from the isotopomer distribution. By the use of this value, and a first order correction for the natural abundance of deuterium in hydrogen (0.79% D) and the imperfect labeling of the deuterated ethylene (0.5% H), theoretical isotopomer distributions for 1-octene and 1-hexene produced by both the metallacyclic mechanism and the Cossee-Arlman linear chain growth mechanism may be calculated. These studies revealed that the correlation of the observed isotopomer distribution with the predicted distribution for the metallacyclic mechanism is excellent for both 1-hexene and 1-octene. Based on these studies, the formation of 1-hexene and 1-octene via the Cossee-Arlman mechanism is excluded.⁵

A number of researchers have also undertaken computational investigations into the changes in selectivity and activity of the trimerization or tetramerization reaction as a function of the different ligand systems on the metal centre.^{7f,8b} These studies offer valuable insights into the factors that need to be taken into consideration for the design of new catalyst systems for selective ethylene trimerization and oligomerization. For instance, Yu and Houk^{8b} carried out density functional investigations into the selective trimerization of ethylene using the tantalum catalyst, [TaCl₃R₂], that was initially reported by Sen and co-workers.^{8a} These studies showed that for this catalyst system, one of the initial and essential processes in the catalytic cycle is the formation of the ethene-TaCl₃ complex **2.66**. The selective generation of 1-hexene over the production of branched oligomers by this catalyst system is attributed to the formation of complex **2.66**, whose formation is energetically favored over that of the terminal alkene-TaCl₃ complex due to steric factors. Furthermore, the conversion of the tantalacycloheptane **2.67** to the η² complex **2.68** occurs as a concerted hydrogen shift process related to the well-known β-agostic interaction between the metal centre and β-hydrogens, in contrast to the two-step β-hydride/reductive elimination process that has been proposed for chromium and platinum systems. These studies show that the dimerization of ethylene to give 1-butene is disfavored by the lack of this kind of concerted reductive elimination process for the tantalacyclopentane whereas bimolecular processes that would lead to tetramerization and possible higher oligomerizations cannot compete with the facile reductive elimination available to the tantalacycloheptane.^{8b}

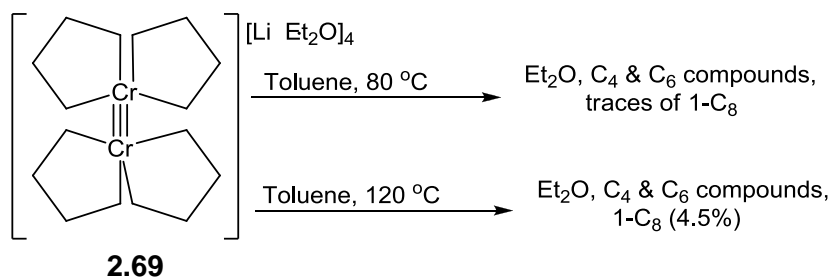


Recently, Muller and Rosenthal proposed an alternative mechanism for the selective tetramerization of ethylene via dimeric catalytic centres to give 1-octene (Scheme 2.12).^{98a} The conceivability of the concept of a binuclear centre for selective ethylene oligomerization was supported by the synthesis of a complex consisting of two chromium centres bridged by a 1,4-butandiyl unit by Theopold and co-workers.^{98b}



Scheme 2.12: Proposed bimetallic mechanism for ethylene tetramerization.

There are also indications for a binuclear mechanism in the Phillips and Union Carbide catalysts systems for ethylene polymerization, in which ethylene inserts between two bridged chromium atoms to form one metallacycle. This postulated mechanism is supported by kinetic investigations^{98c} as well as density functional theory (DFT) studies.^{98d} Experimental support for the postulated bimetallic mechanism is delivered by the thermolysis of defined binuclear chromium complexes with one or more metallacycles such as **2.69** reported by Kurras and co-workers.^{98e}



Without further detailed characterization of catalytically active tetramerization species and their kinetics, primary proof of this concept is not possible. In the mean time, the mononuclear metallacyclic mechanism is still the accepted mechanism for the selective production of high value α -olefins such as 1-hexene and 1-octene mediated by Cr, Ta and Ti catalysts.

2.6 SUMMARY

Metallacyclic compounds of the transition metals are an important class of compounds due to the important role they play in catalytic and stoichiometric reactions. Due to the unstable nature of most metallacyclic compounds, platinacycles are an attractive class of compounds to study as they are relatively stable compared to other metallacycles. In this review, the different methodologies available for the synthesis of platinacyclic complexes have been described. The merits and drawbacks of each synthetic method are presented along with examples of complexes prepared using each method. Also described is the reactivity of platinacycles, with specific focus on the insertion and decomposition reactions as these processes are pertinent to the catalytic processes that involve metallacycles as intermediates. Finally, a brief look at ethylene oligomerization reactions, specifically trimerization and tetramerization reactions has been taken. These processes rely heavily on the intermediacy of metallacycloalkanes for their high selectivity for α -olefins.

2.7 AIMS AND OBJECTIVES

The overall objective of this project is to prepare and study the reactivity and catalytic activity of a series of palladium and platinum complexes based on bidentate iminophosphine ligands.

2.7.1 Specific Aims

- To synthesize a series of bidentate phosphinobenzaldimino ligands (P^AN), and their corresponding palladium and platinum complexes of the types $[Pd(P^AN)Cl_2]$, $[Pd(P^AN)(Me)Cl]$, $[Pt(P^AN)Cl_2]$ and $[Pt(P^AN)(C_4H_9)Br]$ (**Chapter 3**).
- To test a selection of the palladium complexes for catalytic activity in Suzuki-Miyaura coupling reaction (**Chapter 4**).
- To prepare platinacycloalkane complexes of the type $[Pt(P^AN)(CH_2)_n]$, $n = 4$ or 6 (**Chapter 5**).
- To study the decomposition reaction of platinacycloalkane complexes and investigate the β -hydride elimination/reductive elimination reaction mechanism proposed for this decomposition reaction using DFT methods (**Chapter 5**).

2.8 REFERENCES

1. Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G., Principles and Applications of Organometallic Chemistry, University Science Books, Mill Valley, 1987.
2. Blom, B., Clayton, H., Kilkenny, M. and Moss, J. R., *Adv. Organomet. Chem.*, 2006, **54**, 149.
3. Chanda, N. and Sharp, P. R., *Organometallics*, 2007, **26**, 3368.
4. (a) Chapell, S. D. and Cole-Hamilton, D. J., *Polyhedron*, 1982, **1**, 739. (b) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1973, **95**, 4451. (c) Elowe, P. R., McCann, C., Pringle, P. G., Spitzmesser, S. K. and Bercaw, J. E., *Organometallics*, 2006, **25**, 5255.
5. Overett, M. J., Blann, K., Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723.
6. (a) Bollmann, A., Blann, K., Dixon, J. T., Hess, F. M., Killian, E., Maumela, H., McGuinness, D. S., Morgan, D. H., Neveling, A., Otto, S., Overett, M., Slawin, A. M. Z., Wasserscheid, P. and Kuhlmann, S., *J. Am. Chem. Soc.*, 2004, **126**, 14712. (b) Kim, K.-S., Kim, T.-J., Chung, J.-H., Hahn, T.-K., Chae, S.-S., Lee, H.-S., Cheong, M. and Kang, S. O., *Organometallics*, 2010, **29**, 5805. (c) Agapie, T., Schofer, S. J., Labinger, J. A. and Bercaw, J. E., *J. Am. Chem. Soc.*, 2004, **126**, 1304. (d) Janse van Rensburg, W., Grove, C., Steynberg, J. P., Stark, K. B., Huyser, J. J. and Steynberg, P. J., *Organometallics*, 2004, **23**, 1207. (e) McGuinness, D. S., Wasserscheid, P., Morgan, D. H. and Dixon, J. T. *Organometallics*, 2005, **24**, 552. (f) McGuinness, D. S., Brown, D. B., Tooze, R. P., Hess, F. M., Dixon, J. T. and Slawin, A. M. Z., *Organometallics*, 2006, **25**, 3614. (g) Schofer, S. J., Day, M. W., Henling, L. M., Labinger, J. A. and Bercaw, J. E., *Organometallics*, 2006, **25**, 2743. (h) Temple, C., Jabri, A., Crewdson, P., Gambarotta, S., Korobkov, I. and Duchateau, R., *Angew. Chem., Int. Ed.* 2006, **45**, 7050. (i) Janse van Rensburg, W., van den Berg, J.-A. and Steynberg, P. J., *Organometallics*, 2007, **26**, 1000. (j) Nenu, C. N., Bodart, P. and Weckhuysen, B. M., *J. Mol. Catal. A: Chem.* 2007, **269**, 5. (k) McGuinness, D. S., Rucklidge, A. J.; Tooze, R. P. and Slawin, A. M. Z., *Organometallics*, 2007, **26**, 2561. (l) Kuhlmann, S., Blann, K., Bollmann, A., Dixon, J. T., Killian, E., Maumela, M. C., Maumela, H., Morgan, D. H., Pretorius, M., Taccardi, N. and Wasserscheid, P., *J. Catal.* 2007, **245**, 279. (m) McGuinness, D. S., Overett, M., Tooze, R. P., Blann, K., Dixon, J. T. and Slawin, A. M. Z., *Organometallics*, 2007, **26**, 1108. (n) Rucklidge, A. J., McGuinness, D. S., Tooze, R. P., Slawin, A. M. Z., Pelletier, J. D. A., Hanton, M. J. and Webb, P. B., *Organometallics*, 2007, **26**, 2782. (o) Agapie, T., Labinger, J. A. and Bercaw, J. E., *J.*

- Am. Chem. Soc.*, 2007, **129**, 14281. (p) Emrich, R., Heinnemann, O., Jolly, C. W., Kruger, C. and Verhovnik, G. P. J., *Organometallics*, 1997, **16**, 1511. (q) Briggs, J. R., *J. Chem. Soc., Chem. Commun.*, 1989, 674. (r) Tomov, A. K., Chirinos, J. J., Jones, D. J., Long, R. J. and Gibson, V. C., *J. Am. Chem. Soc.*, 2005, **127**, 10166. (s) Tritto, I., Boggioni, L., Sacchi, M. C. and Locatelli, P., *J. Mol. Catal A: Chem.*, 1998, **133**, 139.
7. (a) Tobisch, S and Zeigler, T., *Organometallics*, 2003, **22**, 5392. (b) Deckers, P. J. W. and Hessen, B., *Organometallics*, 2002, **21**, 5564. (c) Deckers, P. J. W., Hessen, B. and Teuben, J. H., *Organometallics*, 2002, **21**, 5122. Deckers, P. J. W., Hessen, B. and Teuben, J. H., *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 2516. (d) Hessen, B., *J. Mol. Catal. A: Chem.*, 2004, **213**, 129. (e) Wang, C. and Huang, J. L., *Chin. J. Chem.*, 2006, **24**, 1397. (f) de Bruin, T., Raybaud, P. and Toulhoat, H., *Organometallics*, 2008, **27**, 4864. (g) Blok, A. N. J., Budzelaar, P. H.M. and Gal, A. W., *Organometallics*, 2003, **22**, 2564.
8. (a) Andes, C., Harkins, S. B., Murtuza, S., Oyker, K. and Sen, A., *J. Am. Chem. Soc.*, 2001, **123**, 7423. (b) Yu, Z.-X. and Houk, K. N., *Angew. Chem. Int. Ed. Engl.*, 2003, **42**, 808.
9. (a) Dyker, G., *Chem. Ber.*, 1997, **130**, 1567. (b) Trost, B. M., *Acc.Chem. Res.*, 1990, **23**, 34. (c) Trost, B. M. and Trost, M. K., *Tetrahedron Lett.*, 1991, **30**, 3647. (d) Trost, B. M. and Trost M. K., *J. Am. Chem. Soc.*, 1991, **113**, 1850. (e) Trost, B. M. and Chang, V. K., *Synthesis*, 1993, 824.
10. Negishi, E. (Ed), *Handbook of Organopalladium Chemistry for Organic Synthesis*, John Wiley and Sons Inc., New York, 2002, Vol 1, p3.
11. Cámpora, J., Palma, P. and Carmona, E., *Coord. Chem. Rev.*, 1999, **193 -195**, 207.
12. Chatt, J. and Shaw, B. L., *J. Chem. Soc.*, 1959, 4020.
13. McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1973, **95**, 4451.
14. McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6521.
15. Biefeld, C., Eick, H. A. and Grubbs, R. H., *Inorg. Chem.*, 1973, **12**, 4166.
16. Whitesides, G. M., Hackett, M., Brainard, R. L., Lavalleye, J. P. P. M., Sowinski, A. F., Izumi, A. N., Moore, S. S., Brown, D. W. and Staudt, E. M., *Organometallics*, 1985, **4**, 1819.
17. Dralle, K., Jaffa, N., L., le Roex, T., Moss, J. R., Travis, S., Watermeyer, N. D. and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865.
18. Sivaramakrishna, A., Hong, S. and Moss, J. R., *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 3543.

19. Mahamo, T., Zheng, F., Sivaramakrishna, A., Moss, J. R. and Smith, G., *J. Organomet. Chem.*, 2008, **693**, 103.
20. Sivaramakrishna, A., Makhubela, B. C. E., Moss, J. R. and Smith, G. S., *J. Organomet. Chem.*, 2010, **695**, 1627.
21. Sivaramakrishna, A., Hong, S. and Moss, J. R., *Dalton Trans.*, 2008, 2228.
22. Lappert, M. F., Martin, T. R., Raston, C. L. and White, A. H., *J. Chem. Soc., Dalton Trans.*, 1982, 1959.
23. (a) Hoberg, H. and Ricuter, W., *J. Organomet. Chem.*, 1980, **195**, 355. (b) Eisch, J. J. and Galle, J. E., *J. Organomet. Chem.*, 1975, **96**, C23. (c) Eisch, J. J., Piotowski, A. M., Aradi, A. A., Kruger, C. And Ramao, M. J., *Z. Naturforsch Teil B*, 1985, **40**, 624.
24. Gardner, S. A., Gordon, H. B. and Raush, M. D., *J. Organomet. Chem.*, 1973, **60**, 179.
25. Uson, R., Vicente, J., Cirac, J. A. and Chicote, M. T., *J. Organomet. Chem.*, 1980, **198**, 105.
26. Brune, H. A., Hohenadel, R., Schmidtberg, G. and Ziegler, U., *J. Organomet. Chem.*, 1991, **402**, 179.
27. (a) Debaedemaeker, T, Hohenadel, R., Brune, H. A., *J. Organomet. Chem.*, 1988, **350**, 109. (b) Debaedemaeker, T, Hohenadel, R., Brune, H. A., *J. Organomet. Chem.*, 1991, **410**, 265.
28. (a) Debaedemaeker, T., Roth, H. and Brune, H. A., *J. Organomet. Chem.*, 1991, **412**, 243. (b) Brune, H. A., Roth, H. and Schmidtberg, *J. Organomet. Chem.*, 1991, **412**, 237.
29. Brune, H. A., Roth, H., Debaedemaeker, T. and Schiebel, H. M., *J. Organomet. Chem.*, 1991, **402**, 435.
30. Plutino, M. R., Scolaro, L. M., Albinati, A. and Romeo, R., *J. Am. Chem. Soc.*, 2004, **126**, 6470.
31. Blanton, C. B., Murtaza, Z., Shaver, R. J. and Rillema, D. P., *Inorg. Chem.*, 1992, **31**, 3230.
32. Cornioley-Deuschel, C. and von Zelewsky, A., *Inorg. Chem.*, 1987, **26**, 3354.
33. Grubbs, R. H., Miyashita, A., Liu, M. and Burk, P., *J. Am. Chem. Soc.*, 1978, **100**, 2418.
34. (a) Fröhlich, H. O., Wyrwa, R., Görls, H. and Pieper, U., *J. Organomet. Chem.*, 1994, **471**, 23. (b) Fröhlich, H. O., Hilper, B. and Hofmann, B., *J. Organomet. Chem.*, 1992, **430**, 133. (c) Wyrwa, R., Fröhlich, H. O. and Görls, H., *J. Organomet. Chem.*, 1995, **491**, 41. (d) Wyrwa, R., Fröhlich, H. O. and Görls, H., *J. Organomet. Chem.*, 1995, **503**, 135. (e) Fröhlich, H. O., Wyrwa, R. and Görls, H., *Angew. Chem.*, 1993, **105**, 425. (f) Fröhlich, H. O., Wyrwa, R. and Görls, H., *J. Organomet. Chem.*, 1993, **456**, 7.

35. Rashidi, M., Esmailbeig, A. R., Shahabadi, N., Tangestaninejad, S and Puddephatt, R. J., *J. Organomet. Chem.*, 1998, **568**, 53.
36. Begum, R. A., Chanda, P., Ramakrishana, T. V. V. and Sharp, P. R., *J. Am. Chem. Soc.*, 2005, **127**, 13494.
37. Tinga, M. A. G. M., Schat, G., Akkerman, O. S., Bickelhaupt, F., Smeets, W. J. J. and Spek, A. L., *Chem. Ber.*, 1994, **127**, 1851.
38. Sharp, P. R., *J. Am. Chem. Soc.*, 2000, **122**, 9880.
39. Brown, J. J. and Sharp, P. R., *Organometallics*, 2003, **22**, 3604.
40. Chanda, N. and Sharp, P. R., *Organometallics*, 2007, **26**, 1635.
41. Robinson Jr., R and Sharp, P. R., *Organometallics*, 2010, **29**, 1388.
42. Cope, A. C and Siekman, R. W., *J. Am. Chem. Soc.*, 1965, **87**, 3272.
43. Jain, V. K. and Jain, L., *Coord. Chem. Rev.*, 2005, **249**, 3075.
44. Ghavale, N, Wadawale, A., Dey, S., Jain, V. K., *J. Organomet. Chem.*, 2010, **695**, 2296.
45. (a) Herrmann, W. A., Brossmer, C., Ofele, K., Reisinger, C.-P., Priermeier, T., Beller, M. and Fischer, H., *Angew. Chem. Int. Ed.*, 1995, **34**, 1844. (b) Rumin, R., *J. Organomet. Chem.*, 1983, **247**, 351.
46. (a) Espinet, P., Esteruelas, M. A., Oro, L. A., Serrano, J. L. and Sola, E., *Coord. Chem. Rev.*, 1992, **117**, 215. (b) Ghedini, M., Pucci, D., Crispini, A. and Barberio, G., *Organometallics*, 1999, **18**, 2116.
47. (a) Williams, J. A. G., Develay, S., Rochester, D. L. and Murphy, L., *Coord. Chem. Rev.*, 2008, **252**, 259. (b) Brooks, J., Babayan, Y. m Lamansky, S., Djurovich. P. I., Tsyba, I., Bau, R. and Thomson, M. E., *Inorg. Chem.*, 2002, **41**, 3055.
48. Ryabov, A., *Chem. Rev.*, 1990, **90**, 403 and references therein.
49. (a) Grice, K. A., Kaminsky, W. and Goldberg, K. I., *Inorg. Chimica Acta*, 2011, **369**, 76. (b) Arndtsen, B. A., Bergman, R. G., Mobley, T. A. and Peterson, T. H., *Acc. Chem. Res.*, 1975, **28**, 154. (c) Gol'dshleger, N.F., Es'kova, V.V., Shilov, A.E. and Shteinman, A.A., *Zhu. Fiz. Khim.*, 1972, **46**, 1353. (d) Lersch, M. and Tilset, M., *Chem. Rev.*, 2005, **105**, 2471.
50. Dehand, J. and Pfeffer, M., *Coord. Chem. Rev.*, 1976, **18**, 327.
51. Newkome, G. R., Puckett, W. E., Gupta, U. and Keifer, G. E., *Chem. Rev.*, 1986, **86**, 451.
52. Carmona, E., Gutierrez-Puebla, E., Marin, J. M., Monge, A., Paneque, M., Poveda, M. L. and Ruiz, C., *J. Am. Chem. Soc.*, 1989, **111**, 2883.
53. (a) Moore, S. S., DiCosimo, R., Sowinski, A. F. And Whitesides, G. M., *J. Am. Chem. Soc.*, 1981, **103**, 948. (b) DiCosimo, R., Moore, S. S., Sowinski, A. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1982, **104**, 124.

54. (a) Griffiths, D. C. and Young, G. B., *Organometallics*, 1989, **8**, 875. (b) Griffiths, D. C. and Young, G. B., *Polyhedron*, 1983, **2**, 1095.
55. (a) Chappell, S. D. and Cole-Hamilton, D. J., *J. Chem. Soc., Dalton Trans.*, 1983, 1051. (b) Chappell, S. D. and Cole-Hamilton, D. J., *J. Chem. Soc., Chem. Commun.*, 1980, 38.
56. Ankianec, B. C., Hardy, D. T., Thomson, S. K., Watkins, W. N. and Young, G. B., *Organometallics*, 1992, **11**, 2591.
57. Tipper, C. F. H., *J. Chem. Soc.*, 1955, 2045.
58. Jennings, P. W. and Johnson, L. L., *Chem. Rev.*, 1994, **94**, 2241.
59. Pudephatt, R. J., Quyser, M. A. and Tipper, C. F. H., *J. Chem. Soc., Chem. Commun.*, 1976, 626.
60. McQuillin, F. J., Powell, K. G., *J. Chem. Soc., Dalton Trans.*, 1972, 2123.
61. Stocker, B. L. and Hoberg, J. O., *Organometallics*, 2006, **25**, 4537.
62. Forcolin, S., Pellicer, G., Graziani, M., Lenarda, M. and Ganzerla, L., *J. Organomet. Chem.*, 1980, **194**, 203.
63. Lenard, M., Bresciani-Phor, N., Calligaris, M., Randaccio, L. and Graziani, M., *Inorg. Chimica Acta*, 1978, **26**, 29.
64. Wong, W., Singer, S. J., Pitts, W. D., Watkins, J. F. and Baddley, W. H., *J. Chem. Soc., Chem. Commun.*, 1972, 672.
65. Burges, J., Haines, R. I., Kemmit, R. D. W. and Smith, I. M. A. R., *J. Chem. Soc., Dalton Trans.*, 1975, 2579.
66. Visser, J. P., Schipperijn, A. J. and Lukas, J., *J. Organomet. Chem.*, 1973, **47**, 433.
67. Tsutsumi, K., Sakai, H., Sakonaka, K., Yabukami, T., Takahashi, Y., Nakagai, Y., Mirimoto, T., Tabata, K. and Kakiuchi, K., *Eur. J. Inorg. Chem.* **2010**, 2361–2368.
68. Stang, P. J., Song, L. and Halton, B., *J. Organomet. Chem.*, 1990, **388**, 215.
69. Evans, J. A., Everitt, G. F., Kemmitt, R. D. and Russel, D. R., *J. Chem. Soc., Chem. Commun.*, 1973, 158.
70. Hamner, E. R., Kemmitt, R. D. and Smith, M. A., R., *J. Chem. Soc., Chem. Commun.*, 1974, 841.
71. Grabowski, N. A., Hughes, R. P., Jaynes, B. S. and Rheingold, A. L., *J. Chem. Soc., Chem. Commun.*, 1986, 1694.
72. Browning, J., Green, M., Laguna, A., Smart, L. E., Spencer, J. E. and Stone, F. G. A., *J. Chem. Soc., Chem. Commun.*, 1975, 723.
73. (a) Briggs, J. R., Hagen, H., Julka, S. and Patton, J. T., *J. Organomet. Chem.*, 2011, **696**, 1677. (b) Jabri, A. and Budzelaar, P. H. M. *Organometallics*, 2011, **30**, 1374. (c) Tschan, M. J.-L., Lopez-Valbuena, J.-M., Freixa, Z., Launay, H., Hagen, H., Benet-Buchholz, J., and van Leeuwen, P. W. N. M., *Organometallics*, 2011, **30**, 792.

74. Muller, C., Lachicotte, R. J. and Jones, W. D., *Organometallics*, 2002, **21**, 1118.
75. (a) Baker, G. K., Green, M., Howard, J. A. K. and Stone, F. G. A., *J. Chem. Soc., Dalton Trans.*, 1978, 1839. (b) Baker, G. K., Green, M., Howard, J. A. K., Spencer, J. L. and Stone, F. G. A., *J. Am. Chem. Soc.*, 1976, **98**, 3373. (c) Benn, R., Jolly, P. W., Joswig, T., Mynott, R. and Schick, K.-P., *Zeitschrift fuer Naturforschung, Teil B: Anorganische Chemie, Organische Chemie*, 1986, **41**, 680.
76. Green, M., Howard, J. A. K., Mitprachachon, P., Pfeffer, M., Spencer, J. L. and Stone, F. G. A., *J. Chem. Soc., Dalton Trans.*, 1979, 306.
77. Szabo, A. A. K. J., Castana, A. M. and Backwell, J.-E., *Organometallics*, 1997, **16**, 1058.
78. (a) Hoffmann, H. R. M., Otte, A. R., Wilde, A., Menzer, S. and Williams, D. J., *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 100. (b) Carfagna, C., Galarini, R., Musco, A. and Santi, R., *Organometallics*, 1991, **10**, 3956. (c) Carfagna, C., Galarini, R., Linn, K., Lopez, J. A., Mealli, C. and Musco, A., *Organometallics*, 1993, **12**, 3019.
79. (a) Aranyos, A., Szabo, K. J., Castano, A. M. and Backvall, J. E., *Organometallics*, 1997, **16**, 1058. (b) Plantevin, V., Blosser, P. W., Galluci, J. C. and Wojcicki, A., *Organometallics*, 1994, **13**, 3651. (c) Huang, T. M., Hsu, H. R., Yang, C. S., Chen, J. T., Lee, G. H. and Wang, Y., *Organometallics*, 1994, **13**, 3657. (d) Blosser, P. W., Schimpff, D. G., Galluci, J. C. and Wojcicki, A., *Organometallics*, 1993, **12**, 1993.
80. Zheng, F. Sivaramakrishana, A. and Moss, J. R., *Coord. Chem. Rev.*, 2007, **251**, 2056.
81. (a) Tobisch, S. and Ziegler, T., *Organometallics*, 2005, **24**, 256. (b) de Bruin, T. J. M., Magna, L., Raybaud, P. and Toulhoat, H., *Organometallics*, 2003, **22**, 3404. (c)
82. Huang, X., Zhu, J. and Lin, Z., *Organometallics*, 2004, **23**, 4154.
83. (a) Miller, T. M. and Whitesides, G. M., *Organometallics*, 1986, **5**, 1473. (b) Young, G. B. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1978, **100**, 5808.
84. DiCosimo, R. and Whitesides, G.M., *J. Am. Chem. Soc.*, 1982, **104**, 3601.
85. Burton, J. T. and Puddephatt, R. J., *Organometallics*, 1986, **5**, 1312.
86. Ling, S. M. and Puddephatt, R. J., *J. Chem. Soc., Chem. Commun.*, 1982, 412.
87. Fischer, W., Hembre, R. T., Sidler, D. R. and Norton, J. R., *Inorg. Chimica Acta*, 1992, **198 – 200**, 57.
88. Grubbs, R. H. and Miyashita, A., *J. Am. Chem. Soc.*, 1978, **100**, 7418.
89. (a) Su, S. R. and Wojcicki, *J. Organomet. Chem.*, 1971, **27**, 231. (b) Calderazzo, F. and Cotton, F., *Inorg. Chem.*, 1962, **1**, 30. (c) Berke, H. and Hoffmann, R., *J. Am. Chem. Soc.*, 1978, **100**, 7224. (d) Behr, A., Kanne, U. and Thelen, G., *J. Organomet. Chem.*, 1984, **269**, C1. (e) Bent, T. L. and Cotton, J. D., *Organometallics*, 1991, **10**, 3165. (f) Calderazzo, *Angew. Chem. Int. Ed. Engl.*, 1977, **16**, 299.
90. Nozaki, K. Hiyama, T., Kacker, S. and Horvath, I. T., *Organometallics*, 2000, **19**, 2031.

91. Klinger, R. J., Huffman, J. C. and Kochi, J. K., *J. Am. Chem. Soc.*, 1982, **104**, 2147.
92. Chiu, K. W., Fawcett, J., Henderson, W., Kemmit, R. D. W. and Russell, D. R., *J. Chem. Soc., Dalton Trans.*, 1987, 733.
93. Tsuchiya, K., Kondo, H. and Nagashima, H., *Organometallics*, 2007, **26**, 1044.
94. Yamazaki, H., Aoki, K., Yamamoto, Y. and Wakatsuki, Y., *J. Am. Chem. Soc.*, 1975, **97**, 3546.
95. Hsiao, J. and Su, M.-D., *Organometallics*, 2008, **27**, 4139.
96. Stephan, C., Munz, C. and tom Dieck, H., *J. Organomet. Chem.*, 1994, **468**, 273.
97. Skupinska, J., *Chem. Rev.*, 1991, **91**, 613.
98. (a) Peitz, S., Aluri, B. R., Peulecke, N., Muller, B. H., Wohl, A., Muller, W., Al-Hazmi, M. H., Mosa, F. M. and Rosenthal. U., *Chem. Eur. J.*, 2010, **16**, 7670. (b) Young, J. F., Yap, G. P. A. and Theopold, K. H., 234th ACS National Meeting 2007, Boston, INORG 554. (c) Rebestorf, B. and Larsson, R., *J. Mol. Catal.*, 1981, **11**, 247. (d) Espelid, O. and Borge, K. J., *J. Catal.*, 2002, **206**, 331.

CHAPTER 3

IMINOPHOSPHINE LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES

3.1 INTRODUCTION

Ligands with phosphorus(III) donor atoms represent the most widely used ligand class in homogeneous catalysis, owing to their synthetic stability and the ease with which their properties can be modified.¹ They are especially attractive ligands for the design of catalysts based on late transition metals as the strong bonds between phosphorus and late metals provide for the stabilization of reactive (unstable) intermediates that form during catalytic cycles.² For example, the use of phosphine ligands in palladium-catalyzed reactions has often circumvented catalyst deactivation by inhibiting the formation of palladium black. In addition, complexes with phosphine ligands are often air and moisture stable, making their preparation and handling relatively easy, and avoiding formation of phosphine oxides due to the strong interaction between the lone pair on the phosphorus atom and the metal centre.^{2,3} This stability towards air and moisture offers the possibility of using these complexes in aqueous media, which is an especially attractive feature as the focus of industrial and academic research is shifting towards more environmentally friendly processes. By choosing the appropriate ligand, the properties and structures of the organometallic and coordination complexes they form can be readily modified.

Complexes of chelating ligands are often more stable than their monodentate counterparts. In addition to the enhanced stability, asymmetry and chirality can be introduced into chelating ligands and their complexes through the use of chiral backbones/substituents and different donor atoms.¹ Developments in the field of functionalized phosphine chemistry continue to draw attention because understanding how these ligands coordinate to metals aids in understanding their influence on the stereoelectronic properties of their complexes.⁴

The past 20 – 30 years have seen considerable interest in metal complexes of bidentate ligands containing both hard and soft donor atoms, in particular where the soft donor is phosphorus and the hard donor is nitrogen.^{5,6} These ligands combine strong coordination via the phosphorus with a hemilabile donor for stabilization of intermediates via the nitrogen donor during the catalytic cycle.⁷ Of the most widely studied bidentate P[^]N ligands are the pyridylphosphines and iminophosphines, whose complexes with palladium,⁸ platinum,⁵ rhodium,⁹ ruthenium,¹⁰ and iridium¹¹ have been reported. Other common ligand classes include aminophosphines,¹² diphenylphosphinomethyl-oxazolines and

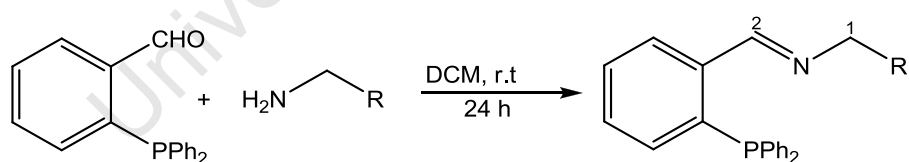
diphenylphosphinomethyl-thiazolines.¹³ The application of such complexes in various catalytic processes has been widely reported and reviewed.^{14,15} These complexes have added great value to the repertoire of transition metals used in a variety of catalytic applications. In fact, there are instances where complexes of bidentate P^N ligands are catalysts of choice. Important examples include carbonylation of alkynes,¹⁶ asymmetric hydrogenation of highly substituted alkenes,¹⁷ asymmetric allylic alkylation,¹⁸ asymmetric hydrocarbonylation,¹⁹ Stille coupling,²⁰ and nickel-catalyzed cycloaddition reactions.²¹

This chapter describes the synthesis and characterization of iminophosphine ligands as well as their neutral [(iminophosphine)palladium(II)(X₂)], where X = Cl or Me, and [(iminophosphine)platinum(II)(Cl₂)] complexes. The compounds were characterized using various analytical and spectroscopic techniques such as ¹H, ¹³C and ³¹P NMR spectroscopy, FTIR spectroscopy, mass spectrometry and elemental analysis. Single crystal structure determination was done for selected palladium and platinum complexes.

3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis and Characterization of Iminophosphine Ligands (3.1 – 3.6)

A convenient method for the preparation of phosphines with P^N donor sets is the condensation of phosphine-substituted aldehydes with amines/hydrazines. This method often proceeds cleanly to give the desired products in quantitative yields.⁶ The iminophosphine ligands in this study were synthesized by a Schiff-base condensation reaction of the commercially available 2-diphenylphosphinobenzaldehyde and the appropriate primary amines (Scheme 3.1).²²



Ligand	R
3.1	Phenyl
3.2	4-Tolyl
3.3	2-Furfuryl
3.4	2-Thionyl
3.5	3-Pyridyl
3.6	Mesityl

Scheme 3.1: Synthesis of iminophosphine ligands 3.1 – 3.6.

The Schiff-base condensation reactions were carried out in DCM in the presence of either Na₂SO₄ or MgSO₄ to remove the water that is formed as a by-product in the reaction. After filtration, the solution was concentrated under reduced pressure, and the crude products

were obtained as yellow/pale orange oils. Solution of the oily materials in hot hexane followed by filtration and cooling to -16 °C overnight yielded the desired ligands as cream-white or pale orange solids (**3.1**, **3.3** – **3.5**) or orange oils (**3.2**, **3.6**). All ligands were obtained as air stable materials in moderate to excellent yields (Table 3.1).

The compounds were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy, FTIR spectroscopy, mass spectrometry and elemental analysis (Table 3.2). The data obtained for these compounds confirmed the proposed structures, and was found to be in agreement with data reported for similar compounds in the literature.

Table 3.1: Isolated yields and melting point and microanalysis data for ligands **3.1** – **3.6**

Ligand	R	Yield	Melting Point (°C)	Microanalysis ^a		
				C	H	N
3.1	Phenyl	96	79 – 80 ²³	82.56 (82.33)	6.11 (5.90)	3.89 (3.91)
3.2	4-Tolyl	81	Oil	82.47 (82.42)	6.61 (6.15)	3.54 (3.56)
3.3	2-Furfuryl	69	75 – 77	77.98 (78.03)	5.51 (5.64)	3.75 (3.79)
3.4	2-Thionyl ^b	64	71 – 72	74.41 (74.78)	5.30 (5.23)	3.59 (3.63)
3.5	3-Pyridyl	74	79 – 81	78.95 (78.93)	5.57 (5.56)	7.32 (7.36)
3.6	Mesityl	77	Oil	82.59 (82.63)	6.65 (6.70)	3.29 (3.32)

^aExpected values in parenthesis. ^bMicroanalytical data for S: 8.28 (8.32).

3.2.1.1 NMR Spectroscopy for **3.1** – **3.6**

The ¹H NMR spectra of the ligands were consistent with the proposed structures and were found to be in agreement with similar compounds reported in the literature.^{24,25}

Product formation was indicated by the disappearance of the signal at δ 10.49 ppm, which is due to the aldehyde proton in 2-diphenylphosphinobenzaldehyde. This was accompanied by the appearance of a doublet in the region δ 8.98 – 9.05 ppm ($J_{HP} = 5.0 - 5.7$ Hz). This doublet is assigned to the imine proton (H2 in Scheme 3.1) and the phosphorus coupling observed is presumably due to through-space coupling, indicating that the preferred conformation of the free ligands is one in which the imine proton points towards the lone pair on the phosphorus atom (Figure 3.1).^{25a,25f} The methylene protons (H1) appear as a singlet in the region δ 4.64 – 4.87 ppm.^{25b,25c} The methyl proton in the 4-tolyl derivative (**3.2**) appears as a singlet integrating for three protons at 2.34 ppm while the methyl protons in the mesityl derivative (**3.6**) appear as singlets integrating for six and three protons at 2.25 ppm and 2.41 ppm respectively. The aromatic protons (phenyl, pyridyl, thiophenyl and furfuryl) appear in the region δ 6.03 – 8.41 ppm as expected (Table 3.2). Figure 3.2 shows the ¹H NMR spectrum of ligand **3.1** with the diagnostic signals for the methylene protons H1 and imine proton H2 highlighted.

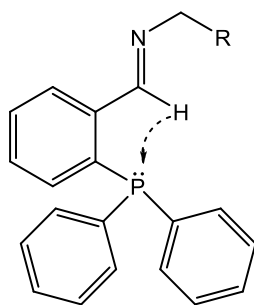


Figure 3.1: Ligand structure showing through-space coupling of the imine proton with phosphorus.

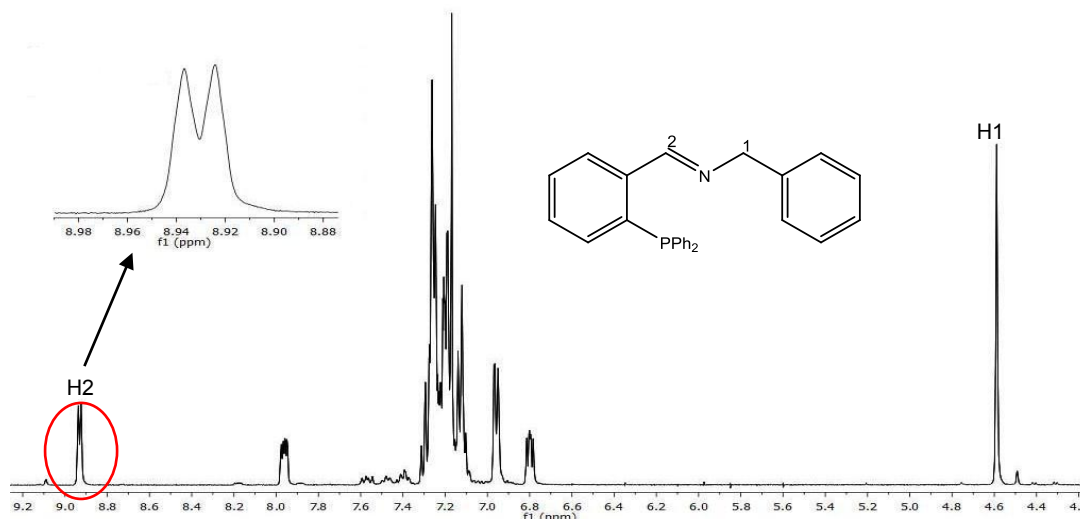


Figure 3.2: ^1H NMR spectrum of ligand **3.1**.

The ^1H NMR results were supported by the data obtained from the ^{13}C NMR spectra of the ligands. Formation of the imine functionality was unambiguously confirmed by the appearance of a doublet ($^3J_{\text{CP}} = 21.1 - 23.4$ Hz) in the region δ 158.9 – 161.4 ppm, which is due to the imine carbon (C2) in Scheme 3.1.^{25a} In addition the benzaldimino and phenyl carbon signals (for the PPh_2 groups) were observed as doublets, indicating that these carbons also couple with the phosphorus atom. The signals for the methylene carbons (C2) appear as a singlet in the region δ 57.6 – 65.1 ppm.^{25a,25b} The methyl carbon in the 4-tolyl derivative **3.5** appears at δ 21.9 ppm, while the methyl carbons in the mesityl derivative **3.6** appear at 19.5 ppm and 21.0 ppm. Signals for the aromatic carbons (phenyl, mesityl, tolyl, pyridyl, furan and thiophenyl) appear in the region 106.9 ppm – 143.2 ppm. The degree of substitution on the phenyl ring of the pendant R group appears to have influence on the shielding experienced by the methylene carbon C1. The shielding effect on this carbon increases with increased electron density on the phenyl ring in the order phenyl < tolyl < mesityl. The signal for this carbon atom appears at 65.1 ppm for ligand **3.1** (R = Ph) whereas this signal appears at 57.6 ppm for ligand **3.6** (R = Mes).

The disappearance of the signal at -11.7 ppm (due to the phosphine in 2-diphenylphosphinobenzaldehyde) and the appearance of only one new singlet in the region

δ -13.4 – -14.5 ppm in the ^{31}P NMR spectra of the ligands further confirmed the formation of the desired iminophosphine ligands (Table 3.2). Analysis of the ligands by ^{31}P NMR also provided valuable insight into the oxidation state of the phosphorus atom of the iminophosphine ligands as phosphorus has distinct chemical shifts in the +3 and +5 oxidation states. In the low +3 oxidation state, high field signals are usually observed whereas for the +5 oxidation state low field signals are expected. This observation is in agreement with reports for similar compounds.^{9,25} The appearance of only one signal indicates the formation of only one product.

3.2.1.2 FTIR Spectroscopy for 3.1 – 3.6

Reaction progress was also followed by IR spectroscopy. A successful reaction is indicated by the disappearance of the carbonyl stretching frequency in the region $1700 - 1800 \text{ cm}^{-1}$ and the appearance of new strong bands in the region $1634 - 1636 \text{ cm}^{-1}$, which are due to the imine stretching vibrations (Table 3.1).^{5,24,25a,25f}

3.2.1.3 Mass Spectrometry and Microanalysis for 3.1 – 3.6

Microanalytical and mass spectral data obtained confirmed the proposed formulations for the ligands. The parent ion, $[\text{M}]^+$ was obtained as the highest molecular weight fragment in all cases (Table 3.2).

Table 3.2: Characterization data for ligands 3.1 – 3.6

Ligand	R	Formula	$\nu_{\text{C=N}}^{\text{a}}$ (cm^{-1})	$\delta_{\text{H}}(\text{H1})$ (ppm)	$\delta_{\text{H}}(\text{H2})$ (ppm)	$\delta_{\text{C}}(\text{C1})$ (ppm)	$\delta_{\text{C}}(\text{C2})$ (ppm)	δ_{P} (ppm)	$[\text{M}+\text{H}]^+$ (calc) m/z
3.1	Phenyl	$\text{C}_{26}\text{H}_{22}\text{NP}$	1636	4.67	9.05 (d, $J = 5.0$ Hz)	65.1	160.6 (d, $^3J_{\text{CP}} = 22.3$ Hz)	-13.8 (s)	379.18 (379.43)
3.2	4-Tolyl	$\text{C}_{27}\text{H}_{24}\text{NP}$	1635	4.64	9.00 (d, $J = 5.1$ Hz)	60.9	161.3 (d, $^3J_{\text{CP}} = 22.9$ Hz)	-13.6 (s)	392.79 (393.46)
3.3	2-Furfuryl	$\text{C}_{24}\text{H}_{20}\text{NOP}$	1635	4.65	8.98 (d, $J = 5.2$ Hz)	57.0	161.4 (d, $^3J_{\text{CP}} = 23.1$ Hz)	-14.5 (s)	369.81 (369.40)
3.4	2-Thionyl	$\text{C}_{24}\text{H}_{20}\text{NPS}$	1634	4.86	9.01 (d, $J = 5.1$ Hz)	59.9	160.8 (d, $^3J_{\text{CP}} = 23.4$ Hz)	-14.5 (s)	385.51 (385.46)
3.5	3-Pyridyl	$\text{C}_{25}\text{H}_{21}\text{N}_2\text{P}$	1634	4.67	8.98 (d, $J = 5.7$ Hz)	62.3	161.3 (d, $^3J_{\text{CP}} = 21.1$ Hz)	-13.4 (s)	379.92 (380.42)
3.6	Mesityl	$\text{C}_{29}\text{H}_{28}\text{NP}$	1636	4.90	8.98 (d, $J = 5.1$ Hz)	57.6	158.9 (d, $^3J_{\text{CP}} = 23.0$ Hz)	-13.5 (s)	422.36 (421.51)

^aIR spectra recorded as KBr pellets.

Table 3.3: Isolated yields and melting point data for complexes 3.7 – 3.12

Complex	R	Yield	Melting Point ($^{\circ}\text{C}$)	Microanalysis ^a		
				C	H	N
3.7	Phenyl	75	199 – 202	55.99 (56.09)	3.78 (3.98)	2.50 (2.54)
3.8	4-Tolyl	50	173 – 175	56.84 (56.81)	4.28 (4.24)	2.39 (2.45)
3.9	2-Furfuryl	72	198 – 199	52.75 (52.72)	3.71 (5.64)	2.56 (2.56)
3.10	2-Thionyl ^b	65	232 – 234	51.33 (51.22)	3.56 (3.58)	2.48 (2.49)
3.11	3-Pyridyl	63	209 – 211	53.91 (53.84)	3.84 (3.80)	4.98 (5.02)
3.12	Mesityl	67	186 – 189	58.37 (58.16)	4.27 (4.17)	2.31 (2.34)

^aExpected values in parenthesis. ^bMicroanalytical data for S: 5.67 (5.70).

3.2.2 Synthesis and Characterization of Palladium Dichloride Complexes (3.7 – 3.12)

A ligand displacement reaction between $[\text{Pd}(\text{COD})\text{Cl}_2]$ and the appropriate P[^]N ligands gave the desired iminophosphine palladium dichloride complexes (Scheme 3.2).²²



Complex	R
3.7	Phenyl
3.8	4-Tolyl
3.9	2-Furfuryl
3.10	2-Thionyl
3.11	3-Pyridyl
3.12	Mesityl

Scheme 3.2: Synthesis of palladium dichloride complexes 3.7 – 3.12.

The DCM solutions were stirred at room temperature overnight, during which time a yellow precipitate formed. At the end of the reactions, the yellow mixtures were concentrated under reduced pressure, filtered and the yellow solids obtained were washed with cold DCM. The products were obtained in moderate to good yields (Table 3.3). The complexes were characterized by ^1H and ^{31}P NMR spectroscopy, FTIR spectroscopy, elemental analysis and mass spectrometry (Table 3.4).

3.2.2.1 NMR Spectroscopy for complexes 3.7 – 3.12

The palladium dichloride complexes proved to be highly insoluble in common organic solvents. As a result, ^1H and ^{31}P NMR spectroscopy for these complexes was performed on $\text{DMSO}-d_6$ suspensions of the material. Due to their insoluble nature, ^{13}C NMR spectroscopy could not be performed.

Coordination of the iminophosphine ligands to the metal centre was shown by the upfield shift of the signal for the imine protons (H2) from δ 8.98 – 9.05 ppm in the free ligands to δ 8.52 – 8.84 ppm in the palladium complexes (Table 3.4), indicating the participation of the imine moiety in ligand coordination to palladium. This upfield shift is thought to be due to back-bonding from the palladium centre to the imine moiety. In addition, this signal appears as a singlet as opposed to the doublet observed for the same protons in the free ligands, which is a common observation for complexes of this type.^{22d} This could be attributed to the ligands being locked in a conformation in which the imine carbon points away from the phosphine group upon coordination to the metal centre. This conformational change was suggested by Liu and co-workers, who proposed that this unexpected upfield shift of the

imine proton signal could be due to the change in the conformation of the ligand in order to facilitate coordination of the imine nitrogen to the metal center.²⁶ A downfield shift of the signal for the methylene protons (H1) from δ 4.63 – 4.87 ppm in the free ligands to δ 5.48 – 5.69 ppm in the palladium complexes was observed (Table 3.4). This downfield shift can be attributed to the imine group coordinating to the metal centre thereby resulting in the deshielding of these neighbouring methylene protons.^{23,25a} This downfield shift further confirms the involvement of the imine moiety in the bidentate coordination of the ligand to the metal centre.

As expected, the signals for the phenyl and pyridyl protons appear in the region δ 6.98 – 8.89 ppm. The appearance of the signals for the thiophenyl and furfuryl groups at δ 6.44 – 7.08 ppm indicates that these groups do not coordinate to the metal centre as these signals appear in a similar region in the free ligands (6.03 – 7.17 ppm).

Further evidence for complex formation between the iminophosphine ligands and the palladium centre is obtained from the ³¹P NMR spectra of the complexes. A significant downfield shift (about 50 ppm) of the phosphine signals from δ -14.5 – -13.4 ppm in the free ligands to δ 30.8 – 35.2 ppm in the palladium complexes is observed (Table 3.4).^{22d,27} Appearance of only one signal in the ³¹P NMR spectra further confirms formation of only one product.

3.2.2.2 FTIR Spectroscopy for 3.7 – 3.12

Further confirmation of ligand coordination to the metal centre comes from IR data obtained for the complexes. The peaks which convey the most important information are those due to the $\nu_{(C=N)}$, which occur as strong peaks between 1624 cm⁻¹ and 1628 cm⁻¹ in the complexes (Table 3.4). Upon coordination, there is a distinct bathochromic shift of between 8 and 11 cm⁻¹ with respect to the free ligands, which is typical for coordinated imines of this type.²⁸

3.2.2.3 Mass Spectrometry and Microanalysis for 3.7 – 3.12

Good microanalytical and mass spectral data were obtained for the complexes (Table 3.4). The microanalytical data obtained corresponds to the proposed structures while the mass spectral data for the complexes showed [M-Cl]⁺ as the highest molecular weight fragment. This observation is consistent with what has been observed for other chloride complexes of iminophosphines.^{24,29,30}

Table 3.4: Characterization data for palladium dichloride complexes **3.7 – 3.12**^a

Complex	R	Formula	$\nu_{C=N}^b$ (cm^{-1})	$\delta_H(\text{H1})$ (ppm)	$\delta_H(\text{H2})$ (ppm)	δ_P (ppm)	$[\text{M}]^+$ (calc) m/z ^c
3.7	Phenyl	$\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{NPPd}$	1628 (1636)	5.48 (s) (4.70)	8.84 (s) (9.05)	34.1 (s) (-13.8)	522.01 (521.31)
3.8	4-Tolyl	$\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{NPPd}$	1628 (1635)	5.47 (s) (4.64)	8.84 (s) (9.00)	30.7 (s) (-13.6)	536.27 (535.33)
3.9	2-Furfuryl	$\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NOPPd}$	1626 (1635)	5.54 (s) (4.64)	8.79 (s) (8.98)	31.3 (s) (-14.5)	511.94 (511.27)
3.10	2-Thionyl	$\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NPPdS}$	1627 (1634)	5.69 (s) (4.87)	8.52 (s) (9.01)	35.2 (s) (-14.5)	527.99 (527.31)
3.11	3-Pyridyl	$\text{C}_{24}\text{H}_{21}\text{Cl}_2\text{N}_2\text{PPd}$	1624 (1634)	5.58 (s) (4.63)	8.61 (s) (8.98)	30.8 (s) (-13.4)	523.21 (522.29)
3.12	Mesityl	$\text{C}_{29}\text{H}_{28}\text{Cl}_2\text{NPPd}$	1630 (1636)	5.50 (s) (4.90)	8.71 (s) (8.98)	31.9 (s) (-13.5)	564.26 (563.39)

^aLigand data in parenthesis. ^bIR spectra recorded as KBr pellets. ^c $[\text{M}]^+$ represents m/z for the fragment $[\text{M}-\text{Cl}]^+$.

3.2.3 Synthesis and Characterization of Palladium Methyl Chloride Complexes (3.13 – 3.18)

The reaction of [Pd(COD)MeCl] and the appropriate ligands gave the desired palladium methylchloride complexes (Scheme 3.3).



Complex	R
3.13	Phenyl
3.14	4-Tolyl
3.15	2-Furfuryl
3.16	2-Thionyl
3.17	3-Pyridyl
3.18	Mesityl

Scheme 3.3: Synthesis of palladium methylchloride complexes **3.13 – 3.18**.

The DCM solutions were stirred at room temperature overnight. Upon completion of the reactions, excess solvent was removed under reduced pressure and the crude products obtained were recrystallised from DCM and hexane. The products were obtained as air and moisture-stable crystalline solids in good yields (Table 3.5).

Table 3.5: Isolated yields, melting point and microanalysis data for **3.13 – 3.18**

Complex	R	Yield	Melting Point (°C)	Microanalysis ^a		
				C	H	N
3.13	Phenyl	65	169 – 171	60.51 (60.46)	4.73 (4.70)	2.57 (2.61)
3.14	4-Tolyl	79	122 – 124	61.54 (61.10)	5.00 (4.94)	2.51 (2.54)
3.15	2-Furfuryl	71	193 – 195	57.56 (57.05)	4.39 (4.40)	2.98 (2.66)
3.16	2-Thionyl ^b	73	188 – 190	55.42 (55.36)	4.25 (4.27)	2.31 (2.58)
3.17	3-Pyridyl	72	180 – 182	58.52 (58.12)	4.56 (4.50)	5.13 (5.21)
3.18	Mesityl	79	135 - 138	62.33 (62.29)	5.42 (5.40)	2.39 (2.42)

^aCalculated values in parenthesis. ^bMicroanalytical data for S: 5.87 (5.91).

The complexes were characterized using spectroscopic and analytical techniques, and the data obtained is in agreement with the proposed structures. Similar trends are observed in the data for both the palladium dichloride (**3.7 – 3.12**) and palladium methylchloride complexes (**3.13 – 3.18**).

3.2.3.1 NMR Spectroscopy for complexes 3.13 – 3.18

In the ^1H NMR spectra of the methyl chloride complexes, the signals for the imine protons (H2) appear as singlets in the region δ 8.16 – 8.80 ppm. Upon ligand coordination there is an upfield shift from δ 8.98 – 9.05 ppm (observed in the free ligand) and this upfield shift has been attributed to the conformational change that occurs in the ligand upon chelation.^{22d,24,31} As in the dichloride complexes, a downfield shift from δ 4.64 – 4.87 ppm in the free ligands to δ 5.09 – 5.49 ppm in the complexes is observed for the methylene protons (N-CH₂-R) upon chelation. This downfield shift is attributed to the deshielding that occurs for these protons when the adjacent imine group coordinates to the metal centre. A slightly greater downfield shift (to δ 5.47 – 5.69 ppm) was observed for the same protons in the palladium dichloride complexes due to the deshielding that occurs for these protons when the adjacent imine group coordinates to the metal centre. The deshielding is, therefore, more significant for the palladium dichloride complexes as there is less electron density on the metal centre in the dichloride complexes due to the electronegative chlorido- ligands than there is in the analogous palladium methyl chloride complexes. As in the dichloride complexes, there is only a slight effect on the signals for the thiophenyl and furfuryl protons, indicating that these groups do not participate in coordinating to the metal centre.

The signals for the methyl protons in Pd-Me appear as doublets in the region δ 0.21 - 0.61 ppm, with coupling constants $^3J_{\text{HP}} = 2.4 - 3.2$ Hz. As a result of the different *trans* influence of the two donor atoms in the ligands, the phosphine is expected to coordinate *trans* to the chlorido ligand. This coordination mode is demonstrated by the small coupling constants between the phosphorus and the Pd-Me protons.^{24,30,32}

In the ^{13}C NMR spectrum of the methyl chloride complexes, the signals for the imine carbons are found in the region 162.4 – 164.7 ppm (Table 3.6). This is a downfield shift from 160.6 – 161.4 ppm observed for the free ligands, further confirming the coordination of the imine group to the metal centre.^{22d} On the contrary, there is an upfield shift of 1.5 – 3.2 ppm with respect to the free ligand in the signals for the methylene carbons (C1) upon coordination to the metal centre.^{25a} The signals for the Pd-Me carbons occur as singlets at δ 0.62 – 2.9 ppm, which is comparable to similar complexes.³⁰

The downfield shift of the phosphine signals from -13.4 – -14.5 ppm in the free ligands to 37.4 – 38.3 ppm in the ^{31}P NMR spectra of the complexes reflects the coordination of the phosphine end of the ligand to the palladium atom.^{24,26,33} This downfield shift is slightly more significant for the methyl chloride complexes (51.0 – 52.1 ppm) than it is for the analogous dichloride complexes (44.2 – 49.7 ppm). The presence of only one signal in the ^{31}P NMR

spectra indicates the formation of only one product. For both palladium dichloride and methyl chloride complexes, the significant downfield shift of the phosphorus signals from *ca.* -14 ppm in the free ligands to *ca.* 30 ppm and *ca.* 38 ppm is due to the effect of coordination to the metal centre, as well as the fact that the phosphorus atom is contained in a ring system.³⁴

3.2.3.2 FTIR Spectroscopy for 3.13 – 3.18

In contrast to their dichloride analogues, the IR spectra of complexes **3.13** – **3.18** show strong peaks for the imine stretch vibrations in region 1635 – 1638 cm^{-1} , which is a slight hypsochromic shift with respect to the free ligands (1634 – 1636 cm^{-1}). Similar observations have been made for similar methyl chloride complexes of transition metals.^{27,28}

3.2.3.3 Mass Spectrometry and Microanalysis for 3.13 – 3.18

Good microanalytical and mass spectral data were obtained for the complexes (Table 3.6). The microanalytical data obtained correspond to the proposed structures. As in the dichloride complexes, the mass spectral data for the complexes showed $[\text{M-Cl}]^+$ as the highest molecular weight fragment. This observation is consistent with what has been observed for other methyl chloride complexes of iminophosphines.^{29,30}

3.2.3.4 X-ray Structure Determination for Complex 3.14

Slow diffusion of hexane into a concentrated DCM solution of complex **3.14** gave greenish-yellow crystals suitable for X-ray analysis. The solid-state structure of the complex (Figure 3.3) was determined by X-ray diffraction analysis in order to complete the characterization of this class of compounds and to gain further insights into the coordination mode of these types of ligands. Selected structural data are listed in Table 3.7.

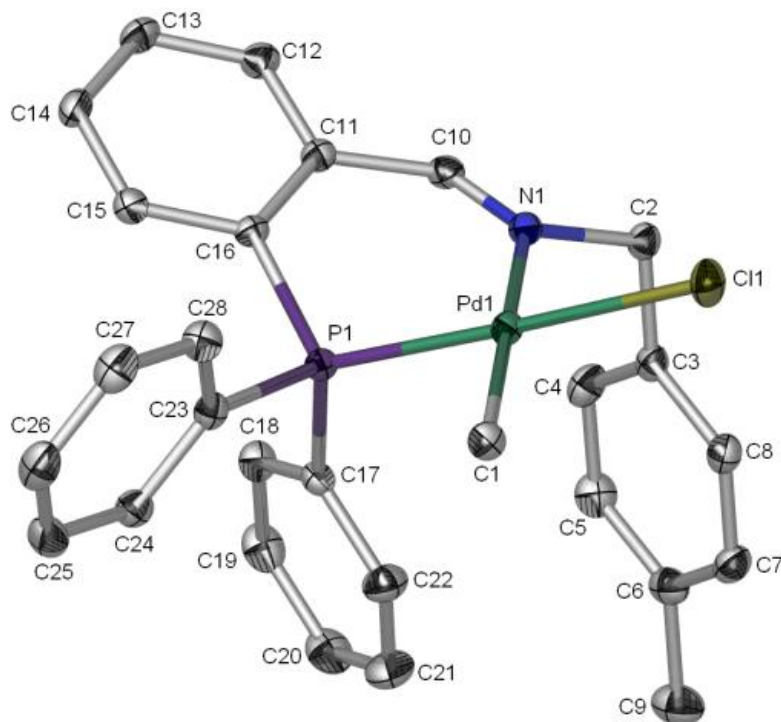


Figure 3.3: The ORTEP plot of the molecular structure of **3.14** showing the atomic numbering.

The *cis* orientation of the phosphine and the methyl groups around the metal centre was confirmed by crystal structure determination. The complex displays a distorted square planar arrangement around the metal centre. The X-ray crystal structure shows that, as expected, the iminophosphine ligand coordinates in a bidentate fashion to the palladium centre, with the phosphine end of the ligand coordinated *trans* to the chloride ligand. The ligand forms a puckered chelate ring with the palladium centre, in which the =CHC₆H₄ unit lies above the Pd(P,N)MeCl plane with the torsion angle Pd(1)-P(1)-C(16)-C(11) being 38.89(17)°. The bite angle N(1)-Pd(1)-P(1) of 87.45(5)° deviates slightly from the expected 90° angle, which can be attributed to the steric strain imposed by the 6-membered chelate ring N(1)-Pd(1)-P(1)-C(16)-C(11)-C(10) that is formed upon coordination to the palladium centre. This reduction in the bite angle of N(1)-Pd(1)-P(1) as well as the compensatory increase in the N(1)-Pd(1)-Cl(1) angle has been observed in other palladium methylhalide complexes of iminophosphines.^{22,24,25} The remaining two angles around the palladium centre are close to the expected 90°, i.e. 89.79(6)° and 89.18(6)° for C(1)-Pd(1)-P(1) and C(1)-Pd(1)-Cl(1) respectively. These values are in good agreement with those obtained for similar complexes.^{32,35,36}

Table 3.6: Characterization data for palladium methyl chloride complexes **3.13** – **3.18**^a

Complex	R	Formula	$\nu_{\text{C=N}}$ (cm^{-1}) ^b	$\delta_{\text{H}}(\text{Pd-CH}_3)$ (ppm)	$\delta_{\text{H}}(\text{H1})$ (ppm)	$\delta_{\text{H}}(\text{H2})$ (ppm)	$\delta_{\text{C}}(\text{Pd-CH}_3)$ (ppm)	$\delta_{\text{C}}(\text{C1})$ (ppm)	$\delta_{\text{C}}(\text{C2})$ (ppm)	δ_{P} (ppm)	[M] ⁺ (calc) m/z ^c
3.13	Phenyl	C ₂₇ H ₂₅ CINPPd	1638 (1636)	0.21 (d, ³ J = 3.2 Hz)	5.09 (4.67)	8.80 (9.05)	0.62	62.5 (65.2)	164.7 (d, ³ J = 5.0 Hz) (160.6)	38.3 (-13.8)	501.10 (500.89)
3.14	4-Tolyl	C ₂₈ H ₂₇ CINPPd	1638 (1635)	0.56 (d, ³ J = 2.9 Hz)	5.40 (4.64)	8.16 (9.00)	2.3	66.6 (64.8)	162.4 (d, ³ J = 4.9 Hz) (161.3)	37.4 (-13.6)	514.10 (514.91)
3.15	2-Furfuryl	C ₂₅ H ₂₃ CINOPPd	1637 (1635)	0.56 (d, ³ J = 2.4 Hz)	5.47 (4.65)	8.24 (8.98)	2.9	59.1 (57.1)	163.7 (d, ³ J = 5.1 Hz) (161.4)	37.7 (-14.5)	490.21 (490.85)
3.16	2-Thionyl	C ₂₅ H ₂₃ CINPPdS	1637 (1634)	0.56 (d, ³ J = 2.9 Hz)	5.48 (4.86)	8.24 (9.01)	2.3	61.5 (60.0)	163.5 (d, ³ J = 5.1 Hz) (160.8)	37.5 (-14.5)	506.83 (506.92)
3.17	3-Pyridyl	C ₂₆ H ₂₄ CIN ₂ PPd	1635 (1634)	0.61 (d, ³ J = 3.0 Hz)	5.49 (4.67)	8.40 (8.98)	2.6	64.4 (62.4)	163.6 (d, ³ J = 4.8 Hz) (161.3)	37.6 (-13.4)	501.11 (501.88)
3.18	Mesityl	C ₃₀ H ₃₁ CINPPd	1638 (1636)	0.59 (d, ³ J = 3.1 Hz)	5.32 (4.90)	8.36 (8.98)	2.1	64.7 (57.6)	162.8 (d, ³ J = 5.0 Hz) (158.9)	38.1 (-13.5)	543.69 (542.97)

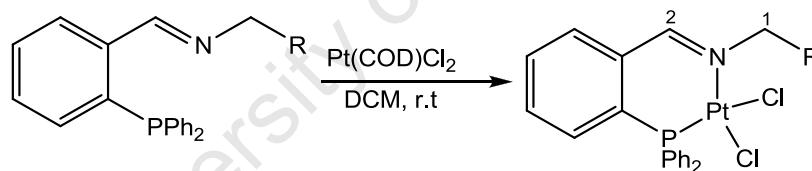
^aLigand data in parenthesis. ^bIR spectra recorded as KBr pellets. ^c[M]⁺ represents m/z for the fragment [M-Cl]⁺

Table 3.7: Selected Bond Lengths (Å) and Angles (°) for **3.14**

Bond Lengths		Bond Angles	
Pd(1)-Cl(1)	2.3985(6)	P(1)-Pd(1)-Cl(1)	177.15(2)
Pd(1)-P(1)	2.1846(5)	N(1)-Pd(1)-(Cl(1)	93.85(5)
Pd(1)-N(1)	2.1595(16)	C(1)-Pd(1)-Cl(1)	89.18(6)
Pd(1)-C(1)	2.0586(19)	N(1)-Pd(1)-P(1)	87.45(5)
P(1)-C(16)	1.8255(19)	C(1)-Pd(1)-P(1)	89.79(6)
P(4)-C(11)	1.824(3)	C(1)-Pd(1)-N(1)	173.39(7)
N(1)-C(10)	1.278(2)		
N(1)-C(2)	1.484(2)		

3.2.4 Synthesis and Characterization of Platinum Dichloride Complexes (3.19 – 3.24)

The platinum dichloride complexes were prepared by the reaction of [Pt(COD)Cl₂] and the appropriate P[^]N ligands (Scheme 3.4). To a DCM solution of the appropriate ligand was added equimolar amount of a DCM solution of [Pt(COD)Cl₂]. A pale yellow precipitate formed immediately and the reaction mixtures were stirred at room temperature overnight, after which the mixture was concentrated under reduced pressure and the precipitates filtered. The yellow solids obtained were washed with aliquots of DCM and Et₂O and then dried under vacuum. The desired products were obtained as pale yellow solids in moderate to good yields (Table 3.8).



Complex	R	Complex	R
3.19	Phenyl	3.22	2-Thionyl
3.20	4-tolyl	3.23	3-pyridyl
3.21	2-furfuryl	3.24	Mesityl

Scheme 3.4: Synthesis of platinum dichloride complexes **3.19 – 3.24**.

The complexes were characterized by various spectroscopic and analytical methods (¹H, ³¹P NMR spectroscopy, IR spectroscopy, mass spectrometry and elemental analysis) and the data obtained corresponds to the proposed structures of the complexes. Due to the insoluble nature, ¹H and ³¹P spectra were performed on DMSO-*d*₆ suspensions of the complexes whereas ¹³C NMR spectrometry could not be performed. The data (Table 3.9) obtained is in agreement with that reported for similar complexes in the literature.

Table 3.8: Isolated yields and melting point data for complexes **3.19** – **3.24**

Complex	R	Yield	Melting Point (°C)	Microanalysis ^a		
				C	H	N
3.19	Phenyl	69	>300	48.01 (48.38)	3.47 (3.44)	2.14 (2.17)
3.20	4-Tolyl	58	275 – 279	48.93 (49.18)	3.64 (3.67)	2.09 (2.12)
3.21	2-Furfuryl	79	>300	45.83 (45.37)	3.19 (3.17)	2.17 (2.20)
3.22	2-Thionyl ^b	87	>300	44.36 (44.25)	3.10 (3.09)	2.13 (2.15)
3.23	3-Pyridyl	70	259 – 261	46.13 (46.45)	3.31 (3.27)	4.30 (4.33)
3.24	Mesityl	68	265 – 267	50.79 (50.66)	4.47 (4.11)	2.00 (2.04)

^aExpected values in parentheses. ^bMicroanalytical data for S: 4.89 (4.92).

3.2.4.1 NMR Spectroscopy for complexes **3.19** – **3.24**

¹H NMR spectra of the complexes show that upon coordination, the signals for the methylene protons H2 experience a downfield shift from 4.63 – 4.90 ppm in the free ligands to 5.67 – 5.89 ppm in the platinum complexes (Table 3.9). This effect is more pronounced for the platinum dichloride complexes than it is for the analogous palladium complexes. The effect on the chemical shifts of the imine protons, on the other hand, is less distinct compared to the palladium complexes. For complexes **3.19**, **3.20** and **3.23**, **3.24**, there is a downfield shift from 8.89 – 9.05 ppm in the free ligands to 9.01 – 9.20 ppm in the complexes indicating that these protons are more deshielded in the platinum complexes than they are in the free ligands. This is consistent with the observation made for analogous palladium dichloride complexes. In contrast, for complexes **3.21** and **3.22** bearing the furfuryl and thionyl groups, the reverse is observed, whereby the imine protons in these complexes are more shielded relative to the free ligands. The ¹H NMR spectra of these complexes show an upfield shift in the signals of the imine protons from 8.98 to 8.90 ppm and 9.01 to 8.98 ppm for **3.21** (R = furfuryl) and **3.22** (R = thionyl) respectively. This indicates that for these complexes there is greater electron density on the metal centre than there is in complexes **3.19**, **3.20**, **3.23** and **3.24**, resulting in shielding of the imine protons in **3.21** and **3.22**. Further confirmation of coordination of the imine moiety to the platinum centre comes from the presence of platinum satellites (³J_{H-Pt} ranging from 100.0 Hz to 109.1 Hz) on the imine proton signals. While several platinum dichloride complexes of the imine ligands have been prepared before,^{22e,33b} there are only a few reports in the literature with ¹H NMR spectral data of these complexes, especially the coupling between platinum and the imine protons, which bears further testimony to ligand coordination to the metal centre.⁵

As in the palladium complexes, the signals for the imine protons appear as singlets as opposed to the doublets observed for the free ligands. The signals for the aromatic protons (phenyl, pyridyl, thiophenyl and furfuryl) appear in the expected regions and do not differ significantly from their values in free ligands, indicating that these groups are not involved in the coordination to the metal centre.

Bidentate coordination of the ligands to the metal centre is confirmed by the ^{31}P NMR spectra of the platinum dichloride complexes **3.19** – **3.24** (Table 3.9), which show a significant downfield shift of the phosphorus signal from -14.5 – -13.4 ppm in the free ligands to 4.29 – 5.87 ppm in the complexes. This observation is consistent with previous reports, where the signals for the phosphorus atom in these types of complexes have been reported to appear in the range *ca.* 4 – 11 ppm.^{4,22e,33b} In addition, these signals appear as singlets with platinum satellites ($^1J_{\text{PPt}} = 3684$ – 3890 Hz), further confirming the coordination of the phosphine moiety to the metal centre. The large coupling constants (Figure 3.4) observed for these complexes are typical for phosphines coordinated to a platinum centre bearing halide ligands.^{22e,33b,37} The chemical shifts for the phosphorus atoms in complexes **3.19** – **3.24** are very similar, indicating that the nature of the pendant R group does not influence the chemical environment around the metal centre.

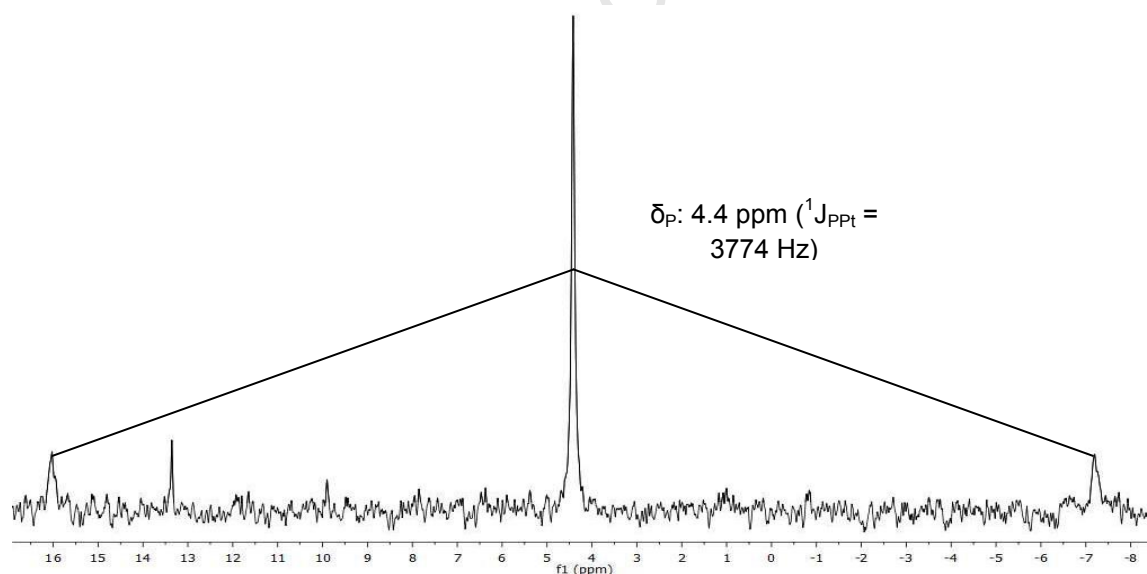


Figure 3.4: ^{31}P NMR spectrum of complex **3.22**.

Table 3.9: Characterization data for platinum dichloride complexes **3.19** – **3.24**^a

Complex	R	Formula	$\nu_{\text{C=N}}$ (cm^{-1}) ^b	δ_{H} (H1) (ppm)	δ_{H} (H2) (ppm)	δ_{P} (ppm)	[M+H] ⁺ (calc) m/z ^c
3.19	Phenyl	C ₂₆ H ₂₂ Cl ₂ NPt	1631 (1636)	5.78 (s) (4.70)	9.09 (s, ³ J _{H-Pt} = 108.8 Hz) (9.05)	4.29 (s, J _{P-Pt} = 3764 Hz) (-13.8)	610.43 (609.96)
3.20	4-Tolyl	C ₂₇ H ₂₄ Cl ₂ NPt	1632 (1635)	5.67 (s) (4.64)	9.01 (s, ³ J _{H-Pt} = 109.1 Hz) (9.00)	4.44 (s, J _{P-Pt} = 3890 Hz) (-13.6)	624.84 (623.99)
3.21	2-Furfuryl	C ₂₄ H ₂₀ Cl ₂ NOPt	1633 (1635)	5.78 (s) (4.64)	8.90 (s, ³ J _{H-Pt} = 106.2 Hz) (8.98)	5.87 (s, J _{P-Pt} = 3760 Hz) (-14.5)	600.76 (599.93)
3.22	2-Thionyl	C ₂₄ H ₂₀ Cl ₂ NPPtS	1630 (1634)	5.89 (s) (4.87)	8.98 (s, ³ J _{H-Pt} = 100.0 Hz) (9.01)	4.41 (s, J _{P-Pt} = 3763 Hz) (-14.5)	616.87 (615.99)
3.23	3-Pyridyl	C ₂₄ H ₂₁ Cl ₂ N ₂ Pt	1629 (1634)	5.81 (s) (4.63)	9.20 (s, ³ J _{H-Pt} = 107.6 Hz) (8.98)	4.72 (s, J _{P-Pt} = 3726 Hz) (-13.4)	611.03 (610.95)
3.24	Mesityl	C ₂₉ H ₂₈ NPt	1634 (1636)	5.74 (s) (4.90)	9.17 (s, ³ J _{H-Pt} = 105.8 Hz) (8.98)	5.71 (s, J _{P-Pt} = 3684 Hz) (-13.5)	652.96 (652.04)

^aLigand data in parenthesis. ^bIR spectra recorded as KBr pellets. ^c[M+H]⁺ represents m/z for the fragment [M-Cl]⁺

3.2.4.2 FTIR Spectroscopy for 3.19 – 3.24

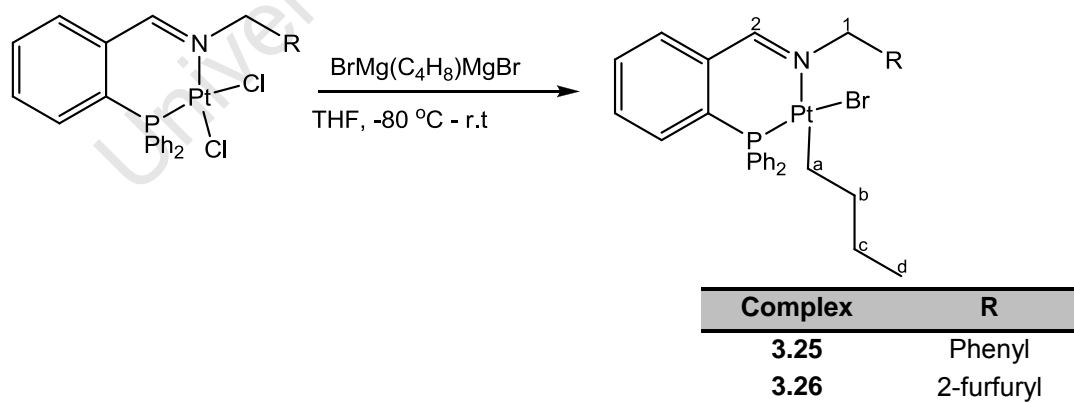
The most informative peak in the IR spectra of the platinum complexes is the imine stretching band, which occurs in the region $1630 - 1634 \text{ cm}^{-1}$. There is a slight shift to lower wavenumbers upon coordination to the metal centre (from $1634 - 1636$ in the free ligands), further confirming the participation of the imine moiety in ligand coordination to the platinum. The direction and magnitude of this shift is in agreement with data reported for similar complexes.⁴

3.2.4.3 Mass Spectrometry and Microanalysis for 3.19 – 3.24

Like the palladium complexes reported herein as well as other iminophosphine complexes of the transition metals,⁶ the highest molecular weight fragment recorded in the mass spectra is the $[\text{M}-\text{Cl}]^+$ fragment. Microanalytical data are in good agreement with the proposed structures for the complexes.

3.2.5 Synthesis and Characterization of Platinum Butyl Bromide Complexes (3.25 – 3.26)

To explore the chemistry of iminophosphine complexes of platinum with alkyl ligands, platinum butyl bromide complexes were prepared and fully characterized and their coordination behaviour studied. The platinum butyl bromide complexes were obtained as products in the reaction of $[\text{Pt}(\text{P}^{\wedge}\text{N})\text{Cl}_2]$ complexes with $\text{BrMg}(\text{C}_4\text{H}_8)\text{MgBr}$. The products were recrystallized from a THF solution by addition of hexane. The products precipitated out as bright yellow or orange solids.



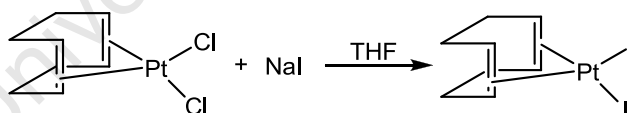
Scheme 3.5: Synthesis of platinum alkyl bromide complexes 3.25 and 3.26.

The majority of $\text{P}^{\wedge}\text{N}$ platinum alkyl halide complexes reported in the literature are $[\text{Pt}(\text{P}^{\wedge}\text{N})(\text{Me})\text{X}]$ complexes where $\text{X} = \text{Cl}, \text{Br}$ or I . The most straight-forward method to synthesize these complexes is by the reaction of $[\text{Pt}(\text{COD})(\text{Me})\text{X}]$ with the appropriate ligands to give the desired products.^{33b,37} A review of the literature shows that, to date, analogous complexes bearing longer alkyl chains have not been reported.

A qualitative comparison of the number of reports on $[M(P^N)(Me)X]$ where $M = Pd$ or Pt and X is a halide, shows that there are, by far, more reports on palladium complexes than there are on platinum complexes. This could be due to the higher activity and a wider scope of application of palladium complexes in catalysis. However, because of the increased stability (and hence lower catalytic activity) of platinum complexes, their study can offer valuable insight into the nature of transient species in catalytic processes catalyzed by analogous palladium complexes.

It has been reported that the direct reaction of $[Pt(L_2)Cl_2]$, with di-Grignard reagents has the drawback of producing a mixture of products containing large quantities of monoalkylated complexes.³⁷ In this study, the reaction of the precursor $[Pt(P^N)Cl_2]$ gave the monoalkylated complexes as the major products (>75%). The rest of the product mixture was composed of some platinacyclic complexes as well as unidentified compounds. While the formation of the monoalkylated complexes was not unexpected, their being the majority product was unexpected. McDermott and co-workers employed the same synthetic procedure for the synthesis of $[Pt(L_2)(C_4H_8)]$, where $L = PPh_3$ and $L_2 =$ diphosphines. They reported that the expected platinacyclopentanes were obtained in yields as high as 62%.³⁸

The expected halide ligand in these complexes would be the chloride ligand. However, the bromide could come from the reaction mixture following the hydrolysis of the excess Grignard reagent. Halide metathesis reactions such as the one depicted in Scheme 3.5, where heavier halides such as iodine replace chlorine in metal complexes are well documented and frequently used.³⁹



Scheme 3.5: Halide metathesis reaction.

The products were obtained as crystalline solids in good yields (Table 3.11). The complexes were characterized by 1H , ^{13}C and ^{31}P spectroscopy as well as mass spectrometry, microanalysis and melting points (Tables 3.10 and 3.11) and the data obtained is in agreement with the proposed structures.

3.2.5.1 NMR Spectroscopy for complexes 3.25 – 3.26

1H NMR spectra of the complexes show the expected signals indicative of complex formation. Upon coordination, the signals for the imine protons appear as a singlet at 8.27 ppm and 8.39 ppm for **3.26** and **3.25** respectively. This is an upfield shift from 8.98 – 9.05 ppm observed for the free ligands. As in the other complexes previously discussed, this

upfield shift is attributed to the conformational changes that occur in the ligands in order to facilitate complex formation. In addition to this upfield shift, further support for coordination of the imine functionality to the metal centre comes from the observation of platinum satellites ($^3J_{\text{HPt}} = 33.1 - 34.8$ Hz) accompanying the signals for the imine protons. As in the dichloride complexes, a downfield shift is observed in the signals for the methylene protons (N-CH₂-R) upon coordination to platinum. These signals appear as broad singlets at 5.79 ppm and 5.67 for **3.25** and **3.26** respectively. Signals for the same protons appear at 4.65 ppm for ligand **3.1** and 4.64 ppm for ligand **3.3**. The magnitude of this downfield shift is comparable to that observed for the dichloride complexes indicating that the chemical environment experienced by these particular protons is similar in both types of complexes.

The alkyl protons in the butyl chains appear in the expected aliphatic region (0.44 – 1.37 ppm). The most deshielded protons are the terminal methyl protons, **H_d**, whose signals appear at 0.58 ppm and 0.44 ppm for **3.25** and **3.26** respectively. As expected, these signals appear as triplets with $^3J_{\text{HH}} = 7.3$ Hz. Signals for the methylene protons adjacent to the metal centre, **H_a**, appear as a doublet of triplets at 0.95 ppm for **3.25** and 0.80 ppm for **3.26**. These protons are more upfield than **H_b** and **H_c**, whose signals appear in the region 1.07 – 1.37 ppm, due to the shielding effect of the d-electron on the metal centre. A similar shielding effect is observed for the methyl protons (Pd-CH₃) in analogous palladium chloromethyl complexes, where these protons appear as doublets in the region between 0.21 ppm and 0.56 ppm (Table 3.6).

The aromatic protons for the ligand backbone as well as the pendant R groups (Ph for **3.25** and furfuryl for **3.26**) appear in the expected regions. The signals for the furfuryl group appear in a similar region for both the free ligand (**3.3**) and the platinum dichloride complex (**3.26**), indicating that, as in the other complexes, this group is not involved in coordination to the metal centre.

Further evidence for imine coordination to the metal centre comes from the ¹³C NMR spectra of the complexes, which show signals for the imine protons as doublets coupling to phosphorus at 161.4 ppm for **3.25** and 162.2 ppm for **3.26**. Signals for the same carbons appear at 160.6 ppm and 161.4 ppm for ligands **3.1** and **3.3** respectively. As in the palladium chloromethyl complexes, this is a slight upfield shift with respect to the same signals in the free ligands. In addition, the difference in the magnitude of the coupling constants between the imine carbons and the phosphorus atoms between the free ligands and the complexes provides further support for the imine coordination to the platinum. $^3J_{\text{CP}}$ for the imine carbons in the free ligands is in the range of 22.3 – 23.1 Hz whereas $^3J_{\text{CP}}$ in the complexes is 4.6 Hz for **3.25** and 4.7 Hz for **3.26**.

Signals for the methylene carbons (N-CH₂-R) appear at 69.0 ppm for **3.25** and 61.3 ppm for **3.26**, a downfield shift from 65.2 ppm (ligand **3.1**) and 57.1 ppm (ligand **3.3**), lending further support to the proposed imine coordination to the metal centre. Signals for the carbons in the butyl chains appear in the aliphatic region between 7.4 ppm and 35.1 ppm. The most shielded carbon is the one adjacent to the metal centre, which appears as a doublet coupling to the phosphorus at 7.4 ppm ($^2J_{CP} = 3.5$ Hz) for complex **3.25** and 7.6 ppm ($^2J_{CP} = 3.7$ Hz) for complex **3.26**. The terminal methyl carbons appear at 13.8 ppm for complex **3.25** and 13.7 ppm for complex **3.26**. The other two methylene carbons (C_b and C_c) appear at 26.3 ppm and 35.1 ppm for complex **3.25**, while they appear at 29.7 ppm and 34.9 ppm for complex **3.26** (Figure 3.5).

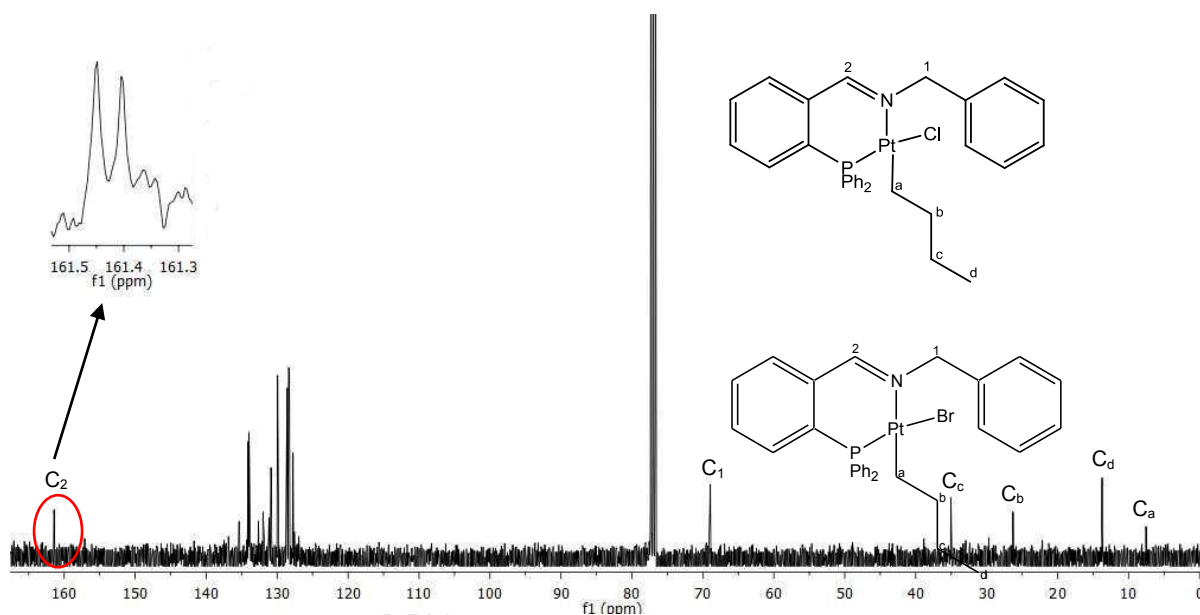


Figure 3.5: ¹³C NMR spectrum of complex **3.25** with signals of interest labelled.

Evidence for phosphine coordination to platinum comes from ³¹P NMR spectra of the complexes. The data obtained for these complexes show similar trends to those obtained for the other metal complexes previously discussed. There is a downfield shift of the phosphorus signals from ca. -14 ppm in the free ligands to ca. 16 ppm in the complexes (Table 3.10). These chemical shifts are in the same range as those reported for similar methyl halide platinum complexes of iminophosphine ligands.^{33b} Further proof for the coordination of the phosphine group to the platinum centre comes from the platinum satellites that accompany these signals. Evidence that these are alkyl halide complexes as opposed to the metallacycloalkanes that are expected to be the product when platinum dichloride precursor complexes react with di-Grignard reagents; comes from the large coupling constants observed between platinum and phosphorus atoms. $^1J_{PPt} = 5000$ for **3.25** (Figure 3.6) and $^1J_{PPt} = 5018$ Hz for **3.26**. Typically, $^1J_{PPt}$ for platinacycloalkanes or dialkyl platinum complexes with phosphine ligands are <2500 Hz^{33b,40} while those for phosphorus

atoms *trans* to a halide ligand in platinum complexes are large, typically >3000 Hz.^{33b,37} In particular, where the halide ligand is a bromide these coupling constants are ca. 5000 Hz.^{33b}

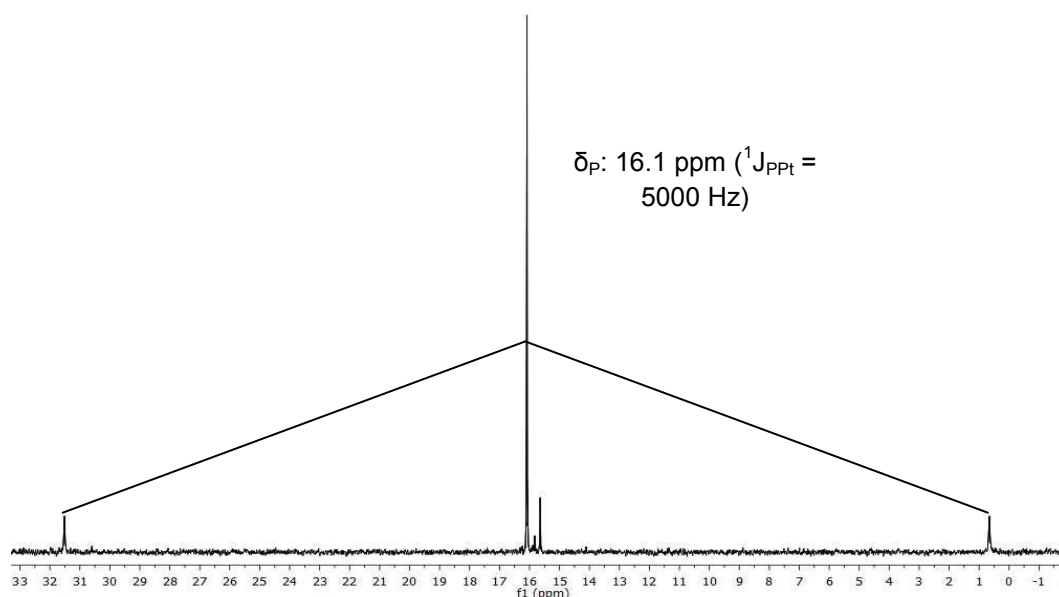


Figure 3.6: ³¹P NMR spectrum of complex 3.25.

3.2.5.2 Mass Spectrometry and Microanalysis for 3.25 – 3.26.

Microanalytical data (Table 3.11) obtained for the complexes is in agreement with the proposed structures while the highest molecular fragment recorded in the mass spectra is the [M-Br]⁺ fragment (Table 3.10).^{29,30}

3.2.5.3 X-ray Structural Determination for Complex 3.26

Crystals (Figure 3.7) suitable for X-ray analysis were obtained by slow diffusion of hexane into a concentrated DCM solution of complex 3.26. The solid-state structure of the complex was determined in order to complete the characterization for the complex and to gain further insight into the structure of this class of compounds as complexes of this type have not been reported and structurally characterized in the literature. Selected structural data are listed in Table 3.12.

As in other alkyl halide complexes of the transition metals bearing iminophosphine ligands, the phosphine group and butyl chain have a *cis* arrangement around the metal centre, with the bromide ligand found *trans* to the phosphine group. As expected, the ligand coordinates in a bidentate fashion to the metal centre. The complex displays a distorted square planar arrangement around the platinum centre.

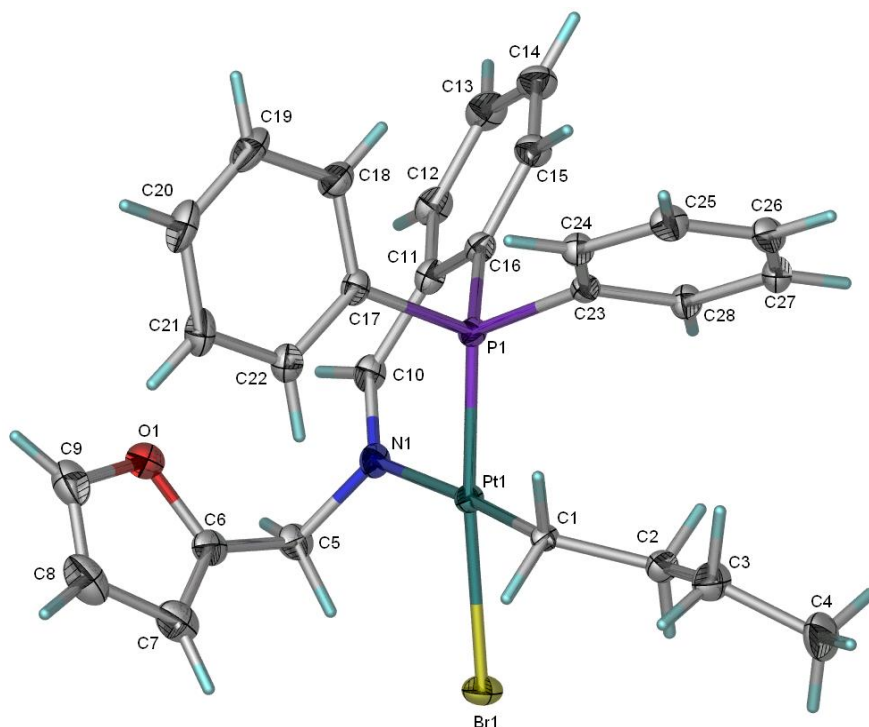


Figure 3.7: The ORTEP plot of the molecular structure of **3.26** showing numbering scheme. All non-hydrogen atoms are shown as ellipsoids with probability level of 40 %.

The ligand forms a puckered chelate ring with the metal centre, with the =CHC₆H₄ fragment lying above the Pt(P[^]N)(C₄H₉)Br plane and the torsion angle Pt(1)-P(1)-C(16)-C(11) being 33.7(2)°. The bite angles around the metal centre slightly deviate from the expected 90°, and this can be attributed to the ring strain imposed by the 6-membered chelate ring N(1)-Pt(1)-P(1)-C(16)-C(11)-C(10) that is formed upon complex formation. In addition, the ligands around the platinum centre have to arrange in such a manner that the relatively large groups found around the metal centre are accommodated. This may lead to further deviation from the expected 90° angles around the metal centre. The angle N(1)-Pt(1)-Br(1) is 93.82(6)°, which is significantly larger than the expected angle. However, this increase is compensated for by the reduction of the bite angle C(1)-Pt(1)-Br(1), which is 86.60(6)°. This reduction in C(1)-Pt(1)-Br(1) and compensatory increase in N(1)-Pt(1)-Br(1) are commonly observed for alkyl halide complexes with iminophosphine ligands.^{22,24,25} The other two bite angles around the platinum centre are close to the expected 90-degree angle with the bite angle C(1)-Pt(1)-P(1) being 90.66(6)° and N(1)-Pt(1)-P(1) being 89.38(6)°.

Table 3.10: Characterization data for platinum butyl bromide complexes **3.25** – **3.26**^a

Complex	R	Formula	$\delta_{\text{H}}(\text{Pt-CH}_2\text{-})$ (ppm)	$\delta_{\text{H}}(\text{H1})$ (ppm)	$\delta_{\text{H}}(\text{H2})$ (ppm)	$\delta_{\text{C}}(\text{Pt-CH}_2\text{-})$ (ppm)	$\delta_{\text{C}}(\text{C1})$ (ppm)	$\delta_{\text{C}}(\text{C2})$ (ppm)	δ_{P} (ppm)	$[\text{M}+\text{H}]^+$ (calc) m/z ^b
3.25	Phenyl	C ₃₀ H ₃₁ BrNPt	0.95 (dt, ³ J = 7.2 Hz, 14.6 Hz)	5.79 (4.67)	8.39 (9.05)	7.4 (d, ² J _{CP} = 3.5 Hz)	69.0 (65.2)	161.4(d, ³ J = 4.7 Hz)(160.6)	16.1 (s, J _{PPt} = 5000 Hz)(- 13.8)	632.56 (631.63)
3.26	2-Furfuryl	C ₂₈ H ₂₉ BrNOPt	0.80 (dt, ³ J = 7.6 Hz, 14.5 Hz)	5.67 (4.65)	8.27 (8.98)	7.6 (d, ² J _{CP} = 3.7 Hz)	61.3 (57.1)	162.2(d, ³ J = 4.6 Hz)(161.4)	16.2 (s, J _{PPt} = 5018 Hz)(- 14.5)	622.32 (621.59)

^aLigand data in parenthesis. ^b[M+H] represents m/z for [M-Br]⁺.

Table 3.11: Isolated yields and melting point data for complexes **3.25** – **3.26**

Complex	R	Yield	Melting Point (°C)	Microanalysis ^a		
				C	H	N
3.25	Phenyl	69	202 – 203	50.71 (50.64)	4.41 (4.39)	1.96 (1.97)
3.26	2-Furfuryl	79	193 – 194	47.99 (47.94)	4.20 (4.17)	1.98 (2.00)

^aExpected values in parentheses.

Table 3.12: Selected Bond Lengths (Å) and Angles (°) for **3.26**

Bond Lengths		Bond Angles	
Pt(1)-Br(1)	2.5032(3)	P(1)-Pt(1)-Br(1)	175.050(18)
Pt(1)-P(1)	2.1722(6)	N(1)-Pt(1)-Br(1)	93.82(6)
Pt(1)-N(1)	2.150(2)	C(1)-Pt(1)-Br(1)	86.60(6)
Pt(1)-C(1)	2.094(2)	N(1)-Pt(1)-P(1)	89.38(6)
P(1)-C(16)	1.821(3)	C(1)-Pt(1)-P(1)	90.66(6)
C(10)-C(11)	1.462(4)	C(1)-Pd(1)-N(1)	173.44(9)
N(1)-C(10)	1.283(3)		
N(1)-C(5)	1.493(3)		

3.3 SUMMARY AND CONCLUSION

A series of bidentate iminophosphine ligands (**3.1 – 3.6**) were successfully prepared by the reaction of 2-diphenylphosphinobenzaldehyde with various primary amines. The ligands were fully characterized using spectroscopic and analytical techniques. The ligands were obtained in good to excellent yields and were found to be air and moisture stable. These ligands were used to prepare palladium(II) complexes of the types $[\text{PdCl}_2(\text{P}^{\wedge}\text{N})]$ (**3.7 – 3.12**) and $[\text{Pd}(\text{Me})\text{Cl}(\text{P}^{\wedge}\text{N})]$ (**3.13 – 3.18**), as well as platinum(II) complexes of the types $[\text{PtCl}_2(\text{P}^{\wedge}\text{N})]$ (**3.19 – 3.24**) and $[\text{Pt}(\text{P}^{\wedge}\text{N})(\text{C}_4\text{H}_8)\text{Br}]$ (**3.25 – 3.26**). All complexes were characterized as fully as possible using various spectroscopic and analytical techniques. For the palladium and platinum dichloride complexes (**3.7 – 3.12** and **3.19 – 3.24** respectively), full characterization by spectroscopic techniques was limited by the poor solubility of these compounds in common organic solvents. All complexes were found to be air and moisture stable.

3.4 REFERENCES

1. Fey, N., Harvey, J. N., Lloyd-Jones, G. C., Murray, P., Orpen, A. G., Orsborne, R. and Purdie, M., *Organometallics*, 2008, **27**, 1372.
2. Hartley, F.R. (Ed.), *The Chemistry of Organophosphorus Compounds*, Vol. 1, Wiley, New York, 1990.
3. Shaffer, A. R. and Schmidt, J. A. R., *Chem. Eur. J.*, 2009, **15**, 2662 – 2673.
4. Duran, S. E., Elsegood, M. R. J., Hammond, S. R. and Smith, M. B., *Dalton Trans.*, 2010, **39**, 7136.
5. Ní Dhubhghaill, O. M., Lennon, J. and Drew, M. G. B., *Dalton Trans.*, 2005, 3213.
6. Clarke, M. L., Slawin, A. M. Z., Wheatley, M. V. and Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 2001, 3421.
7. Sánchez, G., Momblona, F., Serrano, J. L., García, L., Pérez, E. Pérez, J. and López, G., *J. Coord. Chem.*, 2002, **55**, 917.
8. (a) Antonaroli, S. and Crociani, B., *J. Organomet. Chem.*, 1998, **560**, 137. (b) Crociani, L., Bandoli, G., Dolmella, A., Basato, M. and Corain, B., *Eur. J. Inorg. Chem.*, 1988, 1811. (c) Ligtenberg, A. G. J., van den Beuken, E. K., Meetsma, A., Veldman, N., Smeets, W. J. J., Speck, A. L. and Feringa, B. L., *J. Chem. Soc., Dalton Trans.*, 1998, 263.
9. Ghilardi, C. A., Midollini, S., Moneti, S., Orlandini, A. and Scapacci, G., *J. Chem. Soc., Dalton Trans.*, 1992, 3371.
10. Gao, J-X., Ikariya, T. and Noyori, R., *Organometallics*, 1996, **15**, 1087.
11. Barbaro, P., Biachini, C., Laschi, F., Midollini, S., Moneti, S., Scapacci, G., Zanello, G. P., *Inorg. Chem.*, 1994, **33**, 1622.
12. (a) Gwynne, E. A. and Stephan, D. W., *Organometallics*, 2011, **30**, 4128. (b) Yang, M-J., Liu, Y-J., Gong, J-F., and Song, M-P., *Organometallics*, 2011, **30**, 3793. (c) Agrawal, D., Schröder, D. and Frech, C. M., *Organometallics*, 2011, **30**, 3579.
13. Oberbeckmann-Winter, N., Braunstein, P., and Welter, *Organometallics*, 2004, **23**, 6311. (b) Chavez, P., Rios, I. G., Kermagoret, A., Pattacini, R., Meli, A., Bianchini, C., Giambastiani, G., and Braunstein, P., *Organometallics*, 2009, **28**, 1776.
14. (a) Newkome, G. R., *Chem. Rev.*, 1993, **93**, 2067. (b) Cheng, H. and Zhang, Z., *Coord. Chem. Rev.*, 1996, **147**, 1.
15. (a) Rauchfuss, T. B., Clements, J. L., Agnew, S. F. and Roundhill, D. M., *Inorg. Chem.*, 1977, **16**, 775. (b) Andrieu, J., Camus, J-M., Richard, P., Poli, R., Gonsalvi, L., Vizza, F. and Peruzzini, M., *Eur. J. Inorg. Chem.*, 2006, 51. (c) Roundhill, D. M., Bechtold, R. A. and Roundhill, S. G. N., *Inorg. Chem.*, 1980, **19**, 284. (d) Stanfest-Hausser, C., Slugovc, C., Mereiter, K., Schmid, R., Kirchner, K., Xiao, L. and Weissensteiner, W., *J.*

- Chem. Soc., Dalton Trans.*, 2001, 2989. (e) Gravilov, K. N. and Polosukhin, A. I., *Russ. Chem. Rev.*, 2000, **69**, 661. (f) Drent, E., Arnoldy, P. and Budzelaar, P. H. M., *J. Organomet. Chem.*, 1993, **455**, 247. (g) Denis, P. Jean, A., Crizy, J. F., Mortreux, A. and Petit, F., *J. Am. Soc.*, 1990, **112**, 1292. (h) Yang, H., Alvarez, M., Lugan, N. and Mathieu, R., *J. Chem. Soc., Chem. Commun.*, 1995, 1721. (i) Schultz, T., Schmees, N. and Pfaltz, A., *Appl. Organometal. Chem.*, 2004, **18**, 595. (j) Mahamo, T., Mogorosi, M. M., Moss, J. R., Mapolie, S. F., Smith, G. S., Slootweg, J. C. and Lammertsma, K., *J. Organomet. Chem.*, 2012, **703**, 34. (k) Mogorosi, M. M., Mahamo, T., Moss, J. R., Mapolie, S. F., Slootweg, J. C. and Lammertsma, K., Smith, G. S., *J. Organomet. Chem.*, 2011, **696**, 3585. (l) Weng, Z., Teo, S. and Hor, T.S.A., *Organometallics*, 2006, **25**, 4878. (m) Pascu, S. I., Coleman, K. S., Cowley, A. R., Green, M. L. H. and Rees, N. H., *J. Organomet. Chem.* 2005, **690**, 1645. (n) Coleman, K. S., Green, M. L. H., Pascu, S. I., Cowley, A. R., and Rees, L. H., *J. Chem. Soc., Dalton, Trans.*, 2001, 3384.
16. Diversi, A. Edwards, P. G., Newman, P. D. and Tooze, R. P., *J. Chem. Soc., Dalton Trans.*, 2000, 523.
17. Lightfoot, A., Schnider, P. and Pfaltz, A., *Angew. Chem. Int. Ed.*, 1998, **37**, 2897.
18. (a) Williams, J. M. J., *Synlett*, 1996, 705. Von Matt, P. and Pfaltz, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 566. (b) Sawamura, M. and Ito, Y., *Chem. Rev.*, 1992, **92**, 857.
19. (a) Beletskaya, I. and Pelter, A., *Tetrahedron*, 1997, **35**, 4957. (b) Brown, J. M., Hulmes, D. I. and Layzell, T. P., *J. Chem. Soc., Chem. Commun.*, 1993, 1673.
20. Yoshida, H., Shirakawa, E., Kurahashi, T., Nakao, Y. and Hiyama, T., *Organometallics*, 2000, **19**, 5671 and references therein.
21. Tsuda, T., Morikawa, S. and Saegusa, T., *J. Chem. Soc., Chem. Commun.*, 1989, 9.
22. (a) Del Zotto, A., Baratta, W., Ballico M., Herdtweck, E. and Rigo, P., *Organometallics*, 2007, **26**, 5636. (b) Shirakawa, E., Nakao, Y., Murota, Y. and Hiyama, T., *J. Organomet. Chem.*, 2003, **670**, 132. (c) Crossetti, G. L., Filgueiras, C. A., Howie, R. A., Wardell, J. L. and Ziglo, C. M., *Acta Cryst.*, 2001, **C57**, 1279. (d) del Campo, O., Carbayo, A., Cuevas, J. V., Garcia-Herbaso, G. and Munoz, A., *Eur. J. Inorg. Chem.*, 2009, 2254. (e) Thibault, M-H., Lucier, B. E. G., Schurko, R. W. and Fontaine, F-G., *Dalton Trans.*, 2009, 7701.
23. Shirakawa, E., Yoshida, H and Takaya, H., *Tetrahedron Lett.*, 1997, **38**, 3759.
24. Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *J. Chem. Soc., Dalton, Trans.*, 2002, 1776.
25. (a) Rülke, R. E., Kaasjager, V. E., Wehman, P., Elsevier, C. J., van Leeuwen, P. W. N. M., Vrieze, K., Fraanje, J., Goubitz, K. and Spek, A. L. *Organometallics*, 1996, **15**, 3022. (b) Jeffrey, J. C., Rauchfuss, T. B. and Tucker, P. A., *Inorg. Chem.*, 1980, **19**,

3306. (c) Crochet, P., Gimeno, J., Borge, J. and Garcia-Granda, S., *New J. Chem.*, 2003, **27**, 414. (d) Rauchfuss, T. B., *J. Organomet. Chem.*, 1978, 162, C19. (e) Best, J., Wilson, J. M., Adams, H., Gonsalvi, L., Peruzzini, M. and Haynes, A., *Organometallics*, 2007, **26**, 1960. (f) Dilworth, J. R., Howe, S. D., Hutson, A. J., Miller, J. R., Silver, J., Thompson, R. M., Harman, M. and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.*, 1994, 3553.
26. Chen, H-P., Liu, Y-H., Peng, S-M. and Liu, S-T., *Organometallics*, 2003, **22**, 4893.
27. (a) Shaffer, A. R. and Schmidt, J. A. R., *Organometallics*, 2008, **27**, 1259. (b) Shaffer, A. R. and Schmidt, A. R., *Organometallics*, 2009, **28**, 2494.
28. Bhattacharyya, P., Loza, M. L., Parr, J. and Slawin, A. M. Z., *J. Chem. Soc., Dalton Trans.*, 1999, 2917.
29. Stoccorro, S., Cheluci, G., Zucca, A., Cinellu, M. A., Minghetti, G. and Manassero, M., *J. Chem. Soc., Dalton Trans.*, 1996, 1295.
30. Flapper, J., Kooijman, H., Lutz, M., Spek, A. L., van Leeuwen, P. W. N. M., Elsevier, C. J. and Kamer, P. C. J., *Organometallics*, 2009, **28**, 1180.
31. Polosukhin, A. I., Bondarev, O. G., Korostylev, A. V., Hilgraf, R., Davankov, V. A. and Gavrilov, K. N., *Inorg. Chim. Acta.*, 2001, **323**, 55.
32. (a) Ankersmit, H. A., Loken, B. H., Kooijman, H., Spek, A. L., Vrieze, K. and van Koten, G., *Inorg. Chim. Acta.*, 1996, **252**, 141. (b) Brinkmann, P. H. P. and Luinstra, G. A., *J. Organomet. Chem.*, 1999, **572**, 193.
33. (a) Daugulis, O. and Brookhart, M., *Organometallics*, 2002, **21**, 5926. (b) Song, H-B., Zhang, Z-Z. and Mak, T. C. W., *Polyhedron*, 2002, **21**, 1043.
34. Giarrou, P. E., *Chem. Rev.*, 1981, **81**, 229.
35. Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *Organometallics*, 2001, **20**, 1292.
36. van den Beuken, E. K., Smeets, W. J. J., Spek, A. L. and Feringa, B. L., *Chem. Commun.*, 1998, 223.
37. Pattachini, R., Magraf, G., Messaoudi, A., Oberbeckman-Winter, N. and Braunstein, P., *Inorg. Chem.*, 2008, **47**, 9886.
38. (a) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6521. (b) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1973, **95**, 4451.
39. Gracia, C., Marco, G., Navarro, R., Romero, P., Soler, T. and Urriolabeitia, E. P., *Organometallics*, 2003, **22**, 4910.
40. (a) Dralle, K., Jaffa, N., L., le Roex, T., Moss, J. R., Travis, S., Watermeyer, N. D. and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865. (b) Sivaramakrishna, A., Hong, S. and Moss, J. R., *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 3543. (c) Sivaramakrishna, A.,

Makhubela, B. C. E., Moss, J. R. And Smith, G. S., *J. Organomet. Chem.*, 2010, **695**, 1627. (d) Sivaramakrishna, A., Hong, S. and Moss, J. R., *Dalton Trans.*, 2008, 2228.

University of Cape Town

CHAPTER 4

PALLADIUM-CATALYZED SUZUKI-MIYAJURA COUPLING REACTIONS

4.1 INTRODUCTION

Transition metal-catalyzed C-C and C-X (X = heteroatom) bond forming reactions are a powerful synthetic tool in organic chemistry. In this regard, palladium complexes form some of the most versatile and useful catalysts in these organic transformations. Impressive advances have been made in palladium-catalyzed cross-coupling reactions such as the Suzuki-Miyaura, Migita-Kosugi-Stille, Buchwald-Hartwig and Mizoroki-Heck reactions in the last 20 to 30 years.¹⁻³ These processes have historically been used for the construction of carbocycles. However, in recent years interest in their application in the decoration and construction of heterocycles has been steadily growing.⁴ The reason for this interest becomes obvious if one takes into account that the majority of drugs and agrochemicals contain a heterocyclic unit.¹

Interest in palladium chemistry is not limited to academic research. The past few decades have witnessed an increase in the number of palladium-catalyzed reactions being performed on a kilogram-to-few-hundred kilogram scale in the development of new drug or agrochemical candidates in all major agrochemical and pharmaceutical companies.^{1,5} The facile interchange between the two stable oxidation states, Pd^{II} and Pd⁰, and the compatibility of many palladium compounds with most functional groups, are mainly responsible for the rich chemistry enjoyed by palladium compounds⁶ which make these compounds a suitable tool to couple highly functionalized subunits in the synthesis of complex natural products and to perform efficient lead optimization in medicinal chemistry.¹ In recognition of the importance and impact of palladium compounds in organic synthesis, the 2010 Nobel prize in chemistry was awarded for palladium-catalyzed cross couplings.

Among the most utilized palladium-catalyzed reactions is the Suzuki-Miyaura carbon-carbon coupling reaction between an aryl-(pseudo)halide and a boronic acid for the preparation of biaryls; moieties that are found in a wide variety of natural products, chiral reagents, chiral phases for chromatography, chiral liquid crystals and pharmaceutical drugs.⁷

The most common Suzuki-Miyaura catalysts currently in use are based on phosphine complexes with strong P-donors, owing to the stability displayed by these complexes as well as the comparative ease with which their properties can be modified. The accepted mechanism of the C-C coupling reaction (Figure 4.1) begins with the oxidative addition of an

aryl halide to an initial Pd^0 species (I) generating a Pd^{II} intermediate (II). This is followed by a metathetic exchange between this Pd^{II} intermediate and the base (step b), resulting in intermediate (III). This intermediate then undergoes transmetalation (step c) with borane reactants in the presence of base to form the bi-aryl intermediate IV. The product is released by reductive elimination (step d) from the bi-aryl Pd^{II} species regenerating the active Pd^0 species.^{8,9}

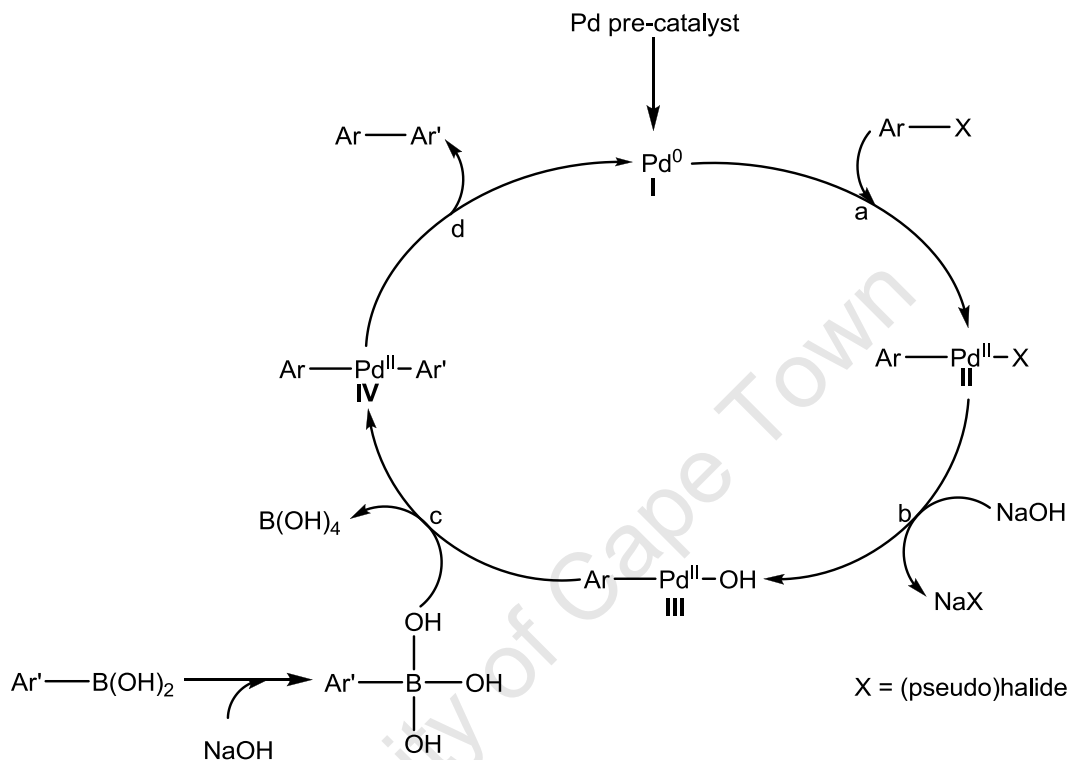


Figure 4.1: Suzuki-Miyaura mechanism. NaOH is used as an example of a typical base.

The rate-limiting steps are typically the oxidative addition¹⁰ or the transmetalation.¹¹ As such, a precatalyst such as $\text{Pd}(\text{PPh}_3)_4$, would need to enter the catalytic cycle through two successive ligand dissociations to give the 14-electron catalytically active complex $\text{Pd}^0(\text{PPh}_3)_2$. Such low-valent, low-coordinate palladium complexes are known to be extremely unstable and their formation is energetically unfavourable. One of the main challenges facing these catalyst systems is therefore the facile decomposition and deactivation of such complexes, which can lead to poor catalyst performance⁹ thereby making the use of high Pd loadings (2 to 12 mol%) necessary.^{3,12-17} It is therefore desirable to design catalysts that are both chemically stable and catalytically active. One way of achieving this is through the use of hemilabile supporting ligands.

The concept of hemilability was introduced in the 1970's by Rauchfuss^{18,19} to describe multidentate ligands that 'would bind well enough to the metal centre to allow isolation of the complex, but would readily dissociate the hard donor component thus generating a vacant

site for substrate binding'.²⁰ This is a particularly desirable characteristic for complexes which might have application in catalysis, and since the majority of metals used in such systems are middle or late transition metals, it is usually the soft donor atom which is continually bound to the metal centre.²¹ An important property of these ligands is that they can stabilize metal ions in a variety of oxidation states and geometries, which normally form during the catalytic cycle.¹⁸ In addition, the hard donor sites are weakly coordinated to the soft metal centre, and can be easily dissociated in solution, affording a vacant site whenever demanded, whereas the chelate effect confers stability to the catalyst precursor in the absence of substrate¹⁸ thereby preventing catalyst decomposition/deactivation.

Over the past few decades, interest in metal complexes of these types of ligands, which are essentially functionalized phosphine ligands, and their role in catalysis has been steadily growing as the different features associated with each donor atom confer unique properties to their metal complexes.²¹⁻²⁴ Unlike homo-donor chelate ligands, hetero-donor ligands have a distinct *trans* effect which can play a role in controlling the selectivity/activity, especially in co- and/or homo-polymerization processes.²⁵ The syntheses and reactivity/catalytic activity of complexes bearing hemilabile ligands of the type P^ΛN^{18,26} and P^ΛO²⁷ have been widely reported.

Significant developments in the chemistry of functionalized phosphine ligands continue to play a crucial role in understanding how these versatile ligands coordinate to metal centres, how they influence metal reactivity and their application in homogeneous catalysis.²⁸ Of the heterodentate ligands, those bearing phosphorus and nitrogen as their donor atoms have emerged as an important class of ligands.²³ The π-acceptor ability of the phosphine can stabilize a metal centre in a low oxidation state, while the nitrogen σ-donor ability makes the metal centre more susceptible to oxidative addition reactions. This electronic asymmetry can also be used to optimize a ligand for a particular reaction by appropriate choice of the properties of the donor atoms. For example, binding the phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen^{23,29} will reduce its electron donating capability while also enhancing its π-acceptor capacity. On the other hand, the presence of an imino rather than amino group will result in a nitrogen donor atom of greater δ-donating capabilities.^{23,30} Moreover, these types of ligands allow modulation of the steric crowding around the metal centre through the simple variation of the substituents on the imine and phosphine groups.³¹ Recent years have seen an increase in the amount of research on the synthesis and application of iminophosphine complexes as catalysts for coupling reactions and it has been found that these complexes show great promise.^{17,32-37}

This chapter describes the application of palladium complexes with hemilabile iminophosphine ligands as pre-catalysts in Suzuki-Miyaura coupling reactions. The effect of such factors as the choice of solvent and base as well as different substituents on both the aryl halides and the arylboronic acids is presented. The bidentate iminophosphine ligand system used in this study was chosen based on several advantages that such ligands offer. These include: 1) their ability to improve the thermal stability of their metal complexes.³⁸ 2) their ability to stabilize complexes in a variety of oxidation states and geometries that can form during the catalytic cycle.¹⁸ 3) their hemilabile nature, which would aid in creating vacant sites on the metal centre,²⁰ allowing easy access to reactants, while 4) helping reduce catalyst deactivation/decomposition.^{20,21}

4.2 RESULTS AND DISCUSSION

Complexes **3.8** – **3.10** and **3.16** (Figure 4.2) were tested for catalytic activity in Suzuki-Miyaura coupling reactions. Complex **3.10** was used in preliminary testing to optimize reaction conditions (temperature, nature of base, solvent type and catalyst loading). The coupling of bromobenzene and phenylboronic acid was chosen as the model reaction and all reactions were carried out under aerobic conditions. Secondly, complexes **3.8**, **3.9**, **3.10** and **3.16** were evaluated for activity in Suzuki-Miyaura coupling reactions to test the effect of palladium precursor (**3.8** and **3.16**) and substituents (**3.8**, **3.9** and **3.10**) that may influence the second coordination sphere of the metal centre.

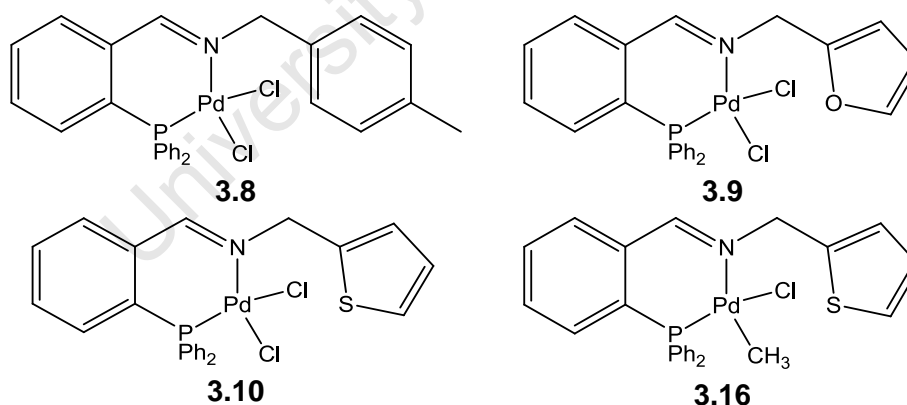


Figure 4.2: Complexes tested for catalytic activity in Suzuki-Miyaura Coupling reactions.

Complex **3.10** was found to be active and full conversion was observed to occur within three hours of reaction under optimized reaction conditions. As a result, the reactions were carried out for a period of 3 h, except in cases where conversion was not observed or was found to be very low in the given period. In such cases the reactions were carried out over a period of 24 h. The molar ratio of bromobenzene : phenylboronic acid : base used was 1.0 : 1.5 : 2.0 for all reactions. The results of these optimization reactions are presented in Table 4.1.

4.2.1 Optimization of Reaction Conditions

4.2.1.1 Effect of Temperature

The reaction was carried out in toluene at 85 °C, 100 °C, 110 °C and 140 °C. The amount of catalyst used was 0.1 mol% and K_2CO_3 was used as base. Complex **3.10** is active even at temperatures as low as 85 °C (entry 1, Table 4.1), with almost complete conversion (94%) being obtained in 3 h. Increasing the temperature to 100 °C (entry 2, Table 4.1) results in an increase in reaction rate, and 92% conversion is reached in 1 h (compared to 77% obtained after 1 h at 85 °C) and 97% conversion at the end of 3 h. Increasing the temperature beyond 100 °C (entries 3 and 4, Table 4.1) does not have a significant beneficial effect on catalyst performance, although complete conversion is reached within 2.5 h at 140 °C. At 110 °C, 90% and 98% conversion were reached within 1 h and 3 h respectively. In all cases, most of the conversion occurs in the first hour of the reaction, with $\geq 90\%$ conversion being reached within an hour at 100 °C and 110 °C (Figure 4.3). Based on the results obtained from the temperature study, all subsequent reactions were carried out at 100 °C.

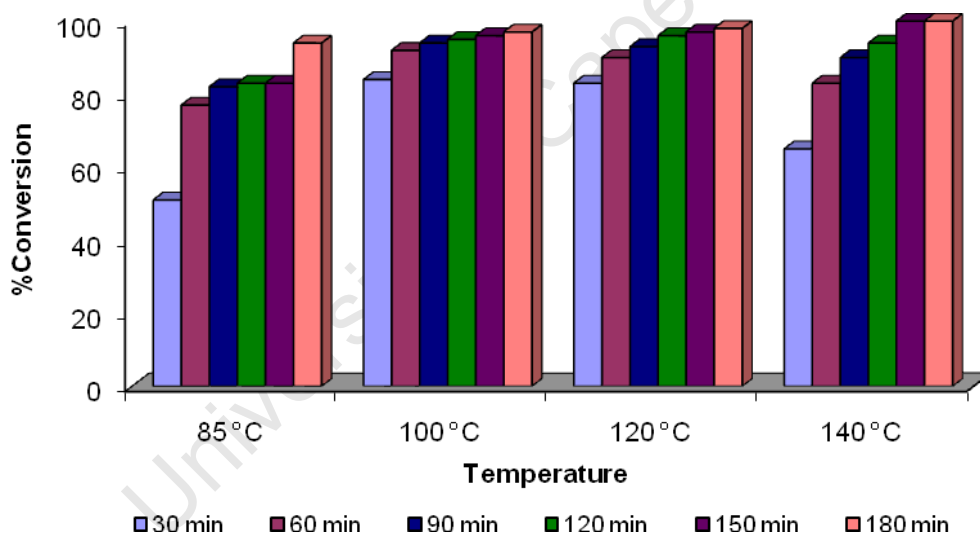


Figure 4.3: Effect of temperature on the production of biphenyl under different temperature conditions with complex **3.10** as catalyst.

4.2.1.2 Catalyst Loading

Entries 1, 5 and 6 in Table 4.1 show the effect of catalyst loading on the performance of complex **3.10**. The best performance is obtained when 0.1 mol% Pd is used. When 0.1 mol% of pre-catalyst is used, 92% conversion is reached within the first hour of the reaction while 87% and 69% conversions are reached in the same amount of time when 1.0 mol% and 5.0 mol%, respectively, are used. Conversion stabilizes at ca. 70% when 5.0 mol% percent of catalyst is used while almost complete conversion (97%) is achieved using 0.1 mol% of catalyst (Figure 4.4).

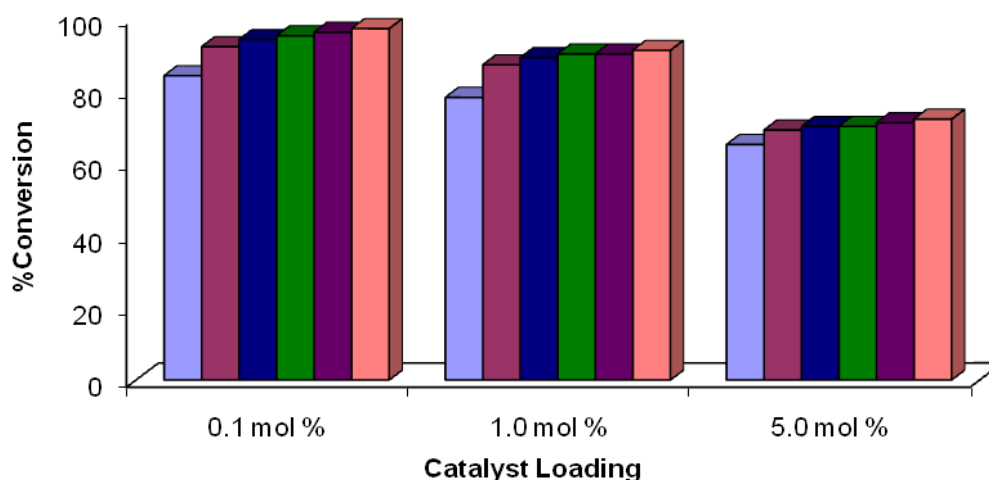


Figure 4.4: Effect of catalyst loading on the production of biphenyl with complex as catalyst **3.10**.

Increasing catalyst loading to 1.0 and 5.0 mol% Pd (entries 5 and 6, Table 4.1) results in catalyst decomposition (shown by formation of palladium black in the reaction mixture) within the first five minutes and one minute, respectively. This observation is in agreement with those by de Vries,³⁹ Rothenberg^{40,41} and others,^{43,44} that only homeopathic amounts of palladium (typically 0.001 - 0.01 mol%) are needed for cross-coupling reactions. This is attributed to the fact that once palladium has been reduced to Pd(0), it tends to form nanoclusters, which have low stability. These clusters eventually aggregate to form palladium black. Therefore, lowering palladium concentration in the reaction mixture favours oxidative addition of the aryl bromide to the Pd(0) species over cluster formation and subsequent catalyst deactivation.^{39a} This result is of particular importance because the use of low catalyst loading is beneficial only when high reaction rates accompanied by almost complete conversions are observed. Otherwise expensive and time-consuming procedures for product separation and purification would be necessary, negating the beneficial effects of using low catalyst loading.

4.2.1.3 Effect of Base

Entries 2 and 7 – 11 in Table 4.1 highlight the effect of various bases on the catalytic performance of complex **3.10**. K_2CO_3 , the relatively cheap and easy to handle base chosen for the preliminary investigations, turned out to be one of the most efficient, along with KOH (entry 7), Cs_2CO_3 (entry 10, Table 4.1) and NaOH (entry 11, Table 4.1), which gave conversions in excess of 96% in 3 h or less. When these bases were used, conversions in excess of 80% were obtained as early in the reaction as 40 minutes, with 91% conversion being reached in this time when Cs_2CO_3 was used as base.

In contrast, the organic base, NaOAc (entry 8, Table 4.1) as well as Na_2CO_3 (entry 9, Table 4.1) performed poorly, with only 42% and 29% conversion, respectively, obtained after 24 h of reaction. Interestingly, comparing entries 2 and 9, a 'potassium effect'³⁴ becomes evident. It seems that the cation plays an important role in determining the efficiency of the base to activate the boronic acid as previously reported.^{34,44-46}

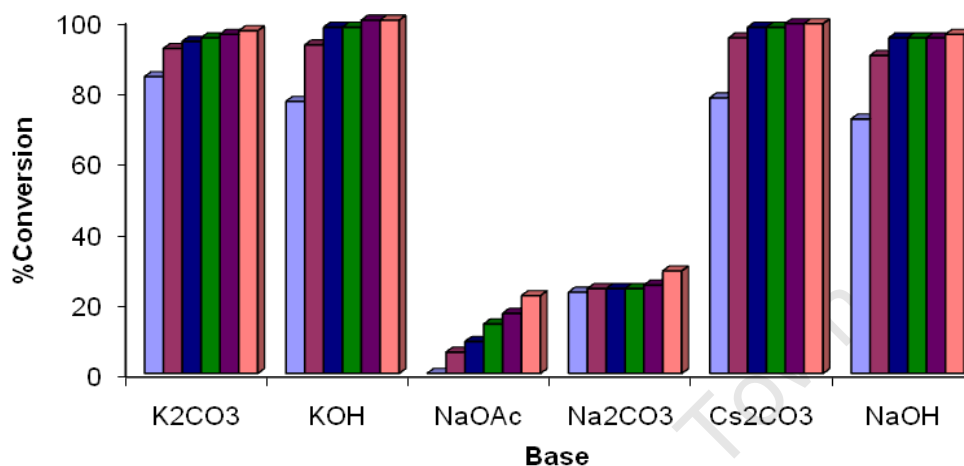


Figure 4.5: Effect of base on the production of biphenyl with complex **3.10** as catalyst.

4.2.1.4 Choice of Solvent

Polar aprotic solvents like THF, DMF and dioxane are often used for coupling reactions as they allow for the best solubility of both the substrates and the catalysts used. As a result, high conversions with high selectivities (depending on the choice of ligand) can be obtained under mild conditions. A study of solvent effects on the activity of complex **3.10** revealed that while the reaction proceeds well in toluene (entry 2, Table 4.1) and 1,4-dioxane (entry 12, Table 4.1), catalytic performance is greatly affected in DMF and even more so in acetonitrile (entries 13 and 14, Table 4.1). Scrivanti and co-workers³⁴ reported that no catalytic activity was observed when they used the heterodonor P[^]O complex $[\text{PdCl}_2\{8\text{-}(\text{di-tertbutylphosphinoxy})\text{quinoline}\}]$ as a pre-catalyst for Suzuki-Miyaura coupling in DMF. They attributed the lack of catalytic activity in this solvent to a possible mechanism whereby these solvents could activate a process such as ligand hydrolysis leading to catalyst decomposition.

Since in our case catalytic activity is just slowed down and not completely suppressed, this mode of catalyst deactivation is not operative. A possible explanation could be that, since both acetonitrile and DMF are basic solvents with N-donor atoms, they could compete with the imine moiety of the ligand in coordinating to the palladium centre and the resultant complexes could be less active than the iminophosphine complex. This possibility is further supported by the fact that in DMF, which is less basic than acetonitrile due to conjugation,

and therefore has a lower coordination ability, the reaction proceeds to almost complete conversion (94% after 24 h), whereas in acetonitrile only 54% conversion is obtained in the same period. The reaction in 1,4-dioxane proceeds at a much faster rate than it does in DMF and the same logic can be applied to explain this. Since the oxygen donor atoms in dioxane are a harder base than the nitrogen donor atom in DMF, this solvent is less likely to coordinate to the palladium centre and therefore it is less likely to interfere with catalyst performance.

Nobre and Monteiro³² reported the use of Pd(OAc)₂ in combination with iminophosphine ligands (2-diphenylphosphino-benzylidene)-2-methylpropan-2-amine or (2-diphenylphosphino-benzylidene)-2,6-diisopropylaniline as catalysts for the coupling of phenylboronic acid and 4-bromotoluene. They also observed that for this catalyst system, dioxane and toluene were the best solvents (with 72% conversion being obtained for both solvents at 50 °C and 1 mol% Pd). Poor results were obtained when acetonitrile was used.³² The graph in Figure 4.6 shows that toluene performed consistently better than the other solvents. However at the end of 3 h the same conversions were obtained for both toluene and 1,4-Dioxane.

The activity of complex **3.10** compares generally favourably with other hetero-donor palladium complexes reported for Suzuki-Miyaura coupling^{17,32,34,35} with lower catalyst loading and shorter reaction times required, while high reaction rates are maintained.

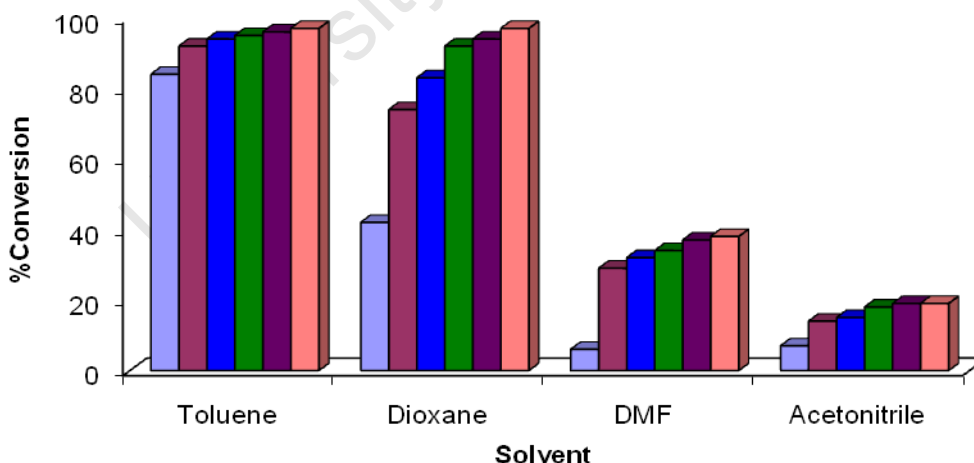


Figure 4.6: Solvent effects on the production of biphenyl using **10**.

4.2.1.5 Mercury Poisoning Test

To determine whether the catalytic species is the molecular iminophosphine palladium complex or nanoparticles (colloids or nanoclusters), a mercury poisoning test was carried out by adding mercury to the reaction mixture before catalytic testing was performed. Mercury is

known to form an amalgam with Pd(0) species, blocking active sites on catalytically active nanoparticles.

The results from the mercury test (entry 15, Table 4.1, Figure 4.7) show an almost complete suppression of catalytic activity in the presence of mercury, indicating that the probability of the actual active species in these reactions being a form of palladium nanoparticles (colloids, nanoclusters, etc) cannot be excluded. It should be noted, however, that not only colloidal Pd(0) but also molecular Pd(0) complexes have been reported to be destroyed by elemental mercury.^{47,48} The results obtained from these tests show that the iminophosphine ligands used in this study are capable of stabilizing the active catalyst.

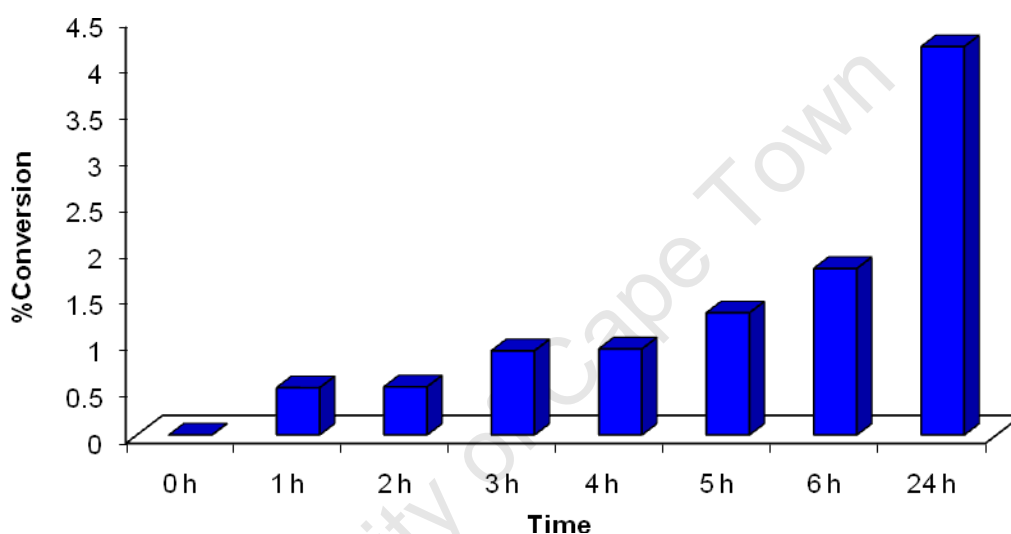


Figure 4.7: Effect of mercury poisoning on biphenyl production using **10** as catalyst.

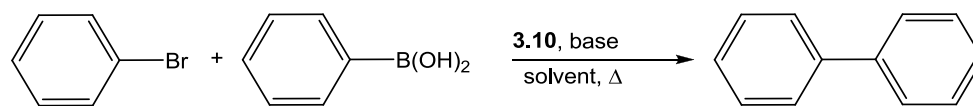
4.2.2 Choice of Arylhalides and Phenylboronic Acids

An investigation into the effect of the use of different aryl halides and substituted phenylboronic acids as substrates on the production of biphenyls under the optimized conditions determined in the preliminary study for **3.10** (0.1 mol% Pd, K₂CO₃, toluene, 100 °C) was carried out. The results from these tests are presented in Table 4.2.

In palladium-catalyzed coupling reactions, oxidative addition to a Pd(0) species is often the rate-determining step in the catalytic cycle,⁸ and the relative reactivity decreases in the order of I > OTf > Br >> Cl because of the different C-X dissociation energies, (e.g. C-I 240 kJ/mol to C-Cl 339 kJ/mol). However, for some catalyst systems, a reversal of reactivity between aryl bromides and aryl iodides has been reported, and in these cases, transmetalation of the Pd^{II}-X species is the rate-determining step. Smith and co-workers^{7j} carried out mechanistic studies of the Suzuki coupling in the production of the drug trityl losartan, an angiotensin II receptor antagonist used for the treatment of high blood pressure, in which they determined

that the rate-determining step depends on the identity of the aryl halide. They found that when using aryl bromide, oxidative addition was rate-determining since the coupling rate was strongly dependent on the concentration of the catalyst and the aryl bromide but independent of the aryl boronic acid.

Table 4.1: Influence of temperature, base, solvent and catalyst loading on the activity of **3.10**^a



Entry	mol% Pd	Conditions	Time (h)	Solvent	Base	%Conversion ^b
1	0.1	85 °C	3	Toluene	K ₂ CO ₃	94
2	0.1	100 °C	3	Toluene	K ₂ CO ₃	97
3	0.1	110 °C	3	Toluene	K ₂ CO ₃	98
4	0.1	140 °C	2.5	Toluene	K ₂ CO ₃	100 ^e
5	1.0	100 °C	3	Toluene	K ₂ CO ₃	91
6	5.0	100 °C	3	Toluene	K ₂ CO ₃	72
7	0.1	100 °C	1.5	Toluene	KOH	98
8	0.1	100 °C	24	Toluene	NaOAc	42
9	0.1	100 °C	24	Toluene	Na ₂ CO ₃	29
10	0.1	100 °C	1.5	Toluene	Cs ₂ CO ₃	98
11	0.1	100 °C	1.5	Toluene	NaOH	95
12	0.1	100 °C	3	1,4-Dioxane	K ₂ CO ₃	97
13	0.1	100 °C	24	DMF	K ₂ CO ₃	95 ^c
14	0.1	100 °C	24	Acetonitrile	K ₂ CO ₃	52
15 ^d	0.1	100 °C	24	Toluene	K ₂ CO ₃ ,	4

^aConditions: Solvent (15 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol). ^bDetermined by GC with n-decane as internal standard. ^c38% conversion observed after 3h. ^d0.1 mol% Hg with respect to bromobenzene. ^eReaction done in a sealed tube.

In contrast, when aryl iodide was used as substrate, the coupling rate was found to be proportional to the concentration of the catalyst and the aryl boronic acid but independent of the concentration of iodotoluene, i.e., the transmetalation was rate-determining. This observation has been attributed to the strength of the Pd^{II}-X bond in the products of the oxidative addition step,⁴⁹⁻⁵¹ and was supported by density functional theory calculations for the Stille cross-coupling reaction, which showed that the overall activation barriers for the transmetalation process increase in the order: X = Cl < Br < I.⁴⁹

Comparing the efficiency of the different aryl halides as substrates in the current study reveals that the best results are obtained when bromobenzene is used (entry 3, Table 4.2, Figure 4.8) and the poorest results are obtained when chlorobenzene is used as substrate (entry 2, Table 4.2). Although a slower reaction rate (compared to bromobenzene) is observed when iodobenzene is used as the substrate (entry 1, Table 4.2), the reaction proceeds almost to completion after 24 h (97%).

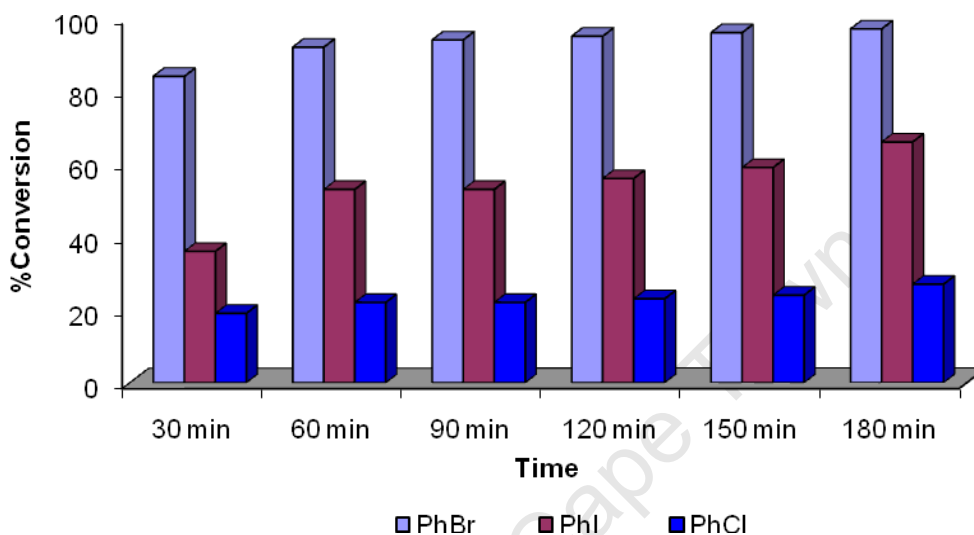


Figure 4.8: Effect of choice of aryl halides on biphenyl production with complex **3.10** as complex.

Complex **3.10** is tolerant of both electron-withdrawing and electron-donating groups on the aryl bromide. The best results were obtained when highly electron-deficient aryl bromides such as 2-bromobenzonitrile (entry 6, Table 4.2) and 4-bromobenzaldehyde (entry 4, Table 4.2) were used. 100% conversion was reached within 50 minutes for both substrates. Using relatively electron-rich aryl bromides slows down the rate of reaction (entries 5 and 7, Table 4.2), with the worst results (80% conversion after 24 h) obtained when 4-bromobenzyl bromide was used as substrate (entry 5, Table 4.2).

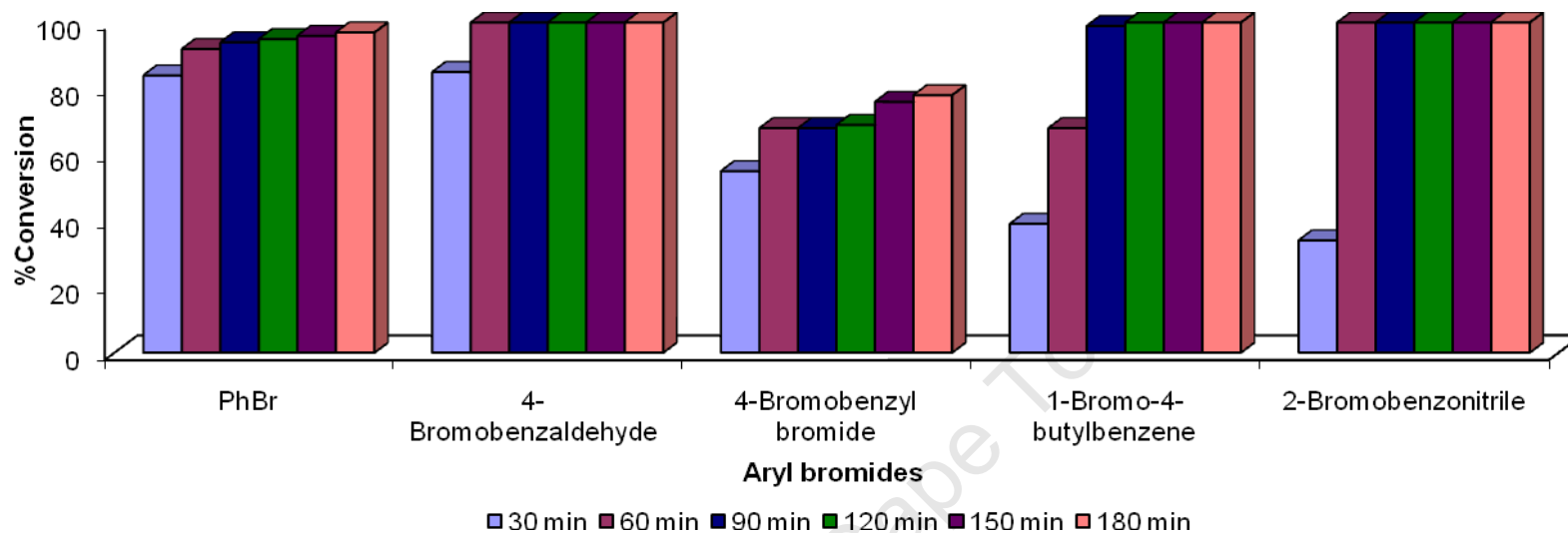


Figure 4.9: Effect of substituents on bromobenzene on catalytic performance of complex 3.10.

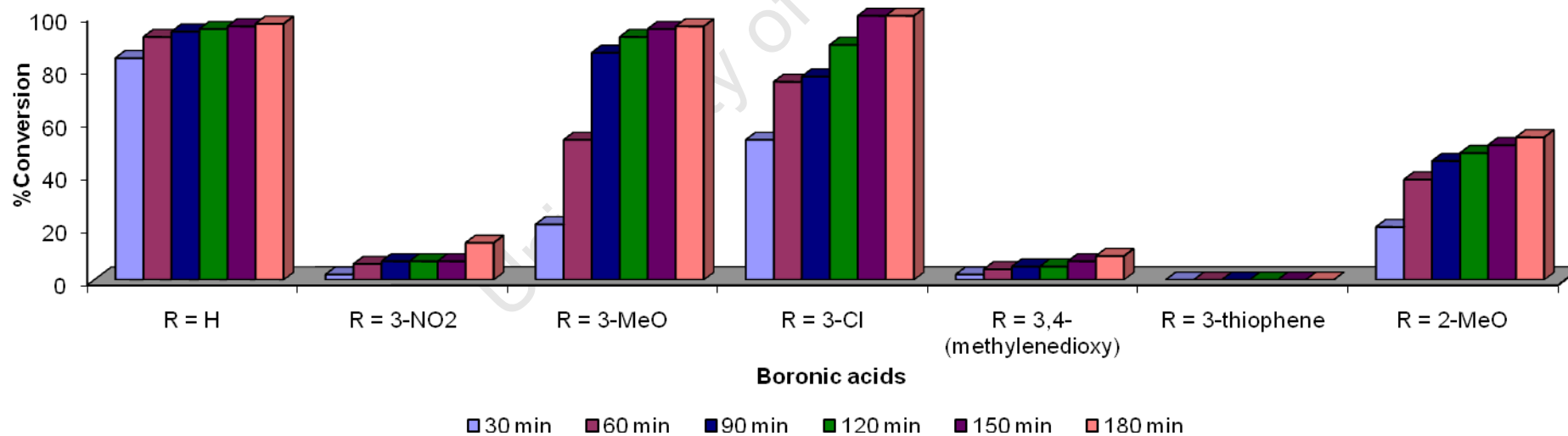
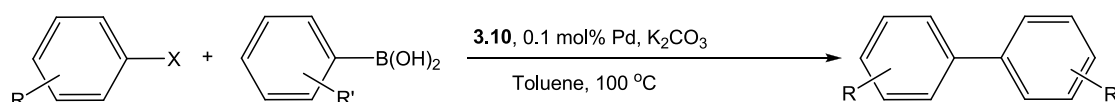


Figure 4.10: Effect of choice of boronic acids on catalytic performance of complex 3.10.

Table 4.2: Suzuki-Miyaura coupling of various aryl halides with phenylboronic acids complex **3.10**^a

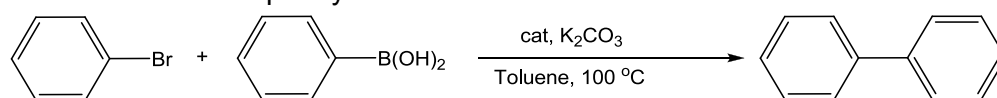
Entry	Ar-X	Ar'-B(OH) ₂	mol% Pd	Time	%Conversion ^b
1			0.1	3 h	66 ^c
2			0.1	24 h	27
3			0.1	3 h	97
4			0.1	50 min	100
5			0.1	24 h	80
6			0.1	50 min	100
7			0.1	2h	100
8			0.1	24 h	19
9			0.1	2 h	92
10			0.1	1.5 h	100
11			0.1	24 h	15
12			0.1	24 h	6
13			0.1	24 h	63

^aConditions: Solvent (15 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol). ^bDetermined by GC with n-decane as internal standard. ^c97% conversion observed after 24 h.

The complex also shows tolerance for electron withdrawing and electron donating substituents on phenylboronic acid. Good conversions were obtained in cases where 3-chloro- and 3-methoxy-substituted phenylboronic acids were used. In the case where 2-methoxyphenylboronic acid was used, only moderate conversion was obtained, and this could be due to steric effects which could come into play due to the close proximity of the methoxy group to the boronic acid moiety. Very little conversion was obtained when 3,4-(methylenedioxy)phenylboronic acid was used, with only 15% conversion being observed after 24 hr. 3-thiopheneboronic acid was also used as substrate and only 6 % conversion to the desired product was obtained after 24 h, possibly due to poisoning of the active catalytic species by substrates with donor sites.

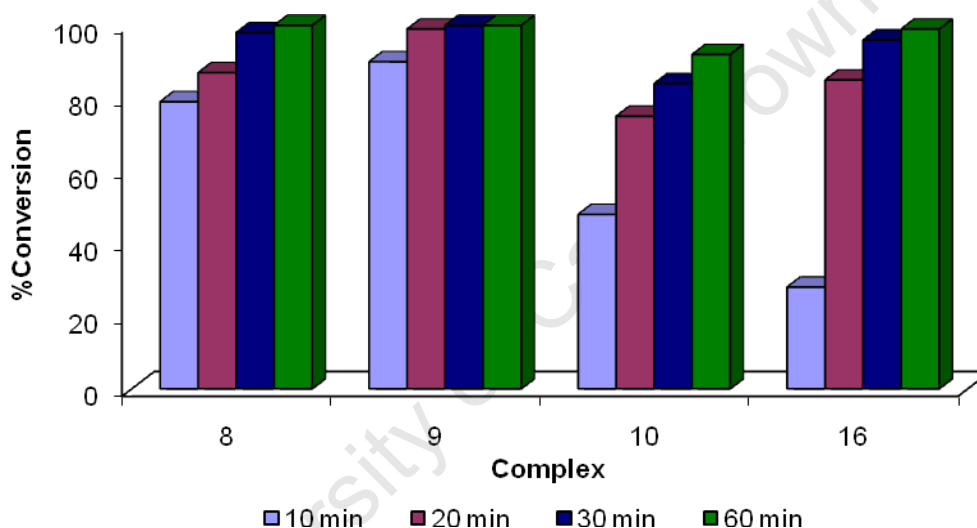
4.2.3 Catalytic Activity of Complexes 3.8, 3.9, 3.10 and 3.16

A comparative study of catalytic activity involving complexes **3.8**, **3.9**, **3.10** and **3.16** was carried out to determine the effects of palladium precursor as well as ligand substituents using conditions optimized for **3.10**. Comparing the results obtained for **3.10** and **3.16** (entries 3 and 4, Table 4.3) it is observed that the methyl chloride complex is slightly more active than its dichloride counterpart. Under the same reaction conditions 100% conversion is reached within 90 minutes with the methyl chloride complex (**3.16**) while only 84% conversion is achieved with the dichloride complex (**3.10**) in 90 minutes and 97% conversion is achieved after 3 h. Furthermore, comparing the results obtained for **3.8**, **3.9** and **3.10** (entries 1 – 3, Table 4.3) it is seen that having a ligand bearing a weakly coordinating donor atom in the second coordination sphere of the metal centre has a beneficial influence on the catalytic activity of the complex. Of the three complexes, complex **3.9**, bearing the furfuryl substituent gave the best results, with 90% and 100% conversion being obtained in 10 min and 30 min respectively (Figure 4.10). Complexes **3.8** and **3.16**, on the other hand, gave 98% and 96% conversion, respectively in 30 min. In all cases, good turn over numbers (>840 mol/mol Pd) and turn over frequencies (>1680 mol/mol Pd/h), based on aryl bromide conversion, were observed.

Table 4.3: Catalytic activity of complexes **3.8** – **3.10**, and **3.16** for the coupling of bromobenzene and phenylboronic acid^a

Entry	Catalyst	R	mol% Pd	%Conversion ^b	TON ^{f,h}	TOF ^{g,h}
1	3.8	4-Tolyl	0.1	98 ^c	980	1960
2	3.9	2-Furfuryl	0.1	100	1000	2000
3	3.10	2-Thionyl	0.1	84 ^d	840	1680
4	3.16	2-Thionyl	0.1	96 ^e	960	1920

^aConditions: Solvent (10 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol), 0.1 mol% Pd, time (30 minutes). ^bDetermined by GC with n-decane as internal standard. ^c100% conversion obtained after 40 minutes. ^d97% conversion obtained after 3 h. ^e100% conversion obtained after 1.5 h. ^fTON: mol of aryl bromide converted/mol catalyst. ^gTOF: mol of aryl bromide converted/mol catalyst per hour. ^hTON and TOF values at 30 minutes of reaction.

**Figure 4.11:** Comparison of catalytic activities of **3.8** – **3.10** and **3.16**.

4.3 SUMMARY AND CONCLUSIONS

A selection of palladium dichloride and palladium methylchloride complexes based on iminophosphine ligands (Chapter 3) was tested for activity in Suzuki-Miyaura coupling reactions. An extensive study on the scope of these complexes was performed and they were found to be compatible with a wide range of reaction conditions as well as functional groups on both the aryl halides and the arylboronic acids. The results show that for these iminophosphine complexes, low catalyst loadings are required while high conversions and short reaction times are maintained. In addition, having a substituent bearing a donor atom on the imine moiety was found to enhance catalytic activity. Palladium methyl chloride complexes were found to be more active than their palladium dichloride counterparts. A

distinct halide effect was observed, whereby there was a reversal in reactivity pattern between bromobenzene and iodobenzene.

University of Cape Town

4.4 REFERENCES

1. Herrebout, W. A., Nagels, N., Verbeeck, S., van der Veken, B. and Maes, B. U. W., *Eur. J. Org. Chem.*, 2010, 3152.
2. Tsuji, J. (Ed.), *Palladium in Organic Synthesis*, 2005, vol. 14, Springer, Dordrecht.
3. Kingston, J. V. and Verkade, J. G., *J. Org. Chem.*, 2007, **72**, 2816.
4. (a) Li, J. J. and Gribble, G. W. (Eds.), *Palladium in Heterocyclic Chemistry*, 2006, vol. 26, Pergamon, Amsterdam. (b) Kotschy, A. and Timári, G. (Eds.: James, B. and van Leeuwen, P. W. N. M.), *Heterocycles from Transition Metal Catalysis*, 2005, vol. 28, Springer, Dordrecht.
5. (a) Buchwald, S. L., Mauger, C., Mignani, G. and Scholz, U., *Adv. Synth. Catal.*, 2006, **348**, 23. (b) Corbet, J. P. and Mignani, G., *Chem. Rev.*, 2006, **106**, 2651. (c) Blaser, H.-U., Indolese, A., Naud, F., Nettekoven, U. and Schnyder, A., *Adv. Synth. Catal.*, 2004, **346**, 1583. (d) Rouhi, A. M., *Chem. Eng. News*, 2004, **82**, 49. (e) Torborg, C. and Beller, M., *Adv. Synth. Catal.*, 2009, **351**, 3027.
6. Dupont, J., Consorti, C. S. and Spencer, J., *Chem. Rev.*, 2005, **105**, 2527.
7. (a) Lloyd-Williams, P. and Giralt, E., *Chem. Soc. Rev.*, 2001, **3**, 145 and references therein. (b) Nicolaou, K. C., Boddy, C. N. C., Brase, S. and Winssinger, N., *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2096. (c) Yuan, X.-Y., Li, H.-Y., Hodge, P., Kilner, M., Tastard, C. Y., and Zhang, Z.-P., *Tetrahedron: Asymmetry*, 2006, **17**, 2401. (d) Inoue, S., Takaya, H. P., Tani, K., Otsuka, S., Sato, T. and Noyori, R., *J. Am. Chem. Soc.*, 1990, **112**, 4897. (e) Noyori, R., *J. Am. Chem. Soc.*, 1989, **18**, 187. (f) Sogah, G. D. Y. and Cram, D. J., *J. Am. Chem. Soc.*, 1976, **98**, 3038. (g) Pu, L., *Chem. Rev.*, 1998, **98**, 2405 and references therein. (h) Larios-Lopez, L., Navarro-Rodriguez, D., Donnio, B. and Guillon, D., *Chem. Lett.*, 2006, **35**, 652 and references therein. (i) Lin, H.-C., Lee, K.-W., Tsai, C.-M. and Wei, K.-H., *Macromolecules*, 2006, **39**, 3808. (j) Smith, G. B., Dezeny, G. C., Hughes, D. L., King, A. O. and Verhoeven, T. R., *J. Org. Chem.*, 1994, **59**, 8151. (k) Birkenhager, W. H. and de Leeuw, P. W., *J. Hypertens.*, 1999, **17**, 873. (l) Goa, K. L. and Wagstaff, A. J., *Drugs*, 1996, **51**, 820.
8. Pudasaini, B. and Janesko, B. J., *Organometallics*, 2011, **30**, 4564.
9. Weng, Z., Teo, S. and Hor, T. S. A., *Acc. Chem. Rev.*, 2007, **40**, 676.
10. Miyaura, N., and Suzuki, A., *Chem. Rev.*, 1995, **95**, 2457.
11. (a) Amatore, C., Jutand, A. and Le Duc, G., *Chem. Eur. J.*, 2011, **17**, 2492. (b) Carrow, B. P. and Hartwig, J. F., *J. Am. Chem. Soc.*, 2011, **133**, 2116.
12. Kirchhoff, J. H., Netherton, M. R., Hills, I. D. and Fu, G. C., *J. Am. Chem. Soc.*, 2002, **124**, 13662.

13. Bermejo, A. A., Ros, A., Fernandez, R. and Lassaletta, J. M., *J. Am. Chem. Soc.*, 2008, **130**, 15798.
14. Molander, G. A., Katona, B. W. and Machruohi, F., *J. Org. Chem.*, 2002, **67**, 8416.
15. Dreher, S. D., Lim, S-E., Sandrock, D. L. and Molander, G. A. *J. Org. Chem.*, 2009, **74**, 3626.
16. Molander, G. A. and Bernardi, C. R., *J. Org. Chem.*, 2002, **67**, 8424.
17. Teo, S., Weng, Z. and Hor, T. S. A., *J. Organomet. Chem.*, 2011, **696**, 2928.
18. P. Espinet, K. Soulantica, *Coord. Chem. Rev.*, 1999, **193 – 195**, 499.
19. Jeffrey, J. C. and Rauchfuss, T. B., *Inorg. Chem.*, 1979, **18**, 2658.
20. Bhattacharya, P., Parr, P. B. J. and Slawin, A. M., *J. Chem. Soc. Dalton Trans.*, 1998, 3609. (b) Linder, R., van den Bosch, B., Lutz, M., Reek, J. N. H. and van der Vlugt, J. I., *Organometallics*, 2011, **30**, 499.
21. Ni Dhubhnhail, O. M., Lennon, J. and Drew, M. G. B., *Dalton Trans.*, 2005, 3213.
22. (a) Davies, J. A. and Hartley, F. R., *Chem. Rev.*, 1979, **81**, 2658. (b) Lindner, E., Haustein, M., Mayer, H. A., Gierling, K., Fawzi, R. and Steinman, M., *Organometallics*, 1995, **14**, 2246. (c) T. B. Higgins, C. A. Mirkin, *Inorg. Chim. Acta*, 1995, **240**, 347.
23. Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *J. Chem. Soc., Dalton Trans.*, 2002, 1776.
24. (a) Shaffer, A. R. and Schmidt, J. A. R., *Organometallics*, 2008, **27**, 1259. (b) A. R. Shaffer, A. R. Schmidt, *Organometallics*, 2009, **28**, 2494.
25. P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.*, 2004, **346**, 497.
26. (a) Slawin, A. M. Z., Smith, M. B., Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 4575. (b) Bhattacharyya, P., Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Inorg. Chem.*, 1996, **35**, 3675. (c) Slawin, A. M. Z., Smith, M. B., Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 1283. (d) Slawin, A. M. Z., Smith, M. B. and Woollins, J. D., *Polyhedron*, 1996, **15**, 1579.
27. Polosukhin, A. I., Bondarev, O. G., Korostylev, A. V., Hilgraf, R., Davankov, V. A. and Gavrilov, K. N., *Inorg. Chim. Acta.*, 2001, **323**, 55.
28. Duran, S. E., Elsegood, M. R. J., Hammond, S. R. and Smith, M. B., *Dalton Trans.*, 2010, **39**, 7136.
29. L. Crociani, G. Bandoli, A. Dolmella, M. Basato, B. Corain, *Eur. J. Chem.*, 1998, 1811.
30. (a) A. Del Zotto, W. Baratta, M. Ballico E. Herdtweck P. Rigo, *Organometallics*, 2007, **26**, 5636. (b) E. Shirakawa, Y. Nakao, Y. Murota, T. Hiyama, *J. Organomet. Chem.*, 2003, **670**, 132. (c) G. L. Crossetti, C. A. Filgueiras, R. A. Howie, J. L. Wardell, C. M. Ziglo, *Acta Cryst.*, 2001, **C57**, 1279. (d) O. del Campo, A. Carbayo, J. V. Cuevas, G. Garcia-Herbaso, A. Munoz, *Eur. J. Inorg. Chem.*, 2009, 2254. (e) M-H. Thibault, B. E. G. Lucier, R. W. Schurko, F-G. Fontaine, *Dalton Trans.*, 2009, 7701.

31. Ghilardi, C.A., Midollini, S., Moneti, S., Orlandini, A. and Scapacci, G., *J. Chem. Soc., Dalton Trans.*, 1992, 3371.
32. Nobre, S. M. and Monteiro, A. L., *J. Mol. Catal. A: Chem.*, 2009, **313**, 65.
33. Crociani, B., Antonaroli, S., Burattini, M., Benetollo, F., Scrivanti, A. and Bertoldini, M., *J. Organomet. Chem.*, 2008, **693**, 3932.
34. Scrivanti, A., Bertoldini, M., Matteoli, U., Antonaroli, S. and Crociani B., *Tetrahedron*, 2009, **65**, 7611.
35. Crociani, B., Antonaroli, S., Burattini, M., Paoli, P. and Rossi, P., *Dalton Trans.*, 2010, 3665.
36. Shaffer, A. R. and Schmidt J. A. R., *Chem. Eur. J.*, 2009, **15**, 2662.
37. Sanchez, G., Garcia, J., Serrano, J. L., Garcia, L., Perez, J., Lopez, G., *Inorg. Chimica Acta*, 2010, **363**, 1084.
38. (a) Guan, Z. and Marshall, W. J., *Organometallics*, 2002, **21**, 3580. (b) Daugulis, O. and Brookhart, M., *Organometallics*, 2002, **21**, 5926. (c) Flapper, J., Kooijman, H., Lutz, M., Spek, A. L., van Leeuwen, P. W. N. M., Elsevier, C. J. and Kamer, P. C. J., *Organometallics*, 2009, **28**, 1180.
39. (a) Alimardanov, A., Schmieder-van de Vondervoort, L., de Vries, A. H. M., and de Vries, J. G., *Adv. Synth. Catal.*, 2004, **346**, 1812. (b) de Vries, A. H. M., Mulders, J., Mommers, J. H. M., Henderickx, H. J. W. and de Vries, J.G., *Org. Lett.* 2003, **5**, 3285. (c) Reetz, M. T. and de Vries, J. G., *Chem. Commun.*, 2004, 1559.
40. Gaikwad, A. V., Holuigue, A., Thathagar, M. B., ten Elshof, J. E. and Rothenberg, G., *Chem. Eur. J.*, 2007, **13**, 6908.
41. Pachon, L. D., Elsevier, C. J. and Rothenberg, G., *Adv. Synth. Catal.*, 2006, **348**, 1705.
42. Schmidt, A. F., Smirnov and V. V., *J. Mol. Catal. A: Chem.*, 2003, **203**, 75.
43. Yao, Q., Kinney, E. P. and Yang, Z., *J. Org. Chem.*, 2003, **68**, 7528.
44. So, C. M., Yeung, C. C., Lau, C. P., Kwong, F. Y., *J. Org. Chem.*, 2008, **73**, 7803.
45. Bedford, R. B., Hazelwood (née Welch), S. L., Horton, P. N., Hursthouse and M. B., *Dalton Trans.*, 2003, 4164.
46. Bedford, R. B., Hazelwood (née Welch), S. L., Limmert, M. E., Albisson, D. A., Draper, S. M., Noelle Scully, P., Coles, S. J., Hursthouse, M. B., *Chem. Eur. J.*, 2003, **9** 3216.
47. Olsson, D. and Wendt, O. F., *J. Organomet. Chem.*, 2009, **694**, 3112.
48. van Asselt, R. and Elsevier, C. J., *J. Mol. Catal.*, 1991, **65**, L13.
49. Ariafard, A., Lin, Z. and Fairlamb I. J. S., *Organometallics*, 2006, **25** () 5788.
50. Casado, A. L. and P. Espinet, *J. Am. Chem. Soc.*, 1998, **120**, 8978.
51. Espinet, P. and Echavarren, A. M., *Angew. Chem. Int. Ed.*, 2004, **43**, 4704.

CHAPTER 5

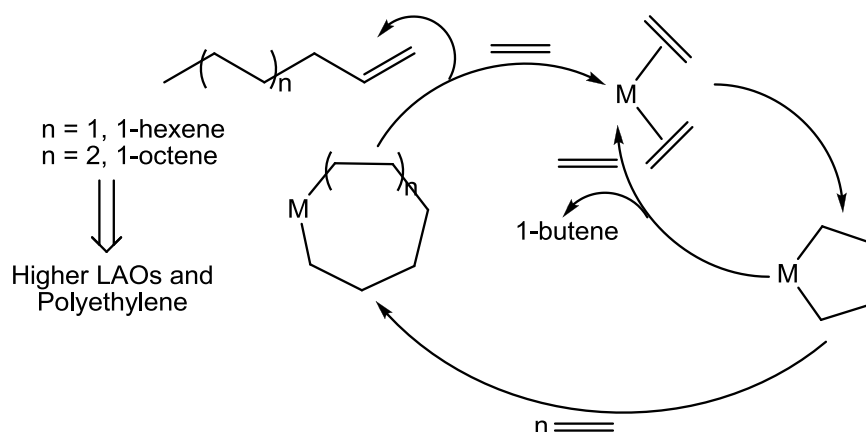
SYNTHESIS, DECOMPOSITION AND DFT STUDIES OF PLATINACYCLOALKANES

5.1 INTRODUCTION

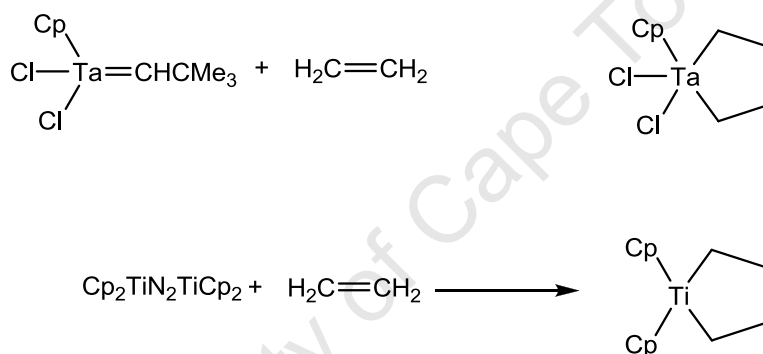
Heterocyclic compounds have played a major role in the development of organic chemistry.¹ Heterocycles containing a transition metal, in particular, are an important class of compounds, which have been shown to be either catalysts² or key intermediates in catalytic transformations of unsaturated compounds such as olefins³ and acetylenes.⁴ Metallacyclobutanes, for example, have been shown to be key intermediates in olefin metathesis reactions catalyzed by metal carbenes.⁵ The good selectivity for high-value α -olefins such as 1-butene, 1-hexene and 1-octene displayed by ethylene oligomerization catalysts based on chromium complexes has been attributed to the involvement of metallacyclo-pentanes, -heptanes and -nonanes as key catalytic intermediates (Scheme 5.1).⁶⁻⁸ As such, metallacycles have achieved a trifecta in terms of selective α -olefin production; all three of the highest volume and highest value co-monomers (i.e. 1-butene, 1-hexene, and 1-octene) can be made selectively through this route. Thus, from their origins in fundamental chemistry, metallacyclic complexes have become extremely important intermediates in large-scale industrial chemistry.⁹

In these ethylene oligomerization systems, the metallacyclic mechanism has been favoured over the Cossee-Arlman mechanism to explain the product distribution observed for the late transition metal catalysts such as those based on nickel and palladium. This is because a Cossee-type mechanism offers no reasonable explanation for the high selectivity for C_6 and/or C_8 α -olefins. Production of higher linear α -olefins (up to C_{30}) has also been proposed to proceed *via* an extended metallacycloalkane mechanism.^{8g} The preparation of tantalum and titanium metallacycles by the reaction of precursor complexes with ethylene and other simple olefins reported by Shrock¹⁰ and Whitesides¹¹ (Scheme 5.2) ultimately paved the way for the development of a catalytic process for ethylene dimerization and oligomerization. The nature of supporting ligands in these complexes plays an important role in the stability as well as the reactivity of the complexes. As a result, these ligands have important implications on the reactivity and catalytic activity of the resulting complexes.^{12,13} For instance, while palladium complexes with phosphine ligands have been successfully applied in ethylene oligomerization and polymerization, complexes with *N*-heterocyclic carbene ligands (NHC's) have not found such widespread use. It has been postulated that this is due to the

propensity of metal alkyl complexes of NHC's to decompose via alkyl-imidazolium reductive elimination.¹²



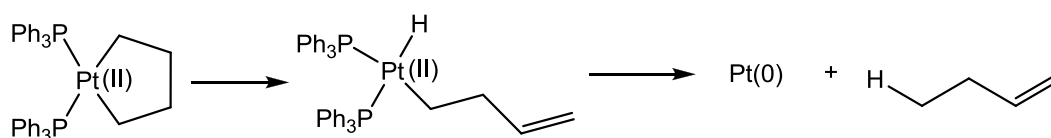
Scheme 5.1: A generalized mechanism for α -olefin production *via* metallacyclic intermediates.



Scheme 5.2: Preparation of tantalacyclopentanes and titanacyclopentanes.

Several metallacyclopentane complexes containing platinum,¹⁴ palladium¹⁵ and nickel¹⁶ have previously been prepared and characterized by spectroscopic and X-ray analysis. Decomposition studies of a range of platinacycloalkanes by Whitesides and co-workers revealed that the major products in each case are α -olefins. The reaction is believed to occur *via* sequential process involving β -hydride elimination to generate a metal-hydride species, and reductive elimination (Scheme 5.3).⁹ Because the metal-hydride species is short-lived, it is expected that little or no isomerisation of the α -olefin product should occur.⁹ Whitesides' studies also showed that metallacyclopentanes are markedly more stable thermally than analogous metallacycloheptanes.^{11,14} This was thought to be due to the constrained geometry of the metallacyclopentanes, which hinders or might even prevent β -hydride elimination. Similar observations have been made with chromacyclopentanes and chromacycloheptanes.¹⁷ However, the precise mechanism for the decomposition reaction of metallacyclopentanes has not been conclusively determined. Studies on platinum complexes indicate that although the elimination of a metal hydride is an important, albeit not

necessarily the rate-determining step in the thermal decomposition of dialkylplatinum(II) complexes and larger platinacycles, other mechanisms such as 3,5-hydrogen transfer⁹ and intermolecular hydrogen transfer¹⁸ might be involved in the decomposition of platinacyclopentanes. However, details of these alternative mechanisms have not been investigated for platinacyclopentanes. Theoretical studies with titanium complexes suggest that despite the challenges presented by constrained geometry of metallacyclopentanes, the step-wise β -hydride elimination/reductive elimination process is still the most likely decomposition pathway for these complexes.¹⁹



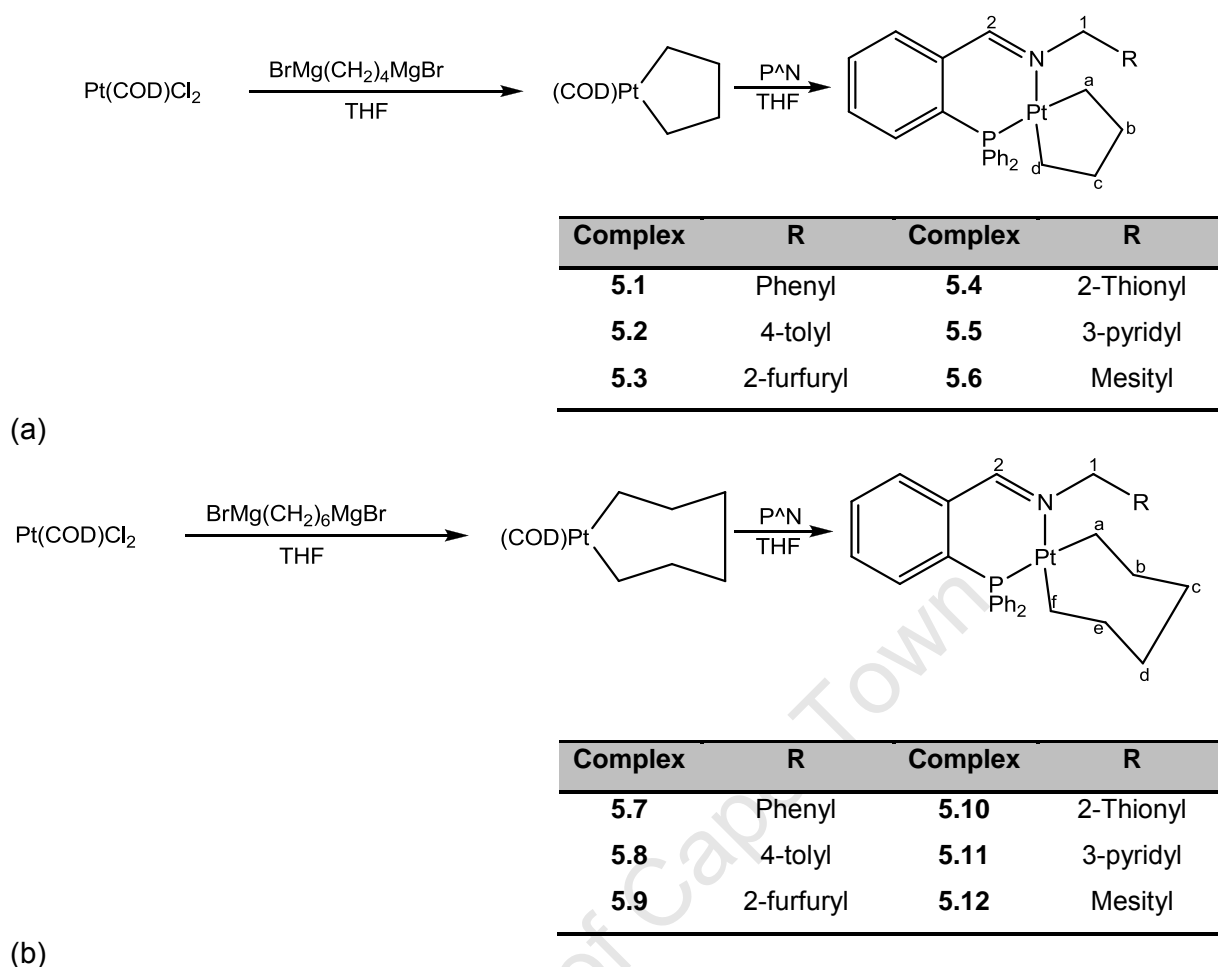
Scheme 5.3: Decomposition platinacyclopentanes.

Due to increased stability of platinacycloalkanes relative to other metallacycloalkanes, their study can offer valuable insight into the nature of transient species in catalytic processes such as ethylene oligomerization, that are proposed to involve metallacycloalkanes as key intermediates. This chapter describes the synthesis and characterization of platinacyclopentanes $[\text{Pt}(\text{P}^{\wedge}\text{N})(\text{C}_4\text{H}_8)]$ and platinacycloheptanes $[\text{Pt}(\text{P}^{\wedge}\text{N})(\text{C}_6\text{H}_{12})]$ bearing iminophosphine ligands that were described in Chapter 3. Thermal decomposition studies were carried out on these complexes. In addition, density functional calculations were carried out to study the β -hydride elimination/reductive elimination reaction sequence for the decomposition of platinacyclopentanes.

5.2 RESULTS AND DISCUSSION

5.2.1 Synthesis and Characterization of Platinacycloalkanes (5.1 – 5.12)

The reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ with the appropriate di-Grignard reagent in THF gave $[\text{Pt}(\text{COD})(\text{CH}_2)_n]$, $n = 4, 6$. The platinacycloalkanes were prepared by displacement of the labile 1,5-cyclooctadienyl ligand from $[\text{Pt}(\text{COD})(\text{C}_4\text{H}_8)]$ complexes (Scheme 5.4 (a)) or $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ complexes (Scheme 5.4 (b)) by the appropriate iminophosphine ligands to give the desired complexes. The products were obtained as yellow or orange solids (**5.1 – 5.6**) or orange oils (**5.7 – 5.12**). All complexes were obtained as air stable materials in moderate to good yields (Table 5.1).



Scheme 5.4: (a) Synthesis of platinacyclopentanes **5.1** – **5.6**. (b) Synthesis of platinacycloheptanes **5.7** – **5.12**.

The complexes were characterized by ^1H , ^{13}C and ^{31}P NMR spectroscopy as well as mass spectrometry, microanalysis and melting points (for **5.1** – **5.6**) (Tables 5.1 – 5.5). The data obtained for the compounds are in agreement with the proposed structures for the complexes. In addition, conclusive structural characterization of complex **5.1** was obtained from X-ray diffraction analysis (see section 5.2.1.4).

5.2.1.1 NMR Spectroscopy for Platinacycloalkanes **5.1** – **5.12**

^1H NMR spectra of the platinacycloalkanes show the expected signals indicative of complex formation. Coordination of the iminophosphine ligands to the metal centre was shown by an upfield shift of the imine protons (H_2 in Scheme 5.4) signals, indicating participation of the imine moiety in coordination to the metal centre. These signals appear in the range of 8.98 – 9.05 ppm in the free ligands, whereas in the platinacycloalkane complexes they appear in the range of 8.13 – 8.43 ppm. The observed upfield shift is attributed to back-bonding from the platinum centre to the imine bond. In addition, these signals appear as singlets, in contrast to the doublets observed for free ligands. This has been attributed to a

conformational change that occurs in the ligand in order to facilitate coordination.²⁰ Furthermore, these signals have platinum satellites with coupling constants in the range of $^3J_{\text{HPt}} = 31.8 - 37.1$ Hz accompanying them (Tables 5.2 and 5.4), which further supports coordination of imine moiety of the ligands to the metal centre.

Table 5.1: Isolated yields and melting point data for complexes **5.1 – 5.12**.

Complex	R	Yield	Melting Point		Microanalysis ^a		
			(°C)		C	H	N
5.1	Phenyl	83	164 – 167		56.91 (57.14)	4.83 (4.80)	2.12 (2.22)
5.2	4-Tolyl	76	142 – 143		57.79 (57.76)	5.03 (5.00)	2.15 (2.17)
5.3	2-Furfuryl	87	146 – 148		54.41 (54.19)	4.82 (4.55)	2.36 (2.26)
5.4	2-Thionyl	81	127 – 129		53.01 (52.82)	4.41 (4.43)	2.17 (2.20)
5.5	3-Pyridyl	76	139 - 142		55.20 (55.15)	4.67 (4.63)	4.39 (4.44)
5.6	Mesityl	85	172 -175		58.97 (58.92)	5.30 (5.39)	2.08 (2.01)
5.7	Phenyl	73	oil		58.37 (58.35)	5.19 (5.20)	2.11 (2.13)
5.8	4-Tolyl	68	oil		58.95 (58.92)	5.40 (5.39)	2.06 (2.08)
5.9	2-Furfuryl	77	oil		55.36 (55.55)	5.00 (4.97)	2.15 (2.16)
5.10	2-Thionyl	71	oil		54.23 (54.21)	4.84 (4.85)	2.09 (2.11)
5.11	3-Pyridyl	65	oil		56.51 (56.44)	5.05 (5.04)	4.24 (4.25)
5.12	Mesityl	60	oil		60.01 (59.99)	5.75 (5.75)	2.00 (1.99)

^aExpected values in parentheses.

As in other iminophosphine complexes discussed in Chapter 3, a downfield shift from 4.64 – 4.87 ppm in the free ligands to 5.25 – 5.77 ppm in the platinacycles is observed in the signals for the methylene protons (N-CH₂-R). This is due to the deshielding that occurs for these protons upon coordination of the adjacent imine group to platinum. The magnitude of this downfield shift is comparable to that observed for the platinum bromobutyl and platinum dichloride complexes discussed in sections 3.2.4 and 3.2.5, indicating that the chemical

environment experienced by these methylene protons is similar in these three types of complexes. In contrast, a less pronounced deshielding effect is experienced by these protons in the palladium complexes discussed in Chapter 3. As in the case of imine protons, the methylene protons (N-CH₂-R) for complexes **5.1** – **5.12** also show platinum satellites (³J_{HPt} = 15.1 – 17.0 Hz).

In addition to these ligand signals, the signals in the aliphatic region of the ¹H NMR spectra, due to the methylene protons in the carbocyclic rings of the metallacycles appear as multiplets in the region 0.72 – 1.91 ppm. The signals of methylene protons adjacent to the metal centre (Pt-CH₂-) appear in the region 0.72-1.01 ppm, and they are, in most cases, more shielded compared to the rest of the carbocyclic methylene protons. This shielding is due to the d-electrons on the metal centre. A similar effect was observed for the bromobutyl complexes **3.25** and **3.26** discussed in Chapter 3. The aromatic protons for the ligand backbone as well as the pendant R groups appear in the expected regions. As with the complexes discussed in Chapter 3, the signals for the furfuryl and thionyl protons in the platinacycloalkanes appear in a similar region as in the free ligands, indicating lack of participation of these pendant groups in metal coordination.

¹³C NMR spectroscopy provided additional evidence for the formation of desired platinacycloalkanes. Upon coordination to the metal centre, the signals for the imine carbons show a slight downfield shift from 160.3 – 161.4 ppm in the free ligands to 161.6 – 163.4 ppm in the platinacycles. As in other iminophosphine complexes, these signals appear as doublets, although the magnitude of the coupling constants is smaller compared to the free ligands. ³J_{CP} is in the range 4.3 – 6.0 Hz for the platinacycles (Tables 5.3 and 5.5) compared to 21.1 – 23.4 Hz observed for the free ligands (Table 3.2). The chemical shifts and coupling constants for imine carbons in the platinacycles are comparable to those of the platinum dichloride and bromobutyl complexes.

A more pronounced downfield shift (of up to 9.1 ppm) is observed for the methylene carbons (N-CH₂-R) upon coordination. Signals for these carbons appear at 57.0 – 65.1 ppm in the free ligands and at 60.9 – 68.8 ppm in the platinacycloalkanes. Signals for the carbon atoms in the carbocycle part of the platinacycloalkanes are observed between 14.9 and 36.1 ppm in the aliphatic region. The carbon atoms adjacent the metal centre (Pt-CH₂-) appear as doublets, due to coupling with the phosphorus atom in the iminophosphine ligand.

Due to the different ligand directing effects of phosphorus and nitrogen donor ligands, the methylene carbons adjacent the metal centre have distinct chemical shifts and coupling constants (²J_{CP}) to the phosphorus atoms in the coordinated ligands. The most shielded

carbons are **Cd** (for the platinacyclopentanes **5.1** – **5.6**) and **Cf** (for the platinacycloheptanes **5.7** – **5.12**), which are *cis* to the phosphine group. Signals for these atoms appear as doublets at 14.9 – 17.3 ppm with $^2J_{CP} = 2.6 - 3.3$ Hz. These values (for the chemical shifts and coupling constants) are similar to those observed for **Ca** in the bromobutyl complexes **3.25** and **3.26**. In these types of complexes, as well as similar palladium complexes, the preferred orientation of the ligand is such that the alkyl group is *cis* to the phosphine group and the halide ligand is *trans* to the phosphine.²¹ In contrast, signals for the methylene carbons *trans* to the phosphine group (**Ca**) are the most deshielded, appearing as doublets at 32.7 – 36.1 ppm. Moreover, coupling constants $^2J_{CP}$ for these carbons range from 4.0 – 6.2 Hz, roughly double the values observed for the carbons *cis* to the phosphine group. Signals for the other methylene carbons in the metallacycles appear as singlets in the expected region.

^{31}P NMR of the platinacycloalkanes further confirmed coordination of the phosphine groups to the metal centre. There is a downfield shift in the phosphorus signals from ca. -14 ppm in the free ligands to 25.0 – 27.1 ppm in the complexes (Tables 5.3 and 5.5). Further proof for the coordination of the phosphine group to the platinum centre comes from the platinum satellites that accompany these signals ($^1J_{PPt} = 1843 - 2066$ Hz). The magnitude of the coupling constants $^1J_{PPt}$ for these signals is in the same range as those reported for platinacyclopentanes, platinum bis(akenyl) and platinum bis(alkyl) complexes with phosphine ligands reported by Moss and co-workers.²²

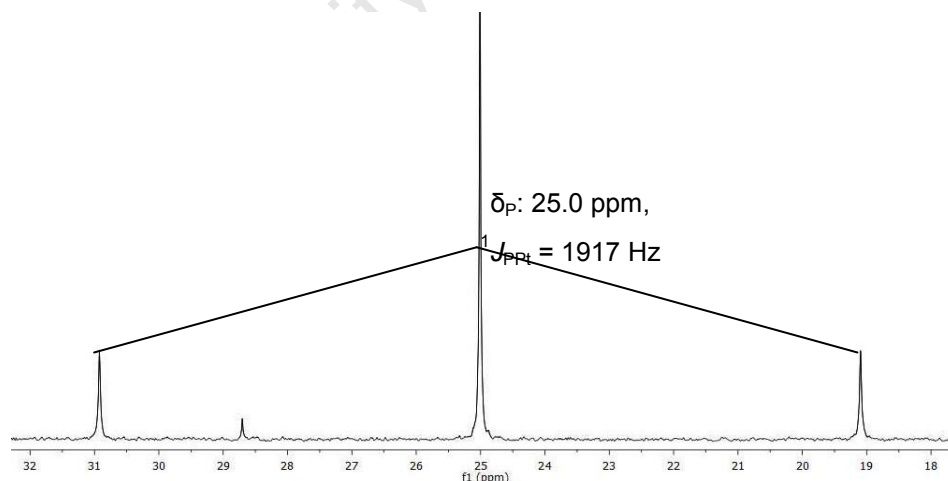


Figure 5.1: ^{31}P NMR spectrum of complex **5.1**.

Table 5.2: IR and ^1H NMR data for complexes 5.1 – 5.6

Complex	R	Formula	$\nu_{\text{C=N}}$ (cm^{-1}) ^{a,b}	$\delta_{\text{H}}(\text{H}_a+\text{H}_d)$ (ppm)	$\delta_{\text{H}}(\text{H1})$ (ppm) ^a	$\delta_{\text{H}}(\text{H2})$ (ppm) ^a
5.1	Phenyl	$\text{C}_{30}\text{H}_{30}\text{NPt}$	1631 (1636)	0.79 – 0.84 (m)	5.50 (s, $^3J_{\text{HPt}} = 16.4$ Hz) (4.67)	8.18 (s, $^3J_{\text{HPt}} = 35.1$ Hz) (9.05)
5.2	4-Tolyl	$\text{C}_{31}\text{H}_{32}\text{NPt}$	1634 (1635)	0.87 – 1.01 (m)	5.25 (s, $^3J_{\text{HPt}} = 15.8$ Hz) (4.64)	8.17 (s, $^3J_{\text{HPt}} = 34.8$ Hz) (9.00)
5.3	2-Furfuryl	$\text{C}_{28}\text{H}_{28}\text{NOPt}$	1630 (1635)	0.86 – 0.88 (m)	5.49 (s, $^3J_{\text{HPt}} = 15.1$ Hz) (4.65)	8.15 (s, $J_{\text{HPt}} = 35.0$ Hz) (8.98)
5.4	2-Thionyl	$\text{C}_{28}\text{H}_{28}\text{NPSPt}$	1630 (1634)	0.80 – 0.83 (m)	5.70 (s, $^3J_{\text{HPt}} = 16.4$ Hz) (4.86)	8.21 (s, $^3J_{\text{HPt}} = 36.4$ Hz) (9.01)
5.5	3-Pyridyl	$\text{C}_{29}\text{H}_{29}\text{N}_2\text{Ppt}$	1633 (1634)	0.89 – 0.93 (m)	5.69 (s, $^3J_{\text{HPt}} = 16.0$ Hz) (4.67)	8.43 (s, $^3J_{\text{HPt}} = 35.7$ Hz) (8.98)
5.6	Mesityl	$\text{C}_{33}\text{H}_{36}\text{NPt}$	1635 (1636)	0.81 – 0.92 (m)	5.27 (s, $^3J_{\text{HPt}} = 17.0$ Hz) (4.90)	8.20 (s, $^3J_{\text{HPt}} = 35.4$ Hz) (8.98)

^aLigand data in parentheses. ^bRecorded as KBr pellets.

Table 5.3: ^{13}C , ^{13}P and Mass Spectral data for complexes 5.1 – 5.6

Complex	R	Formula	$\delta_{\text{C}}(\text{C}_d)$ (ppm)	$\delta_{\text{C}}(\text{C}_a)$ (ppm)	$\delta_{\text{C}}(\text{C1})$ (ppm) ^a	$\delta_{\text{C}}(\text{C2})$ (ppm) ^a	δ_{P} (ppm) ^a	$[\text{M}+\text{H}]^+$ (calc) m/z
5.1	Phenyl	$\text{C}_{30}\text{H}_{30}\text{NPt}$	15.8 (d, $^2J_{\text{CP}} =$ 2.9 Hz)	33.9 (d; $^2J_{\text{CP}} =$ 5.7 Hz)	68.8 (65.1)	162.0 (d, $^3J_{\text{CP}} = 5.5$ Hz) (160.6)	25.0 (s, $J_{\text{PPt}} = 1917$ Hz) (-13.8)	631.18 (630.62)
5.2	4-Tolyl	$\text{C}_{31}\text{H}_{32}\text{NPt}$	16.1 (d, $^2J_{\text{CP}} =$ 3.1 Hz)	33.1 (d; $^2J_{\text{CP}} =$ 6.0 Hz)	67.9 (60.9)	162.2 (d, $^3J_{\text{CP}} = 5.1$ Hz) (161.3)	26.2 (s, $J_{\text{PPt}} = 1920$ Hz) (-13.6)	645.20 (644.64)
5.3	2-Furfuryl	$\text{C}_{28}\text{H}_{28}\text{NOPt}$	15.8 (d, $^2J_{\text{CP}} =$ 2.8 Hz)	33.9 (d, $^2J_{\text{CP}} =$ 5.8 Hz)	60.9 (57.0)	161.6 (d, $^3J_{\text{CP}} = 5.2$ Hz) (161.4)	25.3 (s, $J_{\text{PPt}} = 1904$ Hz) (-14.5)	621.17 (620.58)
5.4	2-Thionyl	$\text{C}_{28}\text{H}_{28}\text{NPtS}$	15.9 (d, $^2J_{\text{CP}} =$ 3.0 Hz)	36.1 (d, $^2J_{\text{CP}} =$ 5.9 Hz)	61.4 (59.9)	162.4 (d, $^3J_{\text{CP}} = 4.3$ Hz) (160.8)	25.7 (s, $J_{\text{PPt}} = 2066$ Hz) (-14.5)	637.13 (636.65)
5.5	3-Pyridyl	$\text{C}_{29}\text{H}_{29}\text{N}_2\text{Pt}$	16.0 (d, $^2J_{\text{CP}} =$ 2.8 Hz)	34.1 (d, $^2J_{\text{CP}} =$ 5.7 Hz)	64.4 (62.3)	162.1 (d, $^3J_{\text{CP}} = 5.3$ Hz) (161.3)	25.7 (s, $J_{\text{PPt}} = 1886$ Hz) (-13.4)	632.27 (631.61)
5.6	Mesityl	$\text{C}_{33}\text{H}_{36}\text{NPt}$	15.8 (d, $^2J_{\text{CP}} =$ 3.0 Hz)	32.7 (d, $^2J_{\text{CP}} =$ 5.9 Hz)	66.7 (57.6)	161.9 (d, $^3J_{\text{CP}} = 5.3$ Hz) (158.9)	26.7 (s, $J_{\text{PPt}} = 1843$ Hz) (-13.5)	673.69 (672.70)

^aLigand data in parenthesis.

Table 5.4: IR and ^1H NMR data for complexes 5.7 – 5.12

Complex	R	Formula	$\nu_{\text{C=N}}$ (cm^{-1}) ^{a,b}	$\delta_{\text{H}}(\text{H}_a+\text{H}_t)$ (ppm)	$\delta_{\text{H}}(\text{H1})$ (ppm) ^a	$\delta_{\text{H}}(\text{H2})$ (ppm) ^a
5.7	Phenyl	$\text{C}_{32}\text{H}_{34}\text{NPt}$	1635 (1636)	0.74 – 0.76 (m)	5.38 (2H, s, $^3J_{\text{HPt}} = 16.8$ Hz) (4.67)	8.33 (s, 1H, $^3J_{\text{HPt}} = 34.7$ Hz) (9.05)
5.8	4-Tolyl	$\text{C}_{33}\text{H}_{36}\text{NPt}$	1635 (1635)	0.76 – 0.89 (m)	5.45 (s, 2H, $^3J_{\text{HPt}} = 16.0$ Hz) (4.64)	8.13 (s, 1H, $^3J_{\text{HPt}} = 33.0$ Hz) (9.00)
5.9	2-Furfuryl	$\text{C}_{30}\text{H}_{32}\text{NOPt}$	1632 (1635)	0.72 – 0.75 (m)	5.77 (s, 2H, $^3J_{\text{HPt}} = 15.7$ Hz) (4.65)	8.16 (s, 2H, $^3J_{\text{HPt}} = 31.8$ Hz) (8.98)
5.10	2-Thionyl	$\text{C}_{30}\text{H}_{32}\text{NPtS}$	1631 (1634)	0.76 – 0.80 (m)	5.50 (2H, s, $^3J_{\text{HPt}} = 16.1$ Hz) (4.86)	8.17 (1H, s, $^3J_{\text{HPt}} = 33.8$ Hz) (9.01)
5.11	3-Pyridyl	$\text{C}_{31}\text{H}_{33}\text{N}_2\text{Pt}$	1634 (1634)	0.76 – 0.81 (m)	5.38 (s, 2H, $^3J_{\text{HPt}} = 15.9$ Hz) (4.67)	8.41 (1H, s, $^3J_{\text{HPt}} = 37.1$ Hz) (8.98)
5.12	Mesityl	$\text{C}_{35}\text{H}_{40}\text{NPt}$	1634 (1636)	0.79 – 0.93 (m)	5.53 (2H, s, $^3J_{\text{HPt}} = 16.4$ Hz) (4.90)	8.17 (s, 1H, $^3J_{\text{HPt}} = 35.0$ Hz) (8.98)

^aLigand data in parentheses. ^bRecorded as KBr pellets.

Table 5.5: ^{13}C , ^{13}P and Mass Spectral data for complexes 5.7 – 5.12

Complex	R	Formula	$\delta_{\text{C}}(\text{C}_f)$ (ppm)	$\delta_{\text{C}}(\text{C}_a)$ (ppm)	$\delta_{\text{C}}(\text{C1})$ (ppm) ^a	$\delta_{\text{C}}(\text{C2})$ (ppm) ^a	δ_{P} (ppm) ^a	$[\text{M}+\text{H}]^+$ (calc) m/z
5.7	Phenyl	$\text{C}_{32}\text{H}_{34}\text{NPt}$	14.9 (d, $^2J_{\text{CP}} = 3.0$ Hz)	34.2 (d, $^2J_{\text{CP}} = 5.0$ Hz)	65.4 (65.1)	162.7 (d, $^3J_{\text{CP}} = 5.5$ Hz) (160.6)	26.8 (s, $J_{\text{PPt}} = 1802$ Hz) (-13.8)	659.34 (658.67)
5.8	4-Tolyl	$\text{C}_{33}\text{H}_{36}\text{NPt}$	17.3 (d, $^2J_{\text{CP}} = 3.1$ Hz)	34.7 (d, $^2J_{\text{CP}} = 6.0$ Hz)	64.9 (60.9)	162.2 (d, $^3J_{\text{CP}} = 5.1$ Hz) (161.3)	25.9 (s, $J_{\text{PPt}} = 1954$ Hz) (-13.6)	671.63 (672.70)
5.9	2-Furfuryl	$\text{C}_{30}\text{H}_{32}\text{NOPt}$	15.1 (d, $^2J_{\text{CP}} = 2.8$ Hz)	33.7 (d, $^2J_{\text{CP}} = 4.9$ Hz)	63.5 (57.0)	162.6 (d, $^3J_{\text{CP}} = 5.4$ Hz) (161.4)	26.4 (s, $J_{\text{PPt}} = 1860$ Hz) (-14.5)	649.69 (648.63)
5.10	2-Thionyl	$\text{C}_{30}\text{H}_{32}\text{NPtS}$	17.1 (d, $^2J_{\text{CP}} = 2.9$ Hz)	34.1 (d, $^2J_{\text{CP}} = 6.0$ Hz)	63.9 (59.9)	163.0 (d, $^3J_{\text{CP}} = 5.1$ Hz) (160.8)	27.1 (s, $J_{\text{PPt}} = 1830$ Hz) (-14.5)	665.59 (664.70)
5.11	3-Pyridyl	$\text{C}_{31}\text{H}_{33}\text{N}_2\text{Pt}$	16.8 (d, $^2J_{\text{CP}} = 3.3$ Hz)	33.5 (d, $^2J_{\text{CP}} = 5.6$ Hz)	67.2 (62.3)	161.9 (d, $^3J_{\text{CP}} = 6.0$ Hz) (161.3)	26.6 (s, $J_{\text{PPt}} = 1835$ Hz) (-13.4)	660.61 (659.66)
5.12	Mesityl	$\text{C}_{35}\text{H}_{40}\text{NPt}$	16.7 (d, $^2J_{\text{CP}} = 2.6$ Hz)	33.3 (d, $^2J_{\text{CP}} = 6.2$ Hz)	65.9 (57.6)	163.4 (d, $^3J_{\text{CP}} = 5.1$ Hz) (158.9)	26.7 (s, $J_{\text{PPt}} = 1863$ Hz) (-13.5)	701.53 (700.25)

^aLigand data in parentheses.

5.2.1.2 FTIR Spectroscopy for 5.1 – 5.12

The most informative peak in the IR spectra of the platinacycles is the imine stretching band, which occurs in the region 1630 – 1635 cm^{-1} . There is a slight shift to lower wavenumbers upon coordination to the metal centre (from 1634 – 1636 cm^{-1} in the free ligands), further confirming the participation of the imine moiety in ligand coordination to the platinum. The direction and magnitude of this shift is in agreement with data reported for other iminophosphine complexes of the transition metals.²³

5.2.1.3 Mass Spectrometry and Microanalysis for 5.1 – 5.12

Microanalytical and mass spectral data were obtained for the complexes and are presented in Tables 5.3 and 5.5. The microanalytical data obtained were consistent with the molecular compositions of the proposed structures of the platinacycloalkane complexes. Mass spectral data showed $[\text{M}+\text{H}]^+$ as the highest molecular weight fragments. In addition, mass spectra showed fragments corresponding to the loss of the carbocyclic fragments of the platinacycles $[\text{M}-(\text{CH}_2)_n]^+$ (where $n = 4$ or 6).

5.2.1.4 X-ray Structure Determination for Complex 5.1

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a concentrated solution of complex **5.1** in DCM. The solid-state structure of the complex was determined in order to complete the characterization for the complex and to gain further insight into the structure of this class of compounds as platinacycloalkanes based on iminophosphine ligands have not been reported in the literature. Selected structural data are listed in Table 5.6.

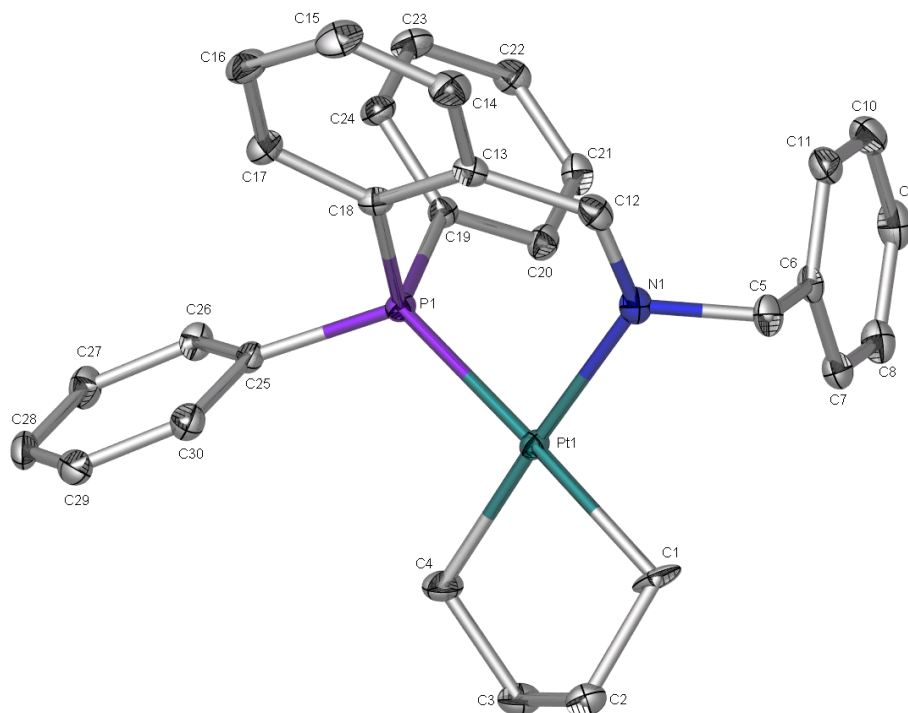


Figure 5.2: The ORTEP plot of the molecular structure of **5.1** showing numbering scheme. All non-hydrogen atoms are shown as ellipsoids with probability level of 30 %.

The X-ray crystal structure of platinacyclopentane **5.1** confirmed the bidentate coordination of the iminophosphine ligand to the metal centre. Because of the ring strain imposed by both the chelate ring N(1)-Pt(1)-P(1)-C(18)-C(13)-C(12) and the metallacycle Pt(1)-C(1)-C(2)-C(3)-C(4), the complex displays a distorted square planar geometry around the metal centre. The iminophosphine ligand forms a puckered chelate ring with platinum, with the fragment =CHC₆H₄ lying above the Pt(P[^]N)(C₄H₈) plane and the torsion angle Pt(1)-P(1)-C(18)-C(13) being 33.6(4)°. The torsion angle Pt(1)-C(1)-C(2)-C(3) is 41.3 (5)°. The bite angles around platinum deviate from the expected 90° angles and this can be attributed to the ring strain imposed by the two ring systems around the metal centre. The bite angles N(1)-Pt(1)-P(1) and C(4)-Pt(1)-C(1) are 88.18(11)° and 84.6(2)°, respectively. These values are significantly smaller than the expected 90° for square planar complexes. However, this reduction is accompanied by a compensatory increase in the other two angles around the platinum atom. C(4)-Pt(1)-P(1) and N(1)-Pt(1)-C(1) are 94.98(15)° and 92.2(2)°, respectively. Grubbs and co-workers²⁴ also observed a similar reduction in the bite angle between platinum and the carbon atoms and a compensatory increase in the bite angle between the metal centre and the phosphorus atoms in the metallacycle for the platinacyclopentane [Pt(PPh₃)₃(C₄H₈)]. In this complex, the bite angle C(37)-Pt(1)-C(40) was found to be 80.9(8)° while P(1)-Pt(1)-P(2) was found to be 98.8(2)° (Figure 5.3). These values deviate quite significantly from the expected 90° angles for the complex reported by

Grubbs compared to complex **5.1**. This can be attributed to the large cone angles for the two triphenylphosphine ligands, which results in a significantly larger than average P(1)-Pt(1)-P(1) angle and a significantly smaller than average C(37)-Pt(1)-C(40) bite angle. In addition, the bidentate nature of the ligand system in complex **5.1** restricts the degree of freedom in the complex, making the larger deviations observed in the monodentate complex [Pt(PPh₃)₃(C₄H₈)] energetically unfavourable.

Table 5.6: Selected Bond Lengths (Å) and Angles (°) for **5.1**

Bond Lengths		Bond Angles	
Pt(1)-C(1)	2.148(5)	C(4)-Pt(1)-N(1)	176.77(18)
Pt(1)-C(4)	2.052(5)	N(1)-Pt(1)-C(1)	92.2(2)
Pt(1)-N(1)	2.118(4)	C(4)-Pt(1)-C(1)	84.6(2)
Pt(1)-P(1)	2.2440(12)	C(4)-Pt(1)-P(1)	94.98(15)
P(1)-C(18)	1.831(5)	C(1)-Pt(1)-P(1)	176.78(14)
C(12)-C(13)	1.469(7)	N(1)-Pt(1)-P(1)	88.18(11)
N(1)-C(12)	1.281(6)		
N(1)-C(5)	1.487(6)		

A comparison of key bond lengths between complex **5.1** and [Pt(PPh₃)₂(C₄H₈)] (Figure 5.3(a)) as well as platinacyclic and bisalkenyl complexes, with monodentate and chelating phosphine ligands which were reported by Moss and co-workers,^{22,25} reveals important differences between these complexes and the iminophosphine complex, **5.1**. Due to the different *trans* effects of phosphine and imine donor groups, the bond lengths Pt(1)-C(1) and Pt(1)-C(4) are different. As expected, Pt(1)-C(1), which is *trans* to the phosphine group is slightly longer than Pt(1)-C(4), which is *trans* to the imine moiety. Pt(1)-C(1) and Pt(1)-C(4) are 2.148(5)Å and 2.052(5)Å, respectively. In contrast, the Pt-C bonds in Grubbs' and Moss' complexes are similar. For example, the bond lengths Pt(1)-C(37) and Pt(1)-C(40) in Grubbs' complex are 2.12(2) Å and 2.05(2) Å, respectively. Analogous bonds in the platinacycloheptene [Pt(PPh₃)₂(C₆H₁₀)] reported by Moss^{22a} are 2.136(3) Å and 2.115 (3)Å for Pt(1)-C(1) and Pt(1)-C(6), respectively (Figure 5.3(b)).

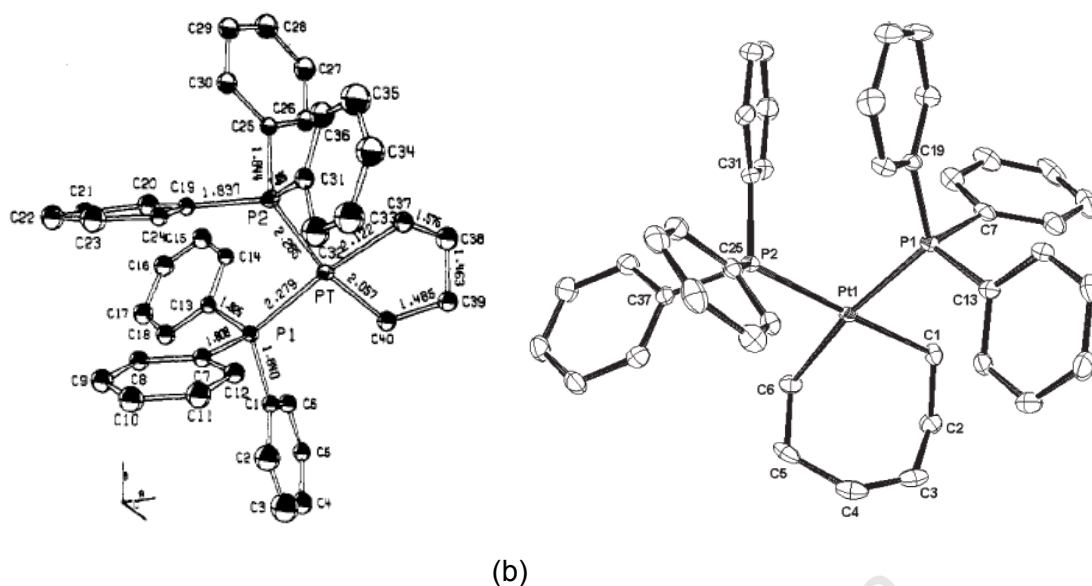
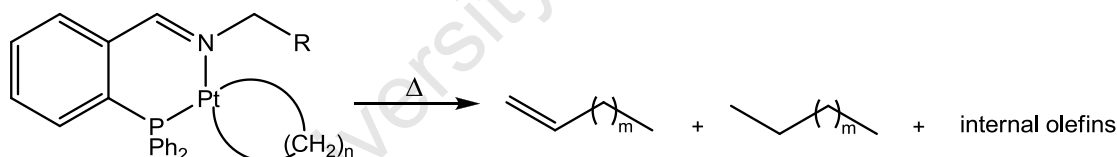


Figure 5.3: (a) ORTEP stereoscopic drawing of a single molecule of [Pt(PPh₃)₂(C₄H₈)] with all hydrogen atoms omitted, 20% probability ellipsoids.²⁴ (b) Molecular structure of [Pt(PPh₃)₂(C₆H₁₀)].^{22a}

5.2.2 Thermal Decomposition of Platinacycloalkanes 5.1 – 5.12

Decomposition products were analyzed by GC-MS. Products were identified by comparison of retention times to those of authentic commercial samples as well as fragmentation patterns obtained from MSD identification. Yields were determined by response relative to an internal standard (*n*-decane). Response factors were obtained from authentic samples.



Scheme 5.5: Decomposition of complexes **5.1** – **5.6** where $n = 4, 6$, and $m = 1, 3$.

5.2.2.1 Effect of Temperature on Product Distribution

One of the aims in this study was to determine the optimal temperature at which selective formation of α -olefins occurs for the metallacycloalkanes studied. The effect of temperature on the decomposition of **5.1** was studied by monitoring the change in the ³¹P NMR spectra of the complex throughout the decomposition process. The results from this study were used to determine the amount of time it takes for complete decomposition of **5.1** at each temperature. In addition, the NMR study was used in an attempt to shed some light on the nature of the platinum-containing fragment after decomposition. Thus far, this fragment has been referred to as the “Pt(0) species”^{14b} in the literature.

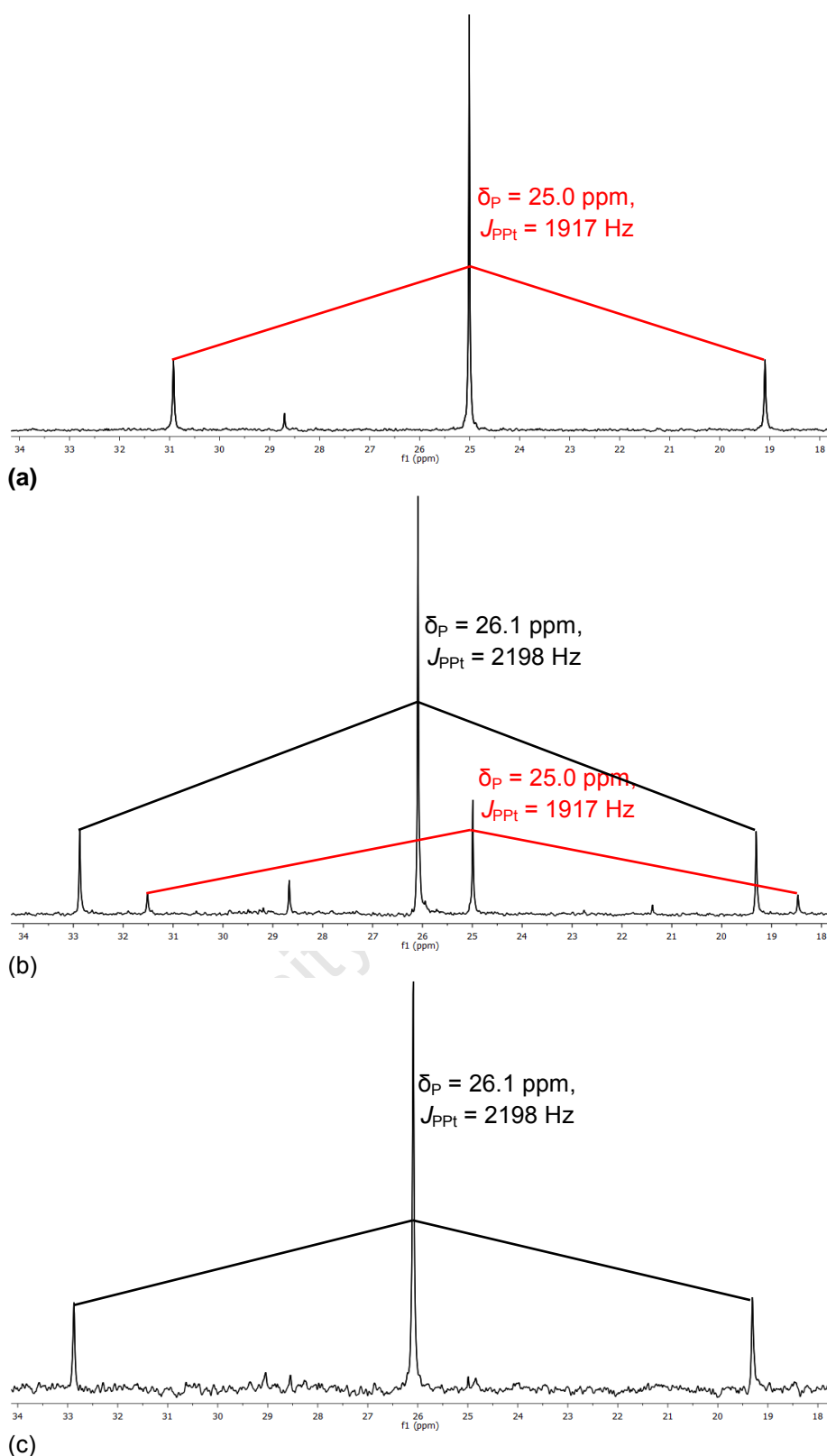
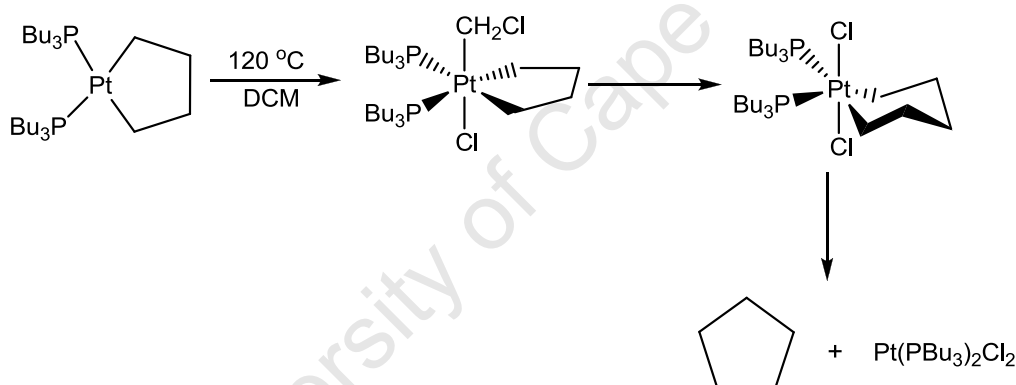


Figure 5.4: ^{31}P NMR spectra of complex **5.1** during heating at 140°C , (a) $t_{0\text{h}}$, (b) $t_{11\text{h}}$, (c) $t_{27\text{h}}$.

Figure 5.4 above shows ^{31}P NMR spectra of **5.1** during heating at 140°C . The spectra show a gradual decrease in the intensity of the signal at 25.0 ppm ($^1J_{PPt} = 1917$ Hz), which is due to the platinacyclopentane **5.1**. The decrease is accompanied by appearance and gradual

increase of a new signal at 26.1 ppm ($^1J_{\text{PPt}} = 2198\text{Hz}$). Only two signals are observed in the ^{31}P NMR spectra during the heating process at all temperatures. This result reveals two observations. The first is that only one phosphorus-containing compound is formed upon decomposition of **5.1**. Secondly, the phosphorus-containing compound is also a platinum complex, as evidenced by the presence of platinum satellites accompanying the new signal.

The magnitude of the coupling constant between the platinum and phosphorus atoms also reveals something about the nature of the platinum fragment formed in this reaction. In decomposition reactions of platinacycloalkanes performed in halogenated solvents such as dichloromethane, cycloalkanes are obtained as a major component of the organic product mixture. In addition, the platinum-containing product has been suggested to be L_2PtX_2 (L = ligand, X = halogen). The reaction in these processes is presumed to proceed *via* the following sequence: 1) Oxidative addition of the C-X bond in the solvent to the metal centre giving a Pt(IV) metallacyclic intermediate. 2) Reductive elimination of the cycloalkane, giving L_2PtX_2 as the metal-containing fragment (Scheme 5.6).²⁶



Scheme 5.6: Decomposition of platinacycloalkanes in halogenated solvents.

This route is not available for the decomposition of **5.1** as the solvent used in this case is non-halogenated. The small magnitude of the coupling constant for the new signal at 26.1 ppm therefore confirms that the metal-containing fragment does not contain any halide ligands. $^1J_{\text{PPt}}$ values for platinum complexes containing halide ligands are typically large ($>3000\text{ Hz}$).²⁷

After determining the time required for complete decomposition of **5.1** at each temperature, the reactions were scaled up (1.5 cm³ solutions) to determine the hydrocarbon product distribution. The organic products were analyzed by GC-MS. The results (Table 5.7) show that the temperature at which the decomposition reaction is carried out has a significant influence on the hydrocarbon distribution obtained. The rate of reaction is significantly higher at elevated temperatures as expected. However, the drawback is that isomerisation and hydrogenation to internal olefins and n-alkanes is also prevalent. Decreasing the

temperature from 170 °C to 120 °C resulted in an increase in the relative amount of 1-butene from 67% to 91%. Further lowering the temperature to 100 °C, however, resulted in no decomposition occurring, reflecting the stability of platinacyclopentanes.^{14a}

Comparing the results obtained under solvent free conditions (Entry 5, Table 5.7) and in toluene (Entry 4, Table 5.7) shows that the product distribution obtained under the different conditions is similar. Under solvent free conditions the amount of n-butane obtained is slightly lower than that obtained in solution. These results indicate that the solvent could act as a hydrogen donor *via* C-H activation in the formation of saturated hydrocarbons from the decomposition reaction. Formation of n-butane from the decomposition of **5.1** under solvent-free conditions, however, indicates that solvent is not the only available source of hydrogen atoms in this process. It is also possible that the hydrogen atoms could come from the C-H activation of coordinated ligands as has been proposed by Whitesides,¹⁸ or platinum hydride species that may form as intermediates or products in the reaction.

Table 5.7: Thermal decomposition of complex **5.1**.^a

Entry	Temp. (°C)	Solvent	Time (h)	1-butene	2-butenes	Butane
1	100	Toluene	120	0	0	0
2	120	Toluene	90	91	8	1
3	140	Toluene	27	81	17	2
4	170	Toluene	6	67	22	11
5	170	-	6	67	26	7

^aReactions done in triplicate. Error: ± 1%.

5.2.2.2 Effect of Time on Product Distribution for **5.1**

A time dependence study in which the relative amounts of hydrocarbons products obtained from the decomposition of **5.1** were compared over time was carried out. The reactions were carried out at 170 °C for two reasons: 1) The rate of decomposition is higher at higher temperatures, therefore appearance of products should be fast. 2) Effect of time on product isomerisation and/or hydrogenation should be detected early. The reaction was followed by monitoring the amounts of 1-butene, 2-butene and n-butane using GC-MS. The results (Figure 5.5) show that the absolute amount of 1-butene obtained increased over time. However, with prolonged heating, the relative amount of 1-butene decreased from 90% after 1 h to 67% after 6 h, and the relative amounts of 2-butenes and n-butane increased. These results further confirm that the primary products in the thermal decomposition of platinacycloalkanes are α -olefins as has been previously reported. Isomerisation and hydrogenation to internal olefins and saturated hydrocarbons are secondary processes. After

complete decomposition, the major product was found to be 1-butene, indicating that these secondary reactions occur at a slower rate than the production of 1-butene.

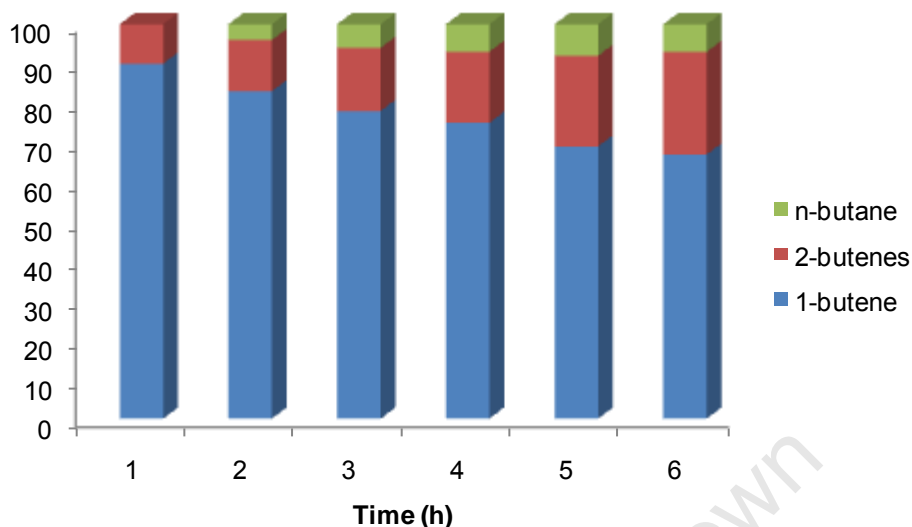


Figure 5.5: Product composition (%) for the thermal decomposition of **5.1** over time.

5.1.1.1 Kinetic Studies of Thermal Decomposition of **5.1** and **5.7**

Knowledge of reaction kinetics is an important component in investigating reaction mechanisms. A number of different analytical techniques can be employed to investigate kinetic behaviour for a given reaction. Spectroscopic tools are particularly useful because, in addition to reaction rates, they can provide structural information of what is going on in the reaction at a molecular level.²⁸ The kinetics of thermal decomposition of complexes **5.1** and **5.7** were followed using two procedures. In the first procedure, samples were taken periodically, cooled in liquid nitrogen and GC-MS analysis of the volatiles in solution was performed. Results were obtained by following the total concentration of the hydrocarbon products relative to that of the internal standard (n-decane). In the second procedure, appearance of the new peak at ~26 ppm and the disappearance of the original peak at ~25 ppm in the ³¹P NMR spectra measured for the reactions were monitored. The results obtained with these two methods were indistinguishable within experimental error. Kinetic data was collected for the decomposition of **5.1** and **5.7** at 140 °C and at 170 °C.

The decomposition reactions were found to follow first-order kinetics for approximately the first 30% to one half-life of the decomposition reaction for both complexes. Beyond this point, the reaction kinetics showed deviations from first order behaviour, indicating increasing involvement of products in the reaction mechanism, most likely the platinum-containing fragment as well as the occurrence of secondary reactions such as isomerisation and hydrogenation. The analysis presented herein is based on the results obtained over the first half life of the decomposition reaction. Rate constants derived from the initial linear regions

of the decomposition curves were calculated according to Equation 5.1 and are presented in Table 5.8.

$$\ln(a_t/a_0) = -kt \quad (\text{Equation 5.1})$$

Where $a = [\text{Complex 5.1}]$ or $[\text{Complex 5.7}]$

Table 5.8: Rate constants for the thermal decomposition of **5.1** and **5.7** in toluene

Complex	Rate Constant (s^{-1}) ^a		Rate ($\text{M}^{-1} \cdot \text{s}^{-1}$) ^b	
	140 °C	170 °C	140 °C	170 °C
5.1	2.90×10^{-5} (0.104 h^{-1})	1.50×10^{-4} (0.525 h^{-1})	4.31×10^{-7} (1.55×10^{-3})	2.02×10^{-6} (7.27×10^{-3})
5.7	9.00×10^{-5} (0.324 h^{-1})	4.37×10^{-4} (1.58 h^{-1})	1.23×10^{-6} (4.44×10^{-3})	6.06×10^{-6} (2.18×10^{-2})

^aRate constants in h^{-1} in parenthesis. ^bReaction rates in $\text{M}^{-1} \cdot \text{h}^{-1}$ in parenthesis.

Figure 5.6 shows plots of kinetic data of the decomposition reaction obtained for **5.1** at 140 °C and 170 °C, while Figure 5.7 shows plots of data obtained for the thermal decomposition of **5.7**. As expected, the rate of decomposition at 170 °C is greater than at 140 °C for both complexes. ³¹P NMR data show that at 140 °C complete decomposition takes 29 h for **5.1** and 10 h for **5.7**. At 170 °C complete decomposition takes only 7 h for **5.1** and 2.5 h for **5.7**. The rate constants for decomposition of **5.1** and **5.7** at 140 °C are 0.104 h^{-1} and 0.324 h^{-1} , respectively. At 170 °C the rate constant for the decomposition of **5.1** is 0.525 h^{-1} , while the rate constant for the decomposition of **5.7** is one order of magnitude higher (1.58 h^{-1}). The decomposition of complex **5.7** (a seven-membered ring) was faster than that of **5.1** at both temperatures under investigation.^{14b}

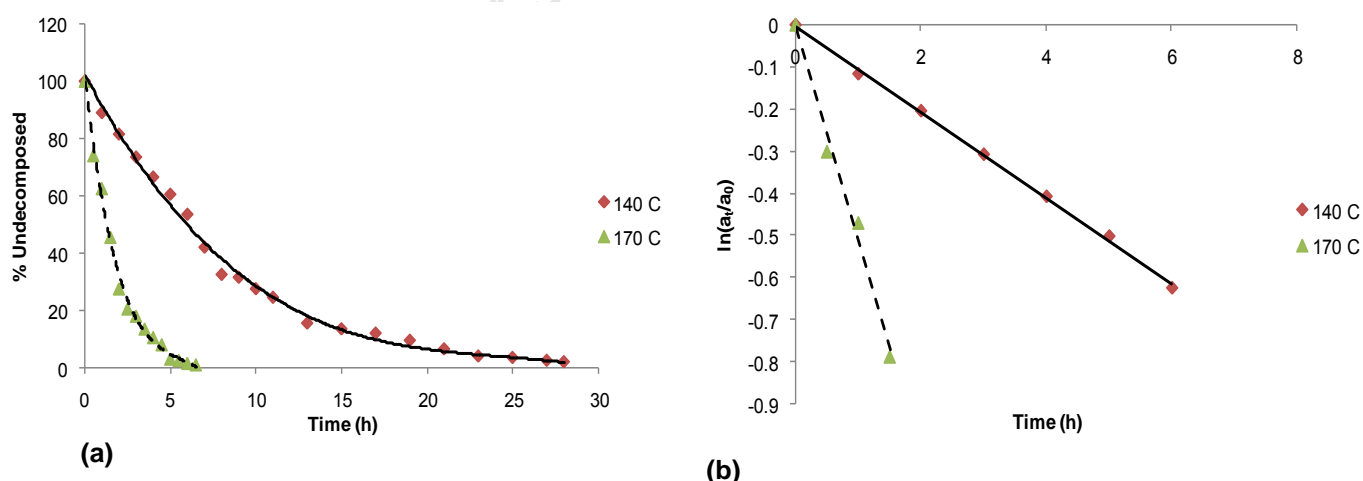
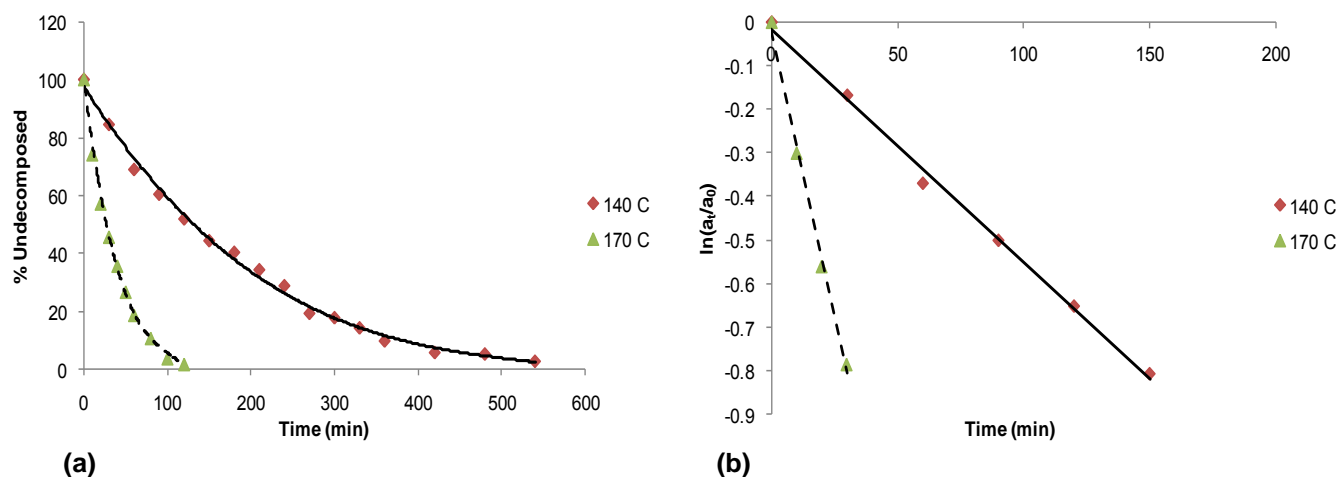


Figure 5.6: Speciation (a) and first order (b) plots for the thermal decomposition of complex **5.1** at 140 °C and 170 °C.



(a) (b)
Figure 5.7: Speciation (a) and first order (b) plots for the thermal decomposition of complex 5.7 at 140 °C and 170 °C.

5.2.2.3 Thermal Decomposition of Complexes 5.2 – 5.12

Decomposition of the rest of the platinacycloalkane complexes in this study was carried out under the following conditions: 140 °C, toluene, 27 h. Results of these reactions are presented in Table 5.9. These conditions were selected because, from the temperature study with 5.1, it was observed that doing the reaction at 140 °C results in good selectivity for 1-butene (~80%). Secondly, whether or not the reaction is done in solution does not seem to significantly affect selectivity for 1-butene. Finally, doing the reaction under the same conditions would allow for direct comparison of results between complexes.

Thermal decomposition of platinacyclopentanes 5.1 – 5.6 (Entries 1 – 6, Table 5.9) shows that similar hydrocarbon product profiles are obtained from the decomposition of these complexes. The nature of the pendant R-group on the imine moiety of the ligand does not seem to have a significant impact on the outcome of the decomposition reaction. A similar observation is made with the platinacycloheptanes 5.7 – 5.12. However, a closer look at entries 3, 4, 9 and 10 (which contain furyl and thionyl groups on the methylene carbon adjacent to the imine functionality) reveals a greater degree of secondary reactions for these complexes. This might indicate that the R-group on the imine moiety is involved in the decomposition and isomerisation reactions. A more noticeable effect is that of the size of the metallacycle ring. It appears that the larger the ring size the greater the propensity for isomerization and hydrogenation. This can be attributed to the fact that, under the same reaction conditions, larger metallacycloalkane complexes will decompose faster than their smaller ring counterparts. This would therefore allow for secondary processes, i.e. isomerisation and hydrogenation, to occur to a larger extent for the larger metallacycles.

Table 5.9: Thermal decomposition of complexes **5.1 – 5.12.**^a

Entry	Complex	n	R	α -olefin	Internal olefins ^b	n-alkanes
1	5.1	4	Phenyl	81	17	2
2	5.2	4	4-Tolyl	85	11	4
3	5.3	4	2-Furfuryl	71	20	9
4	5.4	4	2-Thionyl	76	13	11
5	5.5	4	3-Pyridyl	80	13	7
6	5.6	4	Mesityl	84	11	5
7	5.7	6	Phenyl	50	33	17
8	5.8	6	4-Tolyl	63	27	10
9	5.9	6	2-Furfuryl	56	29	15
10	5.10	6	2-Thionyl	54	35	11
11	5.11	6	3-Pyridyl	52	28	20
12	5.12	6	Mesityl	58	20	22

^aReaction conditions: 0.02M in toluene, 140 °C, 27 h. ^bMixture of cis and trans internal olefins.

5.3 DFT INVESTIGATION INTO THE MECHANISM OF THERMAL DECOMPOSITION OF PLATINACYCLOPENTANES

Studies on the decomposition behaviour of organometallic compounds are fundamental to the development of organometallic chemistry and provide a better understanding of the role of organometallic complexes in synthesis and catalysis.¹⁶ Research in coordination and organometallic chemistry supported by theoretical studies has, in the past two decades, provided much insight into the mechanism of catalytic processes involving M-C and M-H bonds.²⁹ Thermolysis and decomposition reactions of metallacyclic complexes have been used to model catalytic cycles.³⁰ Several researchers have studied the thermal decomposition of metallacycloalkanes and attempts have been made to establish the mechanisms involved in these reactions. However, the mechanism of the thermal decomposition of platinacyclopentanes has not been fully explored. The products from the thermal decomposition of platinacycloalkanes in this study, as well as studies by other researchers, are a mixture of α -olefins and other hydrocarbons whose formation can be rationalized by the widely accepted β -elimination/reductive elimination reaction sequence. These products suggest that formation of a hydridoalkenyl metal complex from which reductive elimination of the α -olefin can occur is an important step. However, it is widely accepted that metallacyclopentanes and other small-ring metallacycloalkanes lack the degree of conformational flexibility required to engage in transannular β -hydrogen agostic interactions that are a prerequisite to the formation of this transition state.³⁰ This is especially true for square planar complexes such as those of platinum and palladium. In this section,

an attempt was made to decipher the structural properties of the proposed intermediates and possible transition state structures in the β -elimination/reductive elimination mechanism using density functional methods. The role played by the supporting ligand in this reaction was also explored.

5.3.1 Selection of Method

Geometry optimization of complex **5.1** was performed using the Gaussian 09 programme. Calculations were carried out with the B3LYP density functional level of theory combined with two different basis sets: Pt was described with the pseudo-potential LANL2DZ, in which an effective core potential was used to describe the inner electrons. For all other elements, the 6-31+G (d,p) basis set was used. The results obtained were compared with the crystallographic data for **5.1** and were found to be an accurate match. The differences in bond lengths were found to be within 0.01 Å and bond angles within 0.2°. The observed differences can be ascribed to packing effects in the crystal structure. A comparison of selected data obtained experimentally and from the geometry optimization is presented in Table 5.10. To reduce computational costs, simplified model complexes, **5.13A** and **5.13B**, were used to explore the mechanism of thermal decomposition for platinacyclopentane complexes. In the model complexes, phenyl groups on the phosphine moiety as well as the pendant group on the imine moiety were replaced with H-atoms. The rigid benzene ring connecting the imine and phosphine functionalities was replaced with a HC=CH fragment. Full geometry optimizations were carried out for the starting structures, all intermediates and products. Frequency calculations were performed to identify all the stationary points as minima (zero imaginary frequency) or transition states (only one imaginary frequency). Transition state structures were further characterized by following the corresponding normal mode (intrinsic reaction coordinate calculations) toward each product and reactant.

Table 5.10: Calculated and experimental data on selected bond lengths and bond angles for complex **5.1**.

	Experimental	B3LYP ^a
Pt(1)-C(1)	2.148(5)	2.148(6)
Pt(1)-C(4)	2.052(5)	2.047(3)
Pt(1)-N(1)	2.118(4)	2.116(4)
Pt(1)-P(1)	2.2440(12)	2.242(9)
P(1)-C(18)	1.831(5)	1.825(10)
C(12)-C(13)	1.469(7)	1.466(8)
N(1)-C(12)	1.281(6)	1.274(8)
N(1)-C(5)	1.487(6)	1.486(4)
C(4)-Pt(1)-N(1)	176.77(18)	176.80(9)
N(1)-Pt(1)-C(1)	92.2(2)	92.16(5)
C(4)-Pt(1)-C(1)	84.6(2)	84.69(1)
C(4)-Pt(1)-P(1)	94.98(15)	95.09(0)
C(1)-Pt(1)-P(1)	176.78(14)	176.70(7)
N(1)-Pt(1)-P(1)	88.18(11)	88.01(7)

^aBasis sets: LANL2DZ for Pt and 6-31+G(d,p) for C, H, N, P.

5.3.2 β -Hydride Elimination

β -Hydride elimination is an important reaction for a variety of transition metal complexes containing β -hydrogens, such as metal alkyl and metal alkoxide complexes. In principle, the agostic interaction between the metal centre and the β -hydrogen in a complex can facilitate the elimination process.³² However, because of the structural rigidity of small ring-sized metallacycloalkanes such as four- to six-membered rings, it has been suggested that these complexes do not readily undergo β -hydride elimination. This has been attributed to the fact that in order for β -elimination to occur, the dihedral angle M-C-C-H should be close to 0° .^{18,33} In small ring metallacycloalkanes, especially those with square planar geometry around the metal centre, these angles are restrained far from 0° .³²

Geometry optimization was performed for two possible conformers (**A** and **B**) of complex **5.13** (Figure 5.8). In each structure, two β -hydrogen atoms, those pointing toward the metal centre, are available for β -elimination. The two conformers were found to be isoenergetic. Conformational change between the two conformers was found to be barrierless. Further calculations were performed using conformer **5.13B**.

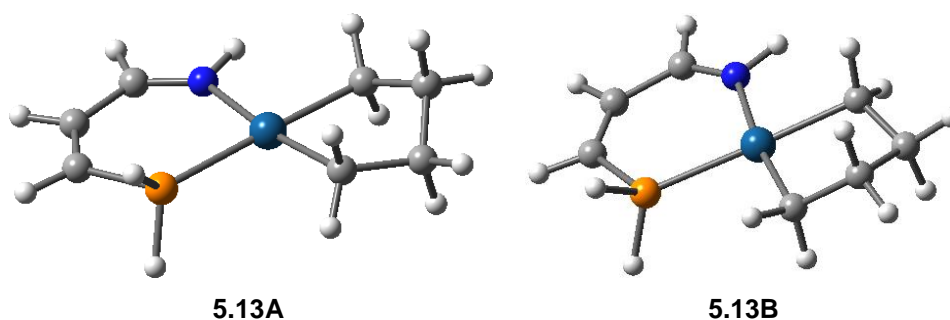
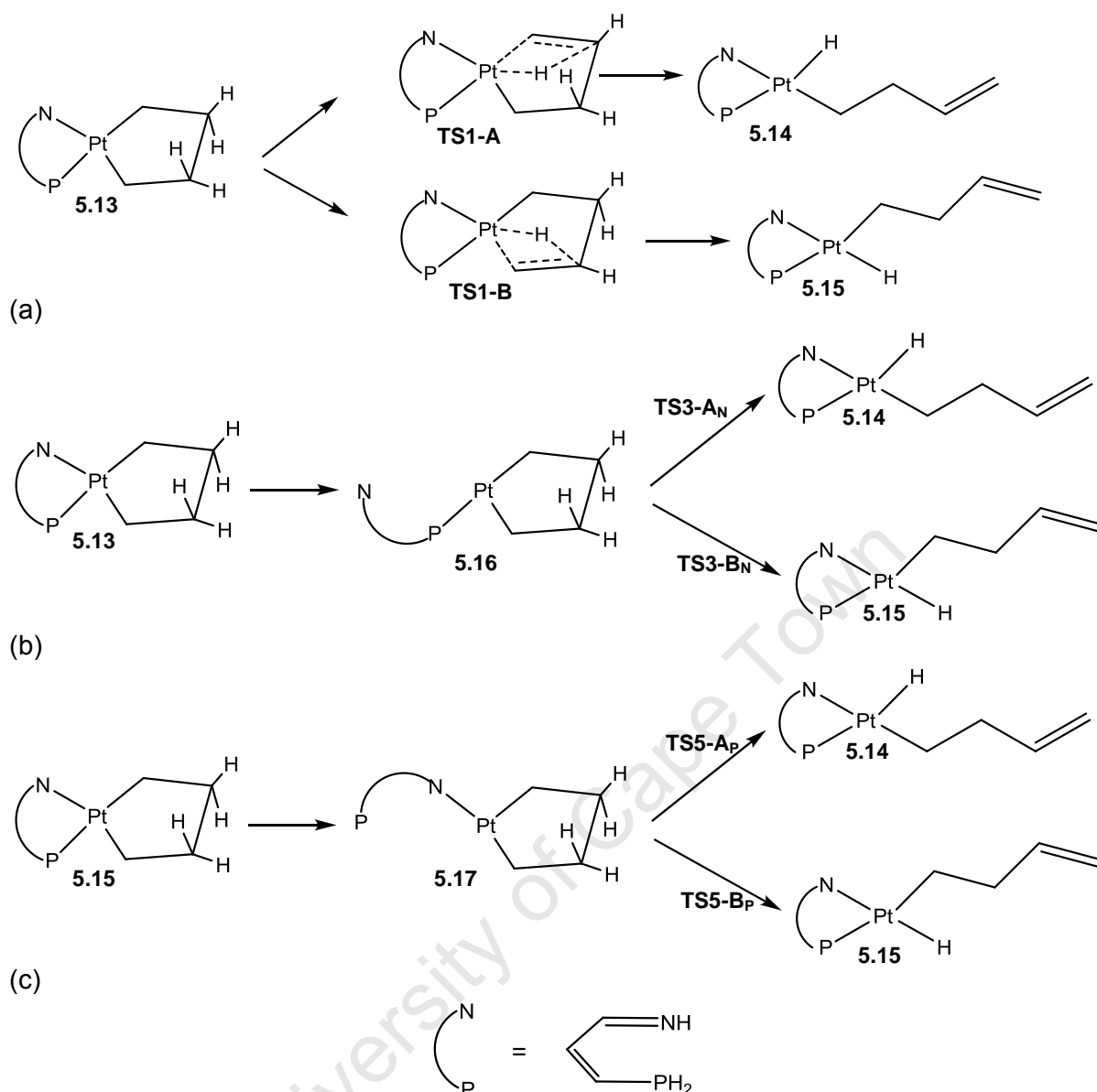


Figure 5.8: GaussView drawings of conformers **A** and **B** of complex **5.13**.

The intramolecular β -elimination reaction of **5.13B** can occur via two possible mechanisms (Scheme 5.7). The first is a concerted S_N2 -like process, in which the β -hydrogen transfer occurs without any ligand dissociation (pathway a, Scheme 5.7). The second is a dissociative pathway in which either the nitrogen (pathway b, Scheme 5.7) or phosphorus donor dissociates (pathway c, Scheme 5.7). In this section these two pathways are investigated. Pt(II) complexes normally adopt a square planar geometry around the metal centre and usually conform to the 16-electron rule. It would, therefore, be insightful to see whether the intramolecular generation of the hydridoalkenyl-platinum complexes **5.14/5.15** proceeds via a 14-electron intermediate, **5.16/5.17**, or it is a concerted process (pathway a).

Two β -hydrogen atoms, H(3) and H(8), are available for elimination from **5.13B** (Figure 5.9). It is expected that due to the different *trans* influences of the donor atoms, there would be differences in the reactivity of H(3) and H(8) toward elimination. In the optimized structure in Figure 5.8, Pt(10)-C(5) (2.088 Å), which is *trans* to the imine donor, is slightly shorter than Pt(10)-C(12) (2.093 Å), which is *trans* to the phosphine donor. Furthermore, the distances between the metal centre and the eliminating β -hydrogen atoms are also different. Pt(10)-H(3) is 3.307 Å while Pt(10)-H(8) is slightly longer (3.326 Å).



Scheme 5.7: Possible pathways for the β -hydrogen elimination reaction of **5.13B**.

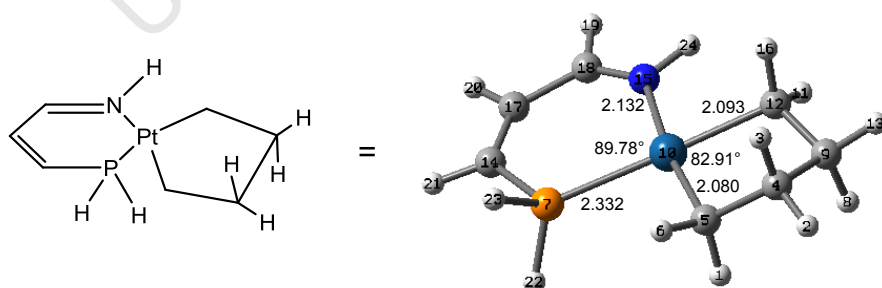


Figure 5.9: Optimized parameters for **5.13B** with atom numbering. Bond lengths (Å): Pt(10)-C(5), 2.080; Pt(10)-C(12), 2.093; Pt(10)-N(15), 2.132; Pt(10)-P(7), 2.332. Bond angles (°): C(5)-Pt(10)-C(12), 82.91; C(5)-Pt(10)-P(7), 97.30; P(7)-Pt(10)-N(15), 89.78; N(15)-Pt(10)-C(12), 90.06. Dihedral angles (°): Pt(10)-C(5)-C(4)-H(3), 78.26; Pt(10)-C(12)-C(9)-H(8), 79.14.

Figure 5.10 shows the energy profile plot for the β -elimination of **5.13B** in the concerted mechanism (pathway (a) in Scheme 5.7). In this pathway, three processes are occurring simultaneously. Pt-C $_{\alpha}$ and C $_{\beta}$ -H $_{\beta}$ bonds are breaking while the Pt-H $_{\beta}$ bond is forming. The reaction coordinate is therefore plotted relative to the increasing Pt-C $_{\alpha}$ and C $_{\beta}$ -H $_{\beta}$ bond distances and the decreasing Pt-H $_{\beta}$ bond distance. Two transition states were located for the process. **TS1-A** results from the elimination of H(8), which is *trans* to the phosphine moiety in the ligand. **TS1-B** results from the elimination of H(3), which is *trans* to the imine moiety.

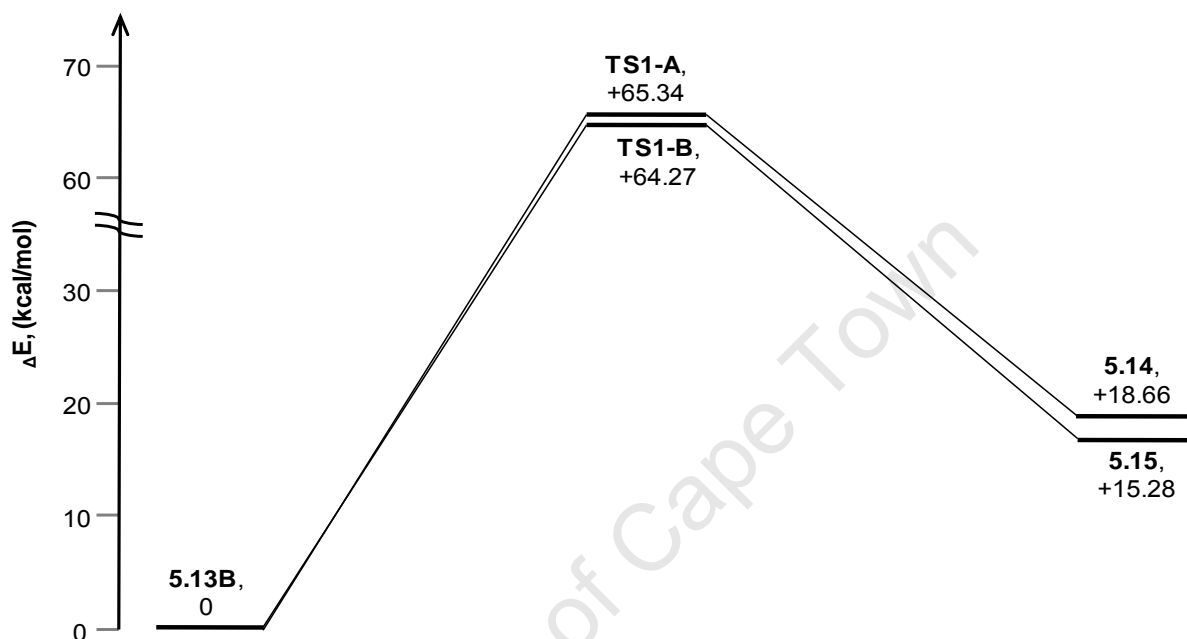


Figure 5.10: Energy profile for the β -elimination reaction of **5.13B** via the concerted, S $_N$ 2-like mechanism. Calculated energies (ΔG) at 298.15 K and 1atm in kcalmol $^{-1}$ relative to **5.13B** are given. Note that the decomposition reaction of **5.1** was carried out at 413.15 K.

The β -hydride elimination reaction of complex **5.13B** requires a high reaction barrier (64.27 kcal·mol $^{-1}$ and 65.34 kcal·mol $^{-1}$ for **TS1-B** and **TS1-A**, respectively). Both transition states have similar features, i.e. elongated Pt-C $_{\alpha}$ and C $_{\beta}$ -H $_{\beta}$ bonds as well as shortened Pt-H $_{\beta}$ distance (Figure 5.11). **TS1-A** and **TS1-B** are five-coordinate structures in which the transferring hydrogen atom is transferred from a direction perpendicular to the square plane.³⁴ In **TS1-A**, where the transferring β -hydrogen is *trans* to the phosphine group of the ligand, Pt-H $_{\beta}$ distance decreases from 3.326 Å in the starting platinacyclopentane to 1.650 Å in the transition state. Pt-C $_{\alpha}$ bond lengthens from 2.093 Å in **5.13B** to 2.228 Å in **TS1-A**. Similarly, C $_{\beta}$ -H $_{\beta}$ bond lengthens from 1.099 Å in **5.13B** to 1.686 Å in **TS1-A**. In addition, C $_{\alpha}$ -C $_{\beta}$ bond gains double bond character. This bond is 1.538 Å long in **5.13B**, 1.424 Å long in **TS1-A** and 1.338 Å in **5.14**. In **TS1-B**, Pt-H $_{\beta}$ distance is longer (1.718 Å) than it is in **TS1-A** while C $_{\beta}$ -H $_{\beta}$ is shorter (1.582 Å). In contrast, Pt-C $_{\alpha}$ is longer (2.269 Å) in **TS1-B**. **TS1-B** is a late transition state with the Pt-H bond almost completely formed (1.650 Å compared to 1.594 Å in the resulting hydridoalkenyl complex **5.14** and 1.718 Å in **TS1-B**).

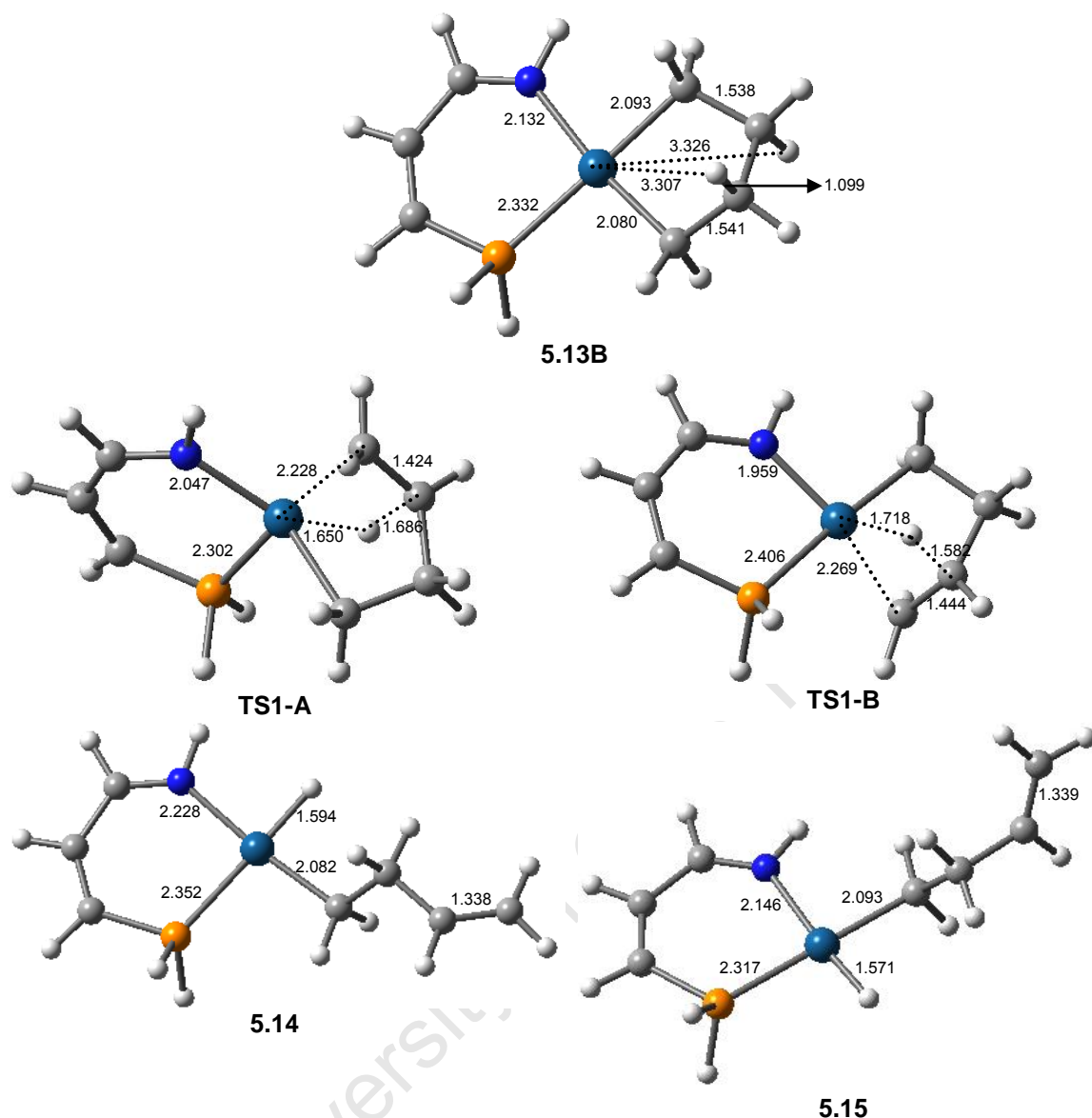


Figure 5.11: Geometrical features of the transition state and product structures for the concerted β -hydrogen elimination of **5.13B**.

Elimination of H(8) (*trans* to the phosphine) is calculated to be less favourable than that of H(3) (*trans* to the imine) by 1.07 kcal·mol⁻¹. Similarly, complex **5.14** formed from the elimination of H(8) is 3.38 kcalmol⁻¹ less stable than the analogous complex **5.15**, formed from the elimination of H(3). The eliminating hydrogen therefore prefers a weak donor in the *trans* position in the hydridoalkenyl metal complex. It is widely accepted that a transition state in which the dihedral angle M-C _{α} -C _{β} -H _{β} is close to 0° is optimal for β -hydride elimination to occur. These angles are 17.20° (**TS1-A**) and 25.38° (**TS1-B**). This is a considerable decrease from 79.14° for Pt(10)-C(12)-C(9)-H(8) and 78.26° for Pt(10)-C(5)-C(4)-H(3) in the starting platinacyclopentane. The dihedral angle is approximately 8° smaller in **TS1-A** than in **TS1-B**. Accordingly, the route involving **TS1-A** would be more favourable than that involving **TS1-B**. However, **TS1-A** and complex **5.14** resulting from it are less

energetically favourable than **TS1-B** and complex **5.15**. These results indicate that the *trans* influence of donor atoms plays a role in stabilizing transition states as well as products formed from the β -hydride elimination reaction of **5.13B**. The reaction pathways presented above have very high energy barriers (65.34 kcal·mol⁻¹ via **TS1-A** and 64.27 kcal·mol⁻¹ via **TS1-B**). As a result, both these decomposition pathways are unlikely to occur.

Heterodonor ligands based on phosphorus and nitrogen donor atoms such as the iminophosphine ligand used in this study confer interesting reactivity to the metal complexes they form. This is due to the different *trans* influence of each donor atom as well as the possibility of ligand hemilability.³⁵ In the absence of substrate, these ligands can stabilize reactive species while in the presence of substrate, the weakly coordinated component can dissociate to create a binding site for the substrate.³⁶ Moreover, such ligands are known to stabilize metal ions in different oxidation states and geometries that form at different stages of catalytic reactions.³⁷ Deckers and co-workers^{38a} as well as Tobisch and Ziegler^{19a,38b} demonstrated the significance of the presence of hemilabile ligands in Ti-catalysts for selective ethylene trimerization. In order to explore this effect on the β -elimination reaction in this study, a DFT analysis of pathways that involve dissociation of either the imine or the phosphine donor groups (pathways b and c in Scheme 5.7) was carried out.

Fully optimized geometrical structures of minima and transition state structures, along with relevant calculated geometrical parameters for the β -hydride elimination reaction of **5.13B** via ligand dissociation are presented in Figure 5.12. Dissociation of the imine or phosphine donor moieties results in three-coordinate complexes, **5.16** and **5.17**, with T-configuration around the metal centre. T-configuration in three-coordinate complexes of palladium and platinum is favoured by Jahn-Teller instability over the alternative Y-configuration.³⁹ β -hydride elimination from the three-coordinate intermediates, **5.16** and **5.17**, proceeds via tetrahedral, four-coordinate transition states, **TS3-A_N** and **TS5-B_P**, respectively. Both transition states display similar characteristics which were also observed for **TS1-A** and **TS1-B**. These include the elongation of Pt-C _{α} and C _{β} -H _{β} bond distances accompanied by the reduction of C _{α} -C _{β} and Pt-H _{β} distances. In **TS3-A_N**, Pt-C _{α} bond is 0.10 Å longer than in **5.16** while C _{β} -H _{β} distance is 0.608 Å longer. Conversely, C _{α} -C _{β} gains double bond character and is 0.095 Å shorter in **TS3-A_N** than in **5.16**. Pt-H _{β} distance is also reduced from 3.327 Å in **5.16** to 1.735 Å in **TS3-A_N**.

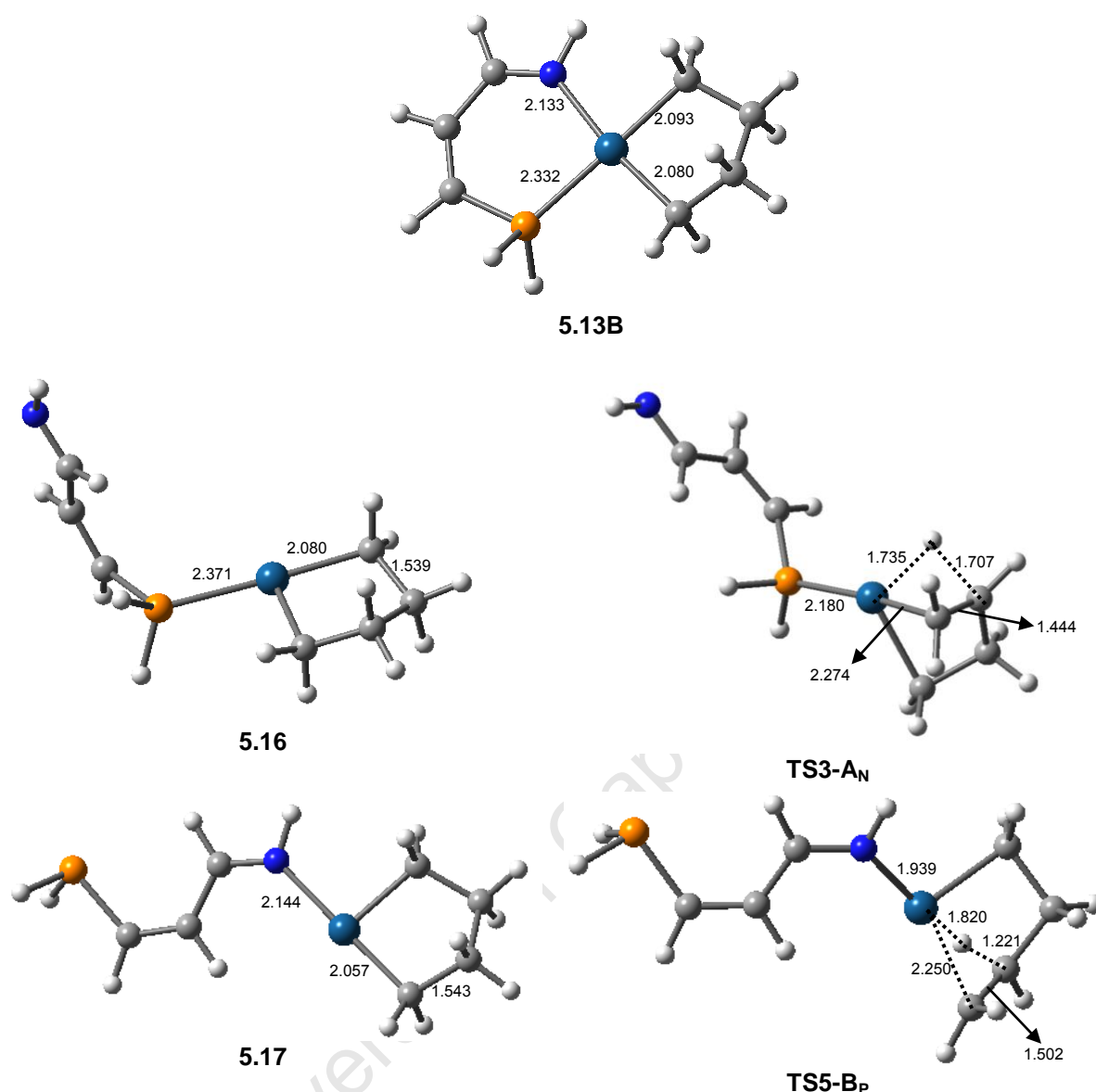


Figure 5.12: Geometrical features of species involved in β -elimination of **5.13B** via imine dissociation and phosphine dissociation.

In **TS5-B_P**, Pt-C _{α} bond is 0.193 Å longer than in **5.17**. C _{α} -C _{β} bond is 0.041 Å shorter in **TS5-B_P** than in **5.17** while C _{β} -H _{β} is 0.122 Å longer. Both transition state structures located in the dissociative pathways show considerable reduction in the Pt-L bond distance relative to the three-coordinate intermediates **5.16** and **5.17**, as well as hydridoalkenyl metal complexes **5.14** and **5.15**. Pt-P bond in **TS3-A_N** is 0.097 Å shorter than in **5.16** and 0.078 Å shorter than in **5.14**. Pt-N bond distance in **TS5-B_P** is 0.205 Å shorter than in the three-coordinate complex **5.17** and 0.027 Å shorter than in the hydridoalkenyl complex **5.15**. Dihedral angle M-C-C-H is 37.37° and -38.86° in **TS3-A_N** and **TS5-B_P**, respectively. These values are considerably larger than the 0° dihedral angle required in the transition state structure in order to facilitate β -hydride elimination, contributing to the very high energy barrier required

for β -elimination from three coordinate species. Furthermore, these values are considerably larger than 17.20° and 25.38° obtained for **TS1-A** and **TS1-B**, respectively.

The energy profile for β -hydride elimination *via* ligand dissociation is shown in Figure 5.13. From chemical intuition, it can be expected that dissociation of the imine component of the ligand would require a lower reaction barrier and the product thereof would be more favourable than the dissociation of the phosphine component. However, the results obtained show that complex **5.16**, from imine dissociation, is only slightly more favourable than complex **5.17**, from phosphine dissociation. Transition states for these dissociation reactions could not be located. This marginal difference is also reflected in the relative stabilities of complexes **5.16** ($18.10 \text{ kcal}\cdot\text{mol}^{-1}$) and **5.17** ($18.87 \text{ kcal}\cdot\text{mol}^{-1}$). Furthermore, the difference in energy barriers for β -hydride elimination from these 14-electron intermediates, **5.16** and **5.17**, is insignificant ($<1 \text{ kcal}\cdot\text{mol}^{-1}$). Reductive elimination from complex **5.17** *via* **TS5-BP** has an energy barrier of $85.99 \text{ kcal}\cdot\text{mol}^{-1}$ while elimination from **5.16** *via* **TS3-A** has a barrier of $85.11 \text{ kcal}\cdot\text{mol}^{-1}$.

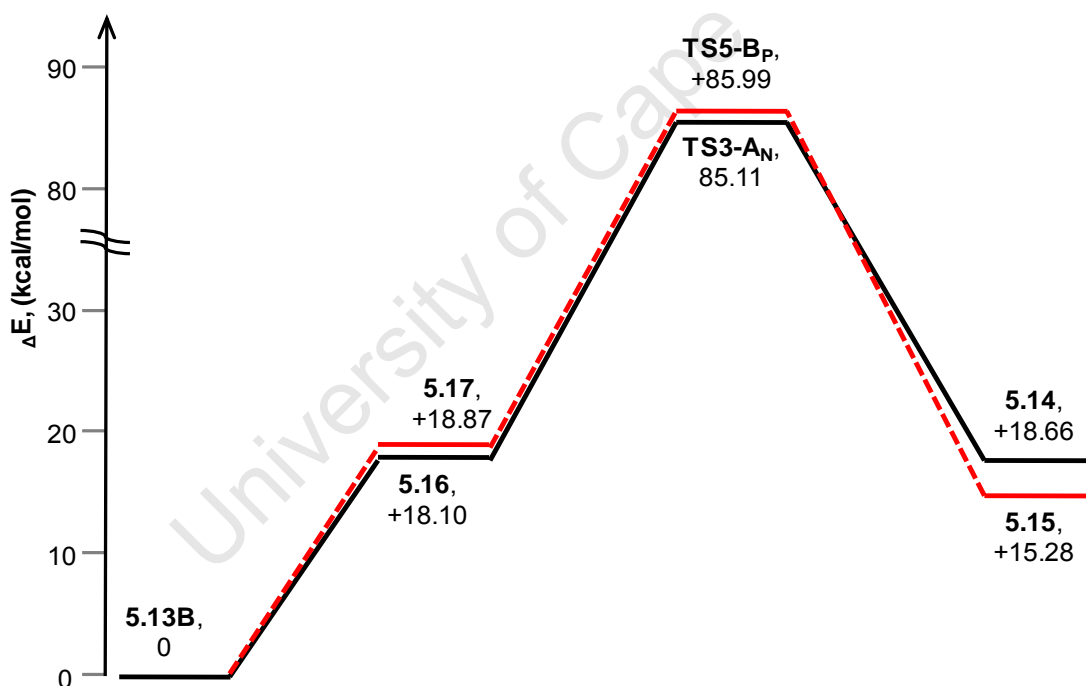


Figure 5.13: Energy profile for the β -elimination of **5.13B** *via* imine dissociation (outlined in black) and phosphine dissociation (outlined in red). Calculated energies (ΔG) at 298.15 K and 1atm in $\text{kcal}\cdot\text{mol}^{-1}$ relative to **5.13B** are given.

Interestingly, the energy barrier for the dissociative pathways is significantly higher ($\sim 20 \text{ kcal}\cdot\text{mol}^{-1}$) than the barrier for the non-dissociative pathway. This supports the proposal that, β -hydrogen transfer in five- and seven-membered ring metallacycloalkanes usually does not require ligand dissociation, unlike in ethylene coordination and insertion reactions, where ligand dissociation is necessary in order to relieve steric crowding on the metal centre.^{28c} In

fact, these calculations reveal that the interaction between the coordinated ligand and the metal centre is stronger in the transition state than in the corresponding starting materials and products. For the concerted β -elimination pathway, Pt-N bond length shortens by 0.085 Å in **TS1-A** and by 0.173 Å in **TS1-B**. Smaller changes are observed for Pt-P bond. This bond shortens by 0.030 Å for **TS1-A** and lengthens by 0.074 Å in **TS1-B**. A similar trend is observed for pathways that involve ligand dissociation. Pt-P bond length decreases by 0.097 Å in **TS3-A_N** while Pt-N bond distance decreases by 0.205 Å in **TS5-B_P**. β -hydride elimination reaction is therefore favoured by non-labile ligands.^{28c} However, due to the extremely high energy barriers for β -elimination calculated for platinacyclopentanes in this study (*via* both the dissociative and non-dissociative pathways), it is difficult to say whether this reaction would benefit from the hemilabile nature of the supporting ligands.

The β -hydride elimination reactions investigated in this section are characterized by late transition states that resemble the product whether the reaction follows the concerted or dissociative route. Like the starting platinacyclopentane, hydridoalkenyl platinum complexes **5.14** and **5.15**, exhibit a square planar geometry around the metal centre. Complex **5.15**, in which the more electronegative alkenyl group is *trans* to the phosphine moiety and the hydride is *trans* to the imine group, is the energetically favoured product of the β -elimination reaction.

These findings are in agreement with those by Huang and co-workers,³² who in their study could not locate transition states for β -hydrogen elimination of platinacyclopentanes with phosphine ligands. The very high energy barrier for β -elimination reaction can be rationalized by the fact that the β -hydrogen atoms in these complexes are not in optimal positions for the elimination reaction. A pseudo-rotation such as the one shown in Figure 5.14(a) is necessary to obtain a conformation in which one of the β -hydrogens is in close proximity to the empty coordination site on the metal centre.³² This pseudo-rotation also serves to reduce the dihedral angle, Pt-C-C-H in order to facilitate formation of the necessary transition state structures. Furthermore, the empty coordination site in **5.13B** and **5.13B*** is not exactly empty. Square planar d^8 complexes such as **5.13B** and **5.13B*** have the d^8 electrons residing in the d_z^2 and t_{2g} orbitals. There appears to be a repulsive interaction between the transferring hydrogen and the metal centre (Figure 5.14(b)), hindering hydride migration to the metal centre. The empty p_z orbital of Pt has high orbital energy and is therefore not involved in the reaction.³² The 14-electron intermediates, **5.16** and **5.17**, have a real vacant site on the metal centre as a result of ligand dissociation. However, in addition to the repulsive interaction between the d_z^2 orbital of Pt and the C-H group, the maximum amplitude of the empty orbital derived from this vacant site is still too

far away from the transferring β -hydrogen to make the elimination reaction possible (Figure 5.14(c)).³²

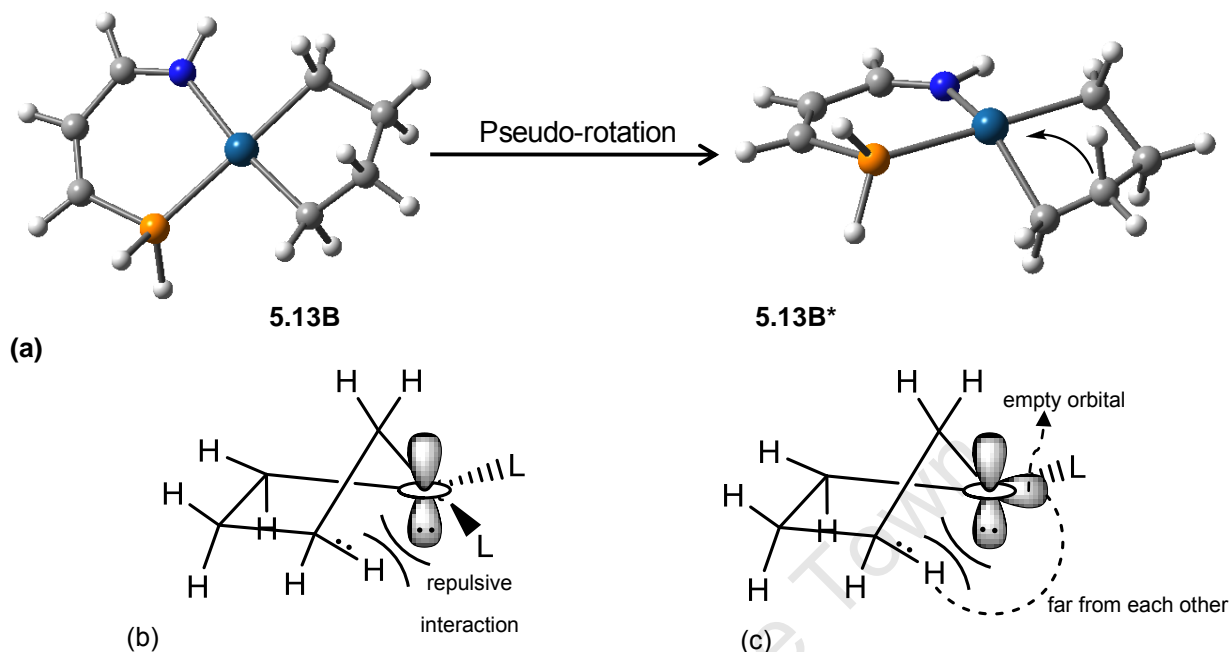


Figure 5.14: Pseudo-rotation in complex **5.13B** to facilitate transition state structure formation.³²

5.3.3 Reductive Elimination

Reductive elimination of transition metal complexes to form C-X bonds (where X = C, H, or heteroatoms) is a fundamental reaction of considerable significance in organometallic chemistry.⁴⁰ It is often the product-forming step in transition metal-mediated homogenous reactions.^{41,42} As such, a number of theoretical⁴³⁻⁴⁷ and experimental⁴⁸⁻⁵⁸ investigations of this reaction have been carried out. Herein, a DFT analysis of the elimination of 1-butene from hydridoalkenyl complexes **5.14** and **5.15** is presented. Reductive elimination of **5.14** leads to formation of **5.18** while elimination of **5.15** leads to formation of **5.19**. Optimized geometries of **5.14**, **5.15**, **5.18** and **5.19**, as well as the transition states connecting them are presented in Figure 5.15.

As with the majority of four-coordinate platinum complexes, **5.14** and **5.15** have a slightly distorted square planar geometry around the metal centre. P-Pt-N bond angle in **5.14** is 89.42° and 90.01° in **5.15** while C-Pt-H bond angle is 85.43° in **5.14** and 85.56° in **5.15**. The most notable change in geometry between the hydridoalkenyl complexes and their corresponding transition states is the decrease in C-H distances as a result of a decrease in C-Pt-H bond angles. C-Pt-H bond angle decreases by 47.60° in going from **5.14** to **TS6**.⁴¹ This results in a 1.132 Å decrease in the C-H bond distance. The same bond angle

decreases by 47.39° in going from **5.15** to **TS7**, resulting in a 1.111 \AA decrease in the C-H bond distance. Although the decrease of C-H bond distances in transition structures are significant, these distances are still considerably longer than C-H bonds lengths calculated for the products.

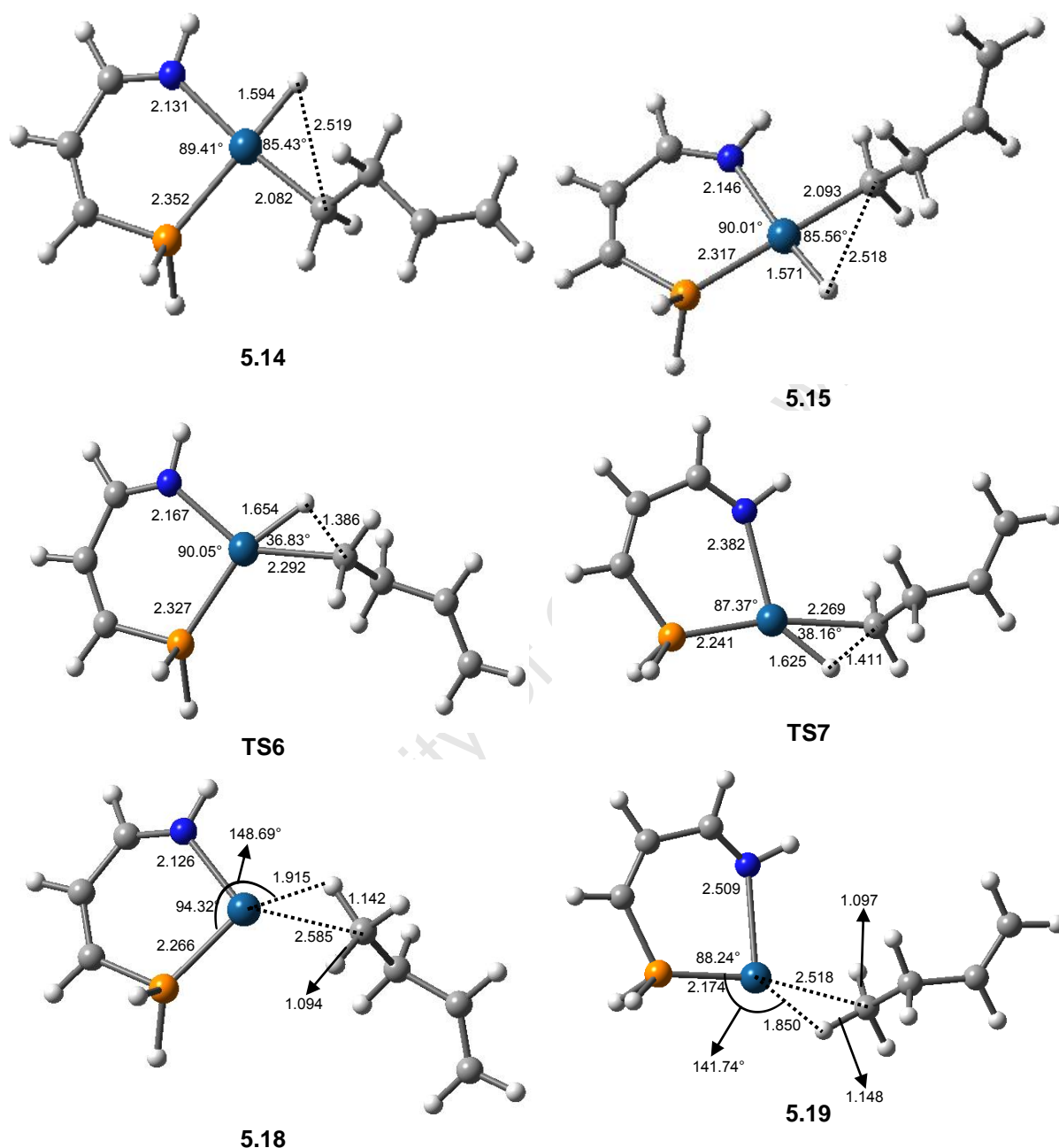


Figure 5.15: Optimized geometries of structures involved in the reductive elimination of **5.14** and **5.15** along with relevant geometrical features.

In contrast, changes in bonds to the metal centre are relatively small in going from hydridoalkenyl complexes to corresponding transition structures. Going from **5.14** (in which the alkenyl group is trans to the imine moiety) to **TS6**, Pt-C bond distance increases by 0.210 \AA while Pt-H bond distance increases by just 0.060 \AA . Similar changes are seen for the formation of **TS7** from **5.15** (in which the alkenyl group is trans to the phosphine moiety).

Pt-C bond distance increases by 0.176 Å and Pt-H bond increases by just 0.054 Å. There is a shortening of Pt-P bond distances and an increase in Pt-N distances in both transition state structures. N-Pt-P bond angle increases by only 0.90° in going from **5.14** to **TS6** a decrease of 2.64° is seen in **TS7** from **5.15**. **TS6** and **TS7** are four-coordinate structures with a highly distorted square planar geometry around the metal centre.⁴¹

The reductive elimination reaction leads to the formation of **5.18** and **5.19** from **TS6** and **TS7**, respectively. **5.18** and **5.19** are complexes of 1-butene with the L₂Pt(0) fragment, where L₂ is the iminophosphine ligand. These 1-butene complexes are held together by a two-electron, three-centre agostic interaction between the metal centre and one of the C-H bonds in 1-butene. Pt-C bond distances lengthen by 0.249 Å from **TS7** to **5.19** and 0.293 Å from **TS6** to **5.18**. The length of the C-H bond that is directed toward platinum is considerably longer than the other two terminal C-H bonds in both 1-butene complexes. In **5.18**, this C-H bond is 1.148 Å while the other two C-H bonds are 1.096 Å and 1.097 Å. In **5.19**, the C-H bond directed toward platinum has a bond length of 1.142 Å while the other two C-H bonds are 1.094 Å and 1.098 Å. The Pt···H distance is 1.850 Å in **5.18** and 1.915 Å in **5.19**. L₂Pt(0)···butene complexes, **5.18** and **5.19**, display a distorted Y-configuration around the metal centre. The bond angles around the metal centre are 141.74° for P-Pt-H, 129.91° for N-Pt-H and 88.24° for N-Pt-P in **5.19**. These angles are 148.69° and 116.99° for P-Pt-H and N-Pt-H, respectively, in **5.18**. N-Pt-P in **5.18** is slightly larger than in **5.19**, with a value of 94.32°. Although T-configuration in three coordinate complexes of palladium and platinum is preferred over Y-configuration, due to the bidentate coordination of the iminophosphine ligand in **5.18** and **5.19**, this orientation is prohibited.

Potential energy profiles for the reductive elimination reaction of 1-butene from hydridoalkenyl complexes **5.14** and **5.15** are presented in Figure 5.16. Elimination of 1-butene from the two complexes has comparable energy barriers. 1-butene elimination from **5.14** to give **5.18** has an energy barrier of 24.55 kcal·mol⁻¹, while elimination from **5.15** to give the more stable product, **5.19** has a barrier of 26.82 kcal·mol⁻¹. In addition, the reductive elimination reaction is endothermic, with complex **5.18** being 18.94 kcal·mol⁻¹ higher in energy than complex **5.14**, while **5.19** is 21.71 kcal·mol⁻¹ higher in energy than the starting complex, **5.15**.

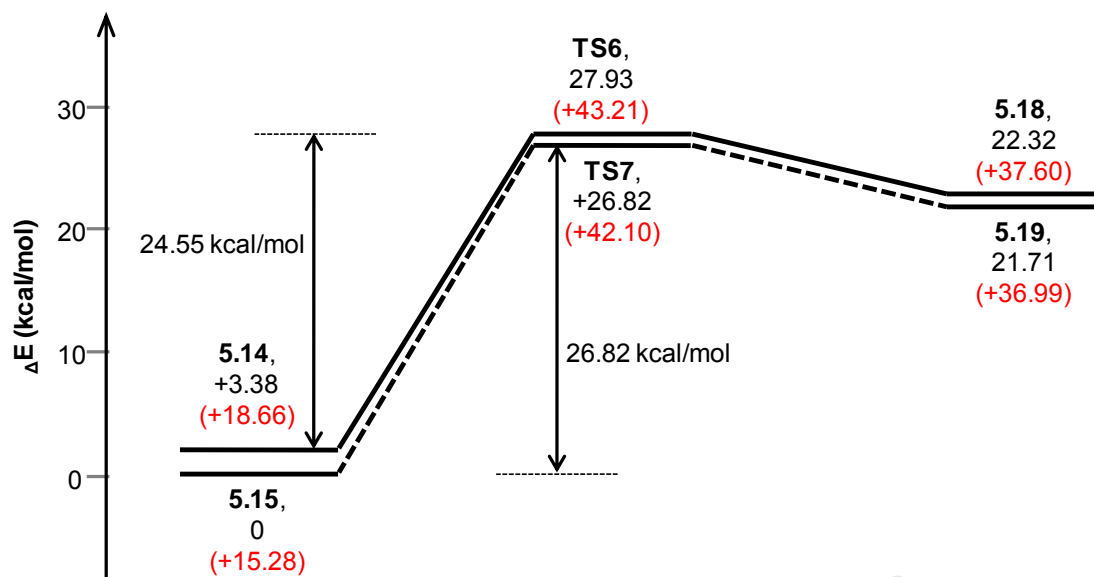
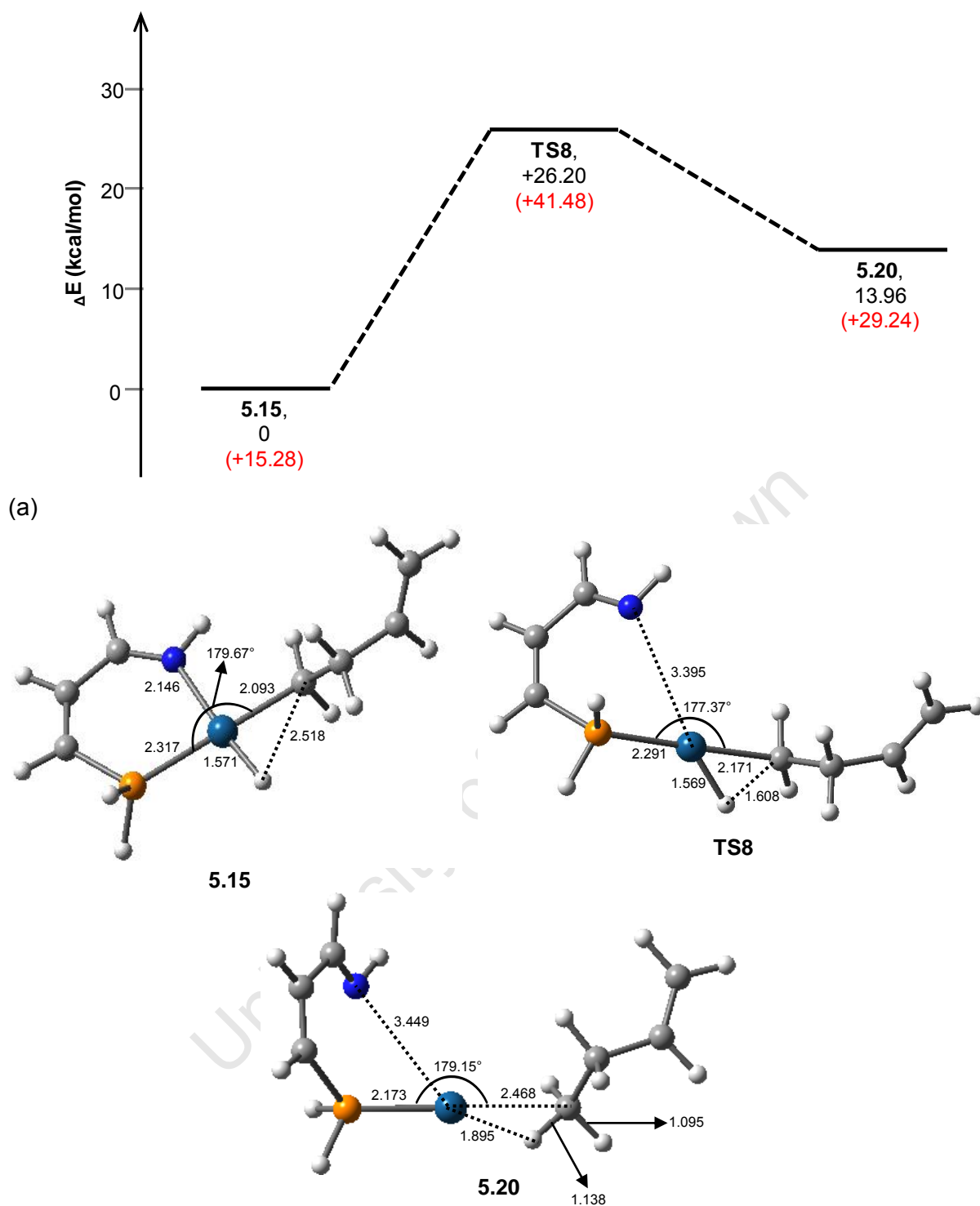


Figure 5.16: Potential energy profile for the reductive elimination of complexes **5.14** and **5.15**. Values in parentheses (red) represent potential energy relative to the metallacyclopentane **5.13B**.

To test whether ligand lability has any effect on the potential energy profile of reductive elimination, calculations on the elimination of 1-butene *via* imine dissociation were performed using complex **5.15**. It is generally accepted that reductive elimination reactions from three-coordinate complexes have lower energy barriers than reductive elimination reactions from corresponding four-coordinate complexes.⁴⁵

The reductive elimination of 1-butene from **5.15** *via* imine dissociation proceeds via a three-coordinate transition state structure, **TS8**. While the energy barrier (Figure 5.17(a)) for the reductive elimination of 1-butene from **5.15** *via* **TS8** is very similar to that of **TS7**, the relative stabilities of the products resulting from these transition state structures are considerably different. **5.20**, resulting from **TS8**, is 12.24 kcal·mol⁻¹ more favourable than **5.19**. Figure 5.17(b) shows that **TS8** exhibits a distorted T-configuration around the metal centre, with the more electronegative alkenyl group maintaining its position *trans* to the phosphine group. P-Pt-C bond angle is almost linear in both **TS8** and **5.20** (177.37° and 179.15°, respectively). Reductive elimination of 1-butene from **5.15** *via* **TS8** (in which the imine end of the ligand dissociates) is <1.0 kcal·mol⁻¹ more favourable than the non-dissociative pathway. However, the more favourable product, **5.20**, makes the dissociative pathway more likely to occur than the non-dissociative pathway.



(b) **Figure 5.17:** (a) Potential energy profile for the reductive elimination of 1-butene from **5.15** via imine dissociation. (b) Optimized geometries of structures involved in the reductive elimination of **5.15** via imine dissociation, along with relevant geometrical features.

The potential energy profile presented in Figure 5.18 shows the lowest energy pathway calculated for the decomposition of **5.13B** via the β -hydride elimination/reductive elimination reaction sequence.

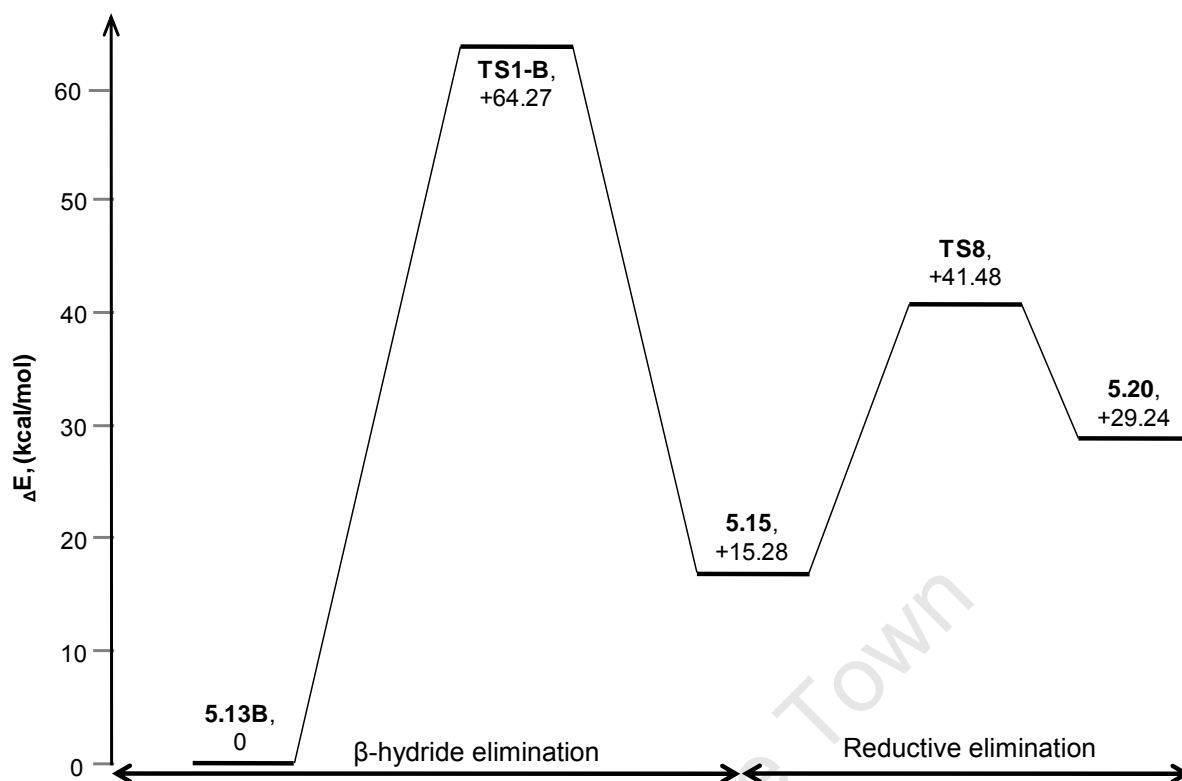


Figure 5.18: The energy profile for a complete, lowest energy, β -hydride elimination/reductive elimination decomposition of the platinacyclopentane complex, **5.13B**.

The energy barriers calculated for β -hydride elimination and reductive elimination of 1-butene from **5.13B** are extremely high ($64.27 \text{ kcal}\cdot\text{mol}^{-1}$ and $26.20 \text{ kcal}\cdot\text{mol}^{-1}$, respectively). The very high energy barrier calculated for the β -elimination reaction supports the proposal that intramolecular β -hydride elimination from the carbocyclic ring of platinacyclopentanes is unlikely to occur. This high barrier is a result of the unfavourable conformational modifications that need to occur in order to bring β -hydrogen atoms into close proximity to the metal centre. In addition to the conformational changes, the repulsive interaction between the transferring hydrogen atom and electrons in the d_z^2 orbital of platinum further increases the energy barrier for this process. Therefore, under the reaction conditions outlined for the decomposition reactions discussed in section 5.2.2, β -hydride elimination to generate the metal hydride intermediate is unlikely to occur. This intermediate could be formed through alternative pathways which were not explored in this study such as C-H activation of supporting iminophosphine ligands.

5.4 SUMMARY

A series of divalent platinacyclopentane and platinacycloheptane complexes with iminophosphine complexes were successfully synthesized and fully characterized using spectroscopic and analytical techniques. The complexes were obtained in moderate to good yields, and were found to be air stable at ambient temperature. Platinacyclopentane complexes, $[\text{Pt}(\text{C}_4\text{H}_8)(\text{P}^{\wedge}\text{N})]$ (**5.1** – **5.6**), were obtained as solids while the larger ring platinacycloheptanes $[\text{Pt}(\text{C}_6\text{H}_{12})(\text{P}^{\wedge}\text{N})]$ (**5.7** – **5.12**) were obtained as oils.

Thermal decomposition behaviour of the platinacyclopentanes was studied at different temperatures and under both solvent free conditions and in solution. The results obtained show that: 1) Platinacyclopentanes are markedly more stable than analogous platinacycloheptanes. 2) The platinacycloalkanes decompose to give α -olefins as the primary, and major products, indicating that formation of a metalhydride intermediate species is an important step in the reaction. 3) Reaction temperature and duration have a significant effect on the organic product distribution. 4) The decomposition reaction follows first order kinetics over the first half life of the decomposition reaction, with deviation from first order behaviour thereafter.

To gain further insight into the mechanism of the decomposition reaction, DFT analysis of the β -hydride elimination/reductive elimination reaction sequence was carried out using a model platinacyclopentane complex **5.13B**. Results from this study show that while transition state structures and intermediates were located for this reaction sequence, energy barriers for β -elimination are extremely high. The high energy barriers are a result of 1) The energetically unfavourable conformational changes that need to occur in the carbocyclic ring of the platinacyclopentane in order to bring β -hydrogen atoms in close proximity to the metal centre. 2) Repulsive interactions between the transferring hydrogen and electrons in the d_z^2 orbital of platinum. Although reductive elimination of 1-butene from hydridoalkenyl platinum complexes **5.14** and **5.15** is endothermic, the energy barrier for this process was found to be relatively low ($26.20 \text{ kcal}\cdot\text{mol}^{-1}$). This process could therefore be possible under experimental conditions. The most stable product from the reductive elimination reaction was found to be a $\text{LPt}(0)$ fragment coordinated to 1-butene through one of the methyl C-H bonds in a two-electron, three centre agostic interaction.

Formation of α -olefins as major products in the decomposition reactions of platinacycloalkanes discussed herein and in previous studies by other researchers suggests that formation of a metal hydride intermediate is necessary. However, results from the DFT calculations presented in this study show that platinacyclopentane complexes do not

decompose *via* intramolecular β -hydride elimination from the carbocyclic ring of the platinacyclopentane complex. Other processes, such as ligand C-H activation, which were not explored as part of the current study, could be involved in the generation of this metal hydride species. In addition to the very high energy barrier for the intramolecular β -hydride elimination ($>64 \text{ kcal}\cdot\text{mol}^{-1}$), reductive elimination from the resultant hydridoalkenyl platinum intermediates, **5.14** and **5.15**, is an endothermic process. These results show that the widely accepted reaction sequence, which involves β -hydride elimination from the carbocyclic ring of the metallacycloalkane, followed by reductive elimination, usually offered to explain the formation of α -olefins from metallacycloalkanes is unlikely to occur in the decomposition of platinacyclopentanes.

University of Cape Town

5.5 REFERENCES

1. Grubbs, R. H., Miyashita, A., Liu, M. and Burk, P., *J. Am. Chem. Soc.* 1978, **100**, 2418.
2. (a) Dyker, G., *Chem. Ber.* 1997, **130**, 1567. (b) Trost, B. M., *Acc. Chem. Res.* 1990, **23**, 34. (c) Trost, B. M. and Trost, M. K., *Tetrahedron Lett.* 1991, **30**, 3647. (d) Trost, B. M. and Trost M. K., *J. Am. Chem. Soc.* 1991, **113**, 1850. (e) Trost, B. M. and Chang, V. K., *Synthesis*, 1993, 824.
3. Overett, M. J., Blann, K., Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723.
4. (a) Collman, J. P., Kang, J. W., Little, W. F. and Sullivan, M. F., *Inorg. Chem.* 1968, **7**, 1298. (b) Eisch, J. J. and Damasavitz, G. A., *J. Organomet. Chem.* 1975, **96**, C19.
5. (a) Grubbs, R. H., Burk, P. L. and Carr, D. D., *J. Am. Chem. Soc.*, 1975, **97**, 3265. (b) Grubbs, R. H., Carr, D. D., Hoppin, C. and Burk, P. L., *J. Am. Chem. Soc.*, 1976, **98**, 3478.
6. (a) Bollmann, A., Blann, K., Dixon, J. T., Hess, F. M., Killian, E., Maumela, H., McGuinness, D. S., Morgan, D. H., Neveling, A., Otto, S., Overett, M., Slawin, A. M. Z., Wasserscheid, P. and Kuhlmann, S., *J. Am. Chem. Soc.*, 2004, **126**, 14712. (b) Kim, K.-S., Kim, T.-J., Chung, J.-H., Hahn, T.-K., Chae, S.-S., Lee, H.-S., Cheong, M. and Kang, S. O., *Organometallics*, 2010, **29**, 5805. (c) Agapie, T., Schofer, S. J., Labinger, J. A. and Bercaw, J. E., *J. Am. Chem. Soc.*, 2004, **126**, 1304. (d) Janse van Rensburg, W., Grove, C., Steynberg, J. P., Stark, K. B., Huyser, J. J. and Steynberg, P. J., *Organometallics*, 2004, **23**, 1207.
7. (a) McGuinness, D. S., Wasserscheid, P., Morgan, D. H. and Dixon, J. T., *Organometallics*, 2005, **24**, 552. (b) McGuinness, D. S., Brown, D. B., Tooze, R. P., Hess, F. M., Dixon, J. T. and Slawin, A. M. Z., *Organometallics*, 2006, **25**, 3614. (c) Schofer, S. J., Day, M. W., Henling, L. M., Labinger, J. A. and Bercaw, J. E., *Organometallics*, 2006, **25**, 2743. (d) Temple, C., Jabri, A., Crewdson, P., Gambarotta, S., Korobkov, I. and Duchateau, R., *Angew. Chem., Int. Ed.* 2006, **45**, 7050. (e) Janse van Rensburg, W., van den Berg, J.-A. and Steynberg, P. J. *Organometallics*, 2007, **26**, 1000. (f) Nenu, C. N., Bodart, P. and Weckhuysen, B. M., *J. Mol. Catal. A: Chem.* 2007, **269**, 5. (g) McGuinness, D. S., Rucklidge, A. J., Tooze, R. P. and Slawin, A. M. Z., *Organometallics*, 2007, **26**, 2561.
8. (a) Kuhlmann, S., Blann, K., Bollmann, A., Dixon, J. T., Killian, E., Maumela, M. C., Maumela, H., Morgan, D. H., Pretorius, M., Taccardi, N. and Wasserscheid, P., *J. Catal.* 2007, **245**, 279. (b) McGuinness, D. S., Overett, M., Tooze, R. P., Blann, K., Dixon, J. T. and Slawin, A. M. Z., *Organometallics*, 2007, **26**, 1108. (c) Rucklidge, A. J.,

- McGuinness, D. S., Tooze, R. P., Slawin, A. M. Z., Pelletier, J. D. A., Hanton, M. J. and Webb, P. B., *Organometallics*, 2007, **26**, 2782. (d) Agapie, T., Labinger, J. A. and Bercaw, J. E., *J. Am. Chem. Soc.*, 2007, **129**, 14281. (e) Emrich, R., Heinemann, O., Jolly, C. W., Kruger, C. and Verhovnik, G. P. J., *Organometallics*, 1997, **16**, 1511. (f) Briggs, J. R., *J. Chem. Soc., Chem. Commun.*, 1989, 674. (g) Tomov, A. K., Chirinos, J. J., Jones, D. J., Long, R. J. and Gibson, V. C., *J. Am. Chem. Soc.*, 2005, **127**, 10166.
9. McGuinness, D. S., *Chem. Rev.* 2011, **111**, 2321.
 10. McLain, S. J., Wood, C. D. and Shrock, R., *J. Am. Chem. Soc.*, 1977, **99**, 3519.
 11. (a) Whitesides, G. M., McDermott, J. X., *J. Am. Chem. Soc.* 1974, **96**, 947. (b) McDermott, J. X., Wilson, M. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6259.
 12. McGuinness, D., *Dalton Trans.*, 2009, 6915.
 13. Cavell, K. J. and McGuinness, D., *Coord. Chem. Rev.*, 2004, **248**, 671.
 14. (a) Whitesides, G. M., White, J. F. and McDermott, J. X., *J. Am. Chem. Soc.* 1973, **95**, 4451. (b) McDermott, J. X., White, J. F. and Whitesides, G. M. *J. Am. Chem. Soc.* 1976, **98**, 6521. (c) Grubbs, R., Eick, H. and Biefield, C., *Inorg. Chem.* 1973, **12**, 2166.
 15. Diversi, P., Ingrosso, G., Lucherini, A. and Murtas, S., *J. Chem. Soc. Dalton Trans.* 1980, 1633.
 16. Doyle, M. J., McMeeking, J. and Binger, P., *J. Chem. Soc. Chem. Commun.* 1976, 376.
 17. Emrich, R., Heinemann, O., Jolly, P. W., Krüger, C. and Verhovnik, G. P. J., *Organometallics*, 1997, **16**, 1511.
 18. Miller, T. M. and Whitesides, G. M., *Organometallics*, 1986, **5**, 1473.
 19. (a) Tobisch, S. and Ziegler, T., *Organometallics*, 2003, **22**, 5392. (b) de Bruin, T. J. M., Magna, L., Raybaud, P. and Toulhoat, H., *Organometallics*, 2003, **22**, 3404. (c) Blok, A. N. J., Budzelaar, P. H. M. and Gal, A. W., *Organometallics*, 2003, **22**, 2564.
 20. Chen, H-P., Liu, Y-H., Peng, S-M. and Liu, S-T., *Organometallics*, 2003, **22**, 4893.
 21. (a) Ankersmit, H. A., Loken, B. H., Kooijman, H., Spek, A. L., Vrieze, K. and van Koten, G., *Inorg. Chim. Acta.*, 1996, **252**, 141. (b) Brinkmann, P. H. P. and Luinstra, G. A., *J. Organomet. Chem.*, 1999, **572**, 193. (c) Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T. and Liu, S-T., *Organometallics*, 2001, **20**, 1292. (d) van den Beuken, E. K., Smeets, W. J. J., Spek, A. L. and Feringa, B. L., *Chem. Commun.*, 1998, 223.
 22. (a) Dralle, K., Jaffa, N., L., le Roex, T., Moss, J. R., Travis, S., Watermeyer, N. D. and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865. (b) Sivaramakrishna, A., Hong, S. and Moss, J. R., *Angew. Chem. Int. Ed. Engl.*, 2007, **46**, 3541. (c) Sivaramakrishna, A., Makhubela, B. C. E., Moss, J. R. and Smith, G. S., *J. Organomet. Chem.*, 2010, **695**,

1627. (d) Sivaramakrishna, A., Hong, S. and Moss, J. R., *Dalton Trans.*, 2008, 2228.
Sivaramakrishna, A., Su, H. and Moss, J. R., *Organometallics*, 2007, **26**, 5786.
23. Duran, S. E., Elsegood, M. R. J., Hammond, S. R. and Smith, M. B., *Dalton Trans.*, 2010, **39**, 7136.
24. Biefeld, C. G., Eick, H. A. and Grubbs, R. H., *Inorg. Chem.*, 1973, **12**, 2166.
25. Sivaramakrishna, A., Makhubela, B. C. E., Zheng, F., Su, H., Smith, G. S. and Moss, J. R., *Polyhedron*, 2008, **27**, 44.
26. Young, G. B. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1978, **100**, 5808.
27. (a) Song, H-B., Zhang, Z-Z. and Mak, T. C. W., *Polyhedron*, 2002, 21, 1043.
(b) Pattachini, R., Magraf, G., Messaoudi, A., Oberbeckman-Winter, N. And Braunstein, P., *Inorg. Chem.*, 2008, 47, 9886.
28. Ciobanu, L., Jayawickrama, D. A., Zhang, X., Webb, A. G. and Sweedler, J. V., *Angew. Chem. Int. Ed.*, 2003, **42**, 4669.
29. (a) Jordaan, M. and Vosloo, H. C. M., *Mol. Simulat.*, 2008, **34**, 997. (b) Forman, G.S., McConnell, A. E., Tooze, R. P., Janse van Rensburg, W., Meyer, W. H., Kirk, M. M., Dwyer, C. L. and Serfontein, D. W., *Organometallics*, 2006, **24**, 4528. (c) de Bruin, T., Raybaud, P. and Toulhoat, H., *Organometallics*, 2008, **27**, 4864. (d) Janse van Rensburg, W., Steynberg, P. J., Kirk, M. M., Meyer, W. H. and Forman, G. S., *J. Am. Chem. Soc.*, 2004, **126**, 14332. (e) Vyboishchikov, S. F., Bühl, M. and Thiel, W., *Chem. Eur. J.*, 2002, **8**, 3962. (f) Zeigler, T., Folga, E. and Berces, A., *J. Am. Chem. Soc.*, 1993, **115**, 636. (g) Adlhart, C. and Chen, P., *Angew. Chem. Int. Ed.*, 2002, **41**, 4484. (h) Fomine, S., Vargas, S. M. and Tlenkopatchev, A., *Organometallics*, 2003, **22**, 93.
30. (a) Overett, M. J., Blann, K., Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723. (b) Chapell, S. D. and Cole-Hamilton, D. J., *Polyhedron*, 1982, **1**, 739.
31. Epshtyn, A., Trunkely, E. F., Kissounko, D. A., Fettinger, J. C. and Sita, L. R., *Organometallics*, 2009, **28**, 2520.
32. Huang, X., Zhu, J. and Lin, Z., *Organometallics*, 2004, **23**, 4154.
33. Thorn, D. L., Hoffmann, R., *J. Am. Chem. Soc.*, 1978, **100**, 2079.
34. Ng, S. M., Zhao, C. and Lin, Z., *J. Organomet. Chem.*, 2002, **662**, 120.
35. (a) Jeffrey, J. C. and Rauchfuss, T. B., *Inorg. Chem.*, 1979, **18**, 2658. (b) Espinet, P. and Soulantica, K., *Coord. Chem. Rev.*, 1999, **193 – 195**, 499.
36. (a) Bhattacharyya, P., Parr, P. B. J. and Slawin, A. M., *J. Chem. Soc., Dalton Trans.*, 1998, 3609. (b) Lindner, R., van den Bosch, B., Lutz, M., Reek, J. N. H. and van der Vlugt, *Organometallics*, 2011, **30**, 499.
37. Ni Dhubhnaill, O. M., Lennon, J. and Drew, M. G. B., *Dalton Trans.*, 2005, 3213.

38. (a) Deckers, P. J. W., Hessen, B., Teuben, J., *Organometallics*, 2002, **21**, 5122. (b) Tobisch, S. and Zeigler, T., *Organometallics*, 2004, **23**, 4077.
39. Guido, E., D'Amico, G., Russo, N., Sicilia, E., Rizzato, S., Albinati, A., Romeo, A., Plutino, M. R. and Romeo, R., *Inorg. Chem.*, 2011, **50**, 2224.
40. Parshall, G. W. and Ittel, S. D., *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 1992, 2nd Ed., Wiley-Intersciences, New York.
41. Bartlett, K. L., Goldberg, K. I. and Borden, W. T., *J. Am. Chem. Soc.*, 2000, **122**, 1456.
42. (a) Su, M.-D. and Chu, S.-Y., *Inorg. Chem.*, 1998, **37**, 3400. (b) Low, J. J. and Goddard, W. A., III, *J. Am. Chem. Soc.*, 1986, **108**, 6115. (c) Obara, S., Kitaura, K. and Morokuma, *J. Am. Chem. Soc.*, 1984, **106**, 7482. (d) Balazs, A. C., Johnson, K. H. and Whitesides, G. M., *Inorg. Chem.*, 1982, **21**, 2162.
43. (a) McGuinness, D. S., Saendig, N., Yates, B. F. and Cavell, K. J., *J. Chem. Soc.*, 2001, **123**, 4029. (b) Tatsumi, K., Hoffmann, R., Yamamoto, A. and Stille, K., *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857.
44. Hill, G. S. and Puddephatt, R. J., *Organometallics*, 1998, **17**, 1478.
45. Siegbahn, P. E. M. and Crabtree, R. H., *J. Am. Chem. Soc.*, 1996, **118**, 4442.
46. (a) Espinosa-Garcia, J., Corchado, J. C. and Truhlar, D. G., *J. Am. Chem. Soc.*, 1997, **119**, 9891. (b) Avdeev, V. I. and Zhidomirov, G. M., *Kinet. Catal.*, 1998, **39**, 476. (c) Niu, S. and Hall, M. B., *J. Am. Chem. Soc.*, 1998, **120**, 6169. (d) Sakaki, S., Biswas, B. and Sugimoto, M., *Organometallics*, 1998, **17**, 1278.
47. Collman, J. P., Hegedus, L. S. and Norton, J. R., and Finke, R. G., *Applications of Organotransition Metal Chemistry*, 1987, University Science Books, Mill Valley, CA.
48. Gillie, A. and Stille, J. K., *J. Am. Chem. Soc.*, 1980, **102**, 4933.
49. DiCosimo, R. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1982, **104**, 3601.
50. Yamamoto, T. and Abla, M., *J. Organomet. Chem.*, 1997, **535**, 209.
51. Abis, L., Sen, A. and Halpern, J., *J. Am. Chem. Soc.*, 1978, **100**, 2915.
52. Michelin, R. A., Faglia, S. and Uguagliati, P., *Inorg. Chem.*, 1983, **22**, 1831.
53. Stang, P. J. and Kowalski, M. H., *J. Am. Chem. Soc.*, 1989, **111**, 3356.
54. Edelbach, B. L., Lachicotte, R. J. and Jones, W. D., *J. Am. Chem. Soc.*, 1998, **120**, 2843.
55. (a) Williams, B. S., Holland, A. W. and Goldberg, K. I., *J. Am. Chem. Soc.*, 1999, **121**, 252. (b) Hill, G. S., Yap, G. P. A. and Puddephatt, R. J., *Organometallics*, 1999, **18**, 1408. (c) Crumpton, D. M. and Goldberg, K. I., *J. Am. Chem. Soc.*, 2000, **122**, 962.
56. (a) Stahl, S. S., Labinger, J. A. and Bercaw, J. E., *J. Am. Chem. Soc.*, 1996, **118**, 5961. (b) Jenkins, H. A., Yap, G. P. A. and Puddephatt, R. J., *Organometallics*, 1997, **16**, 1946. (c) Fekl, U., Zhal, A. and van Eldik, R., *Organometallics*, 1999, **18**, 4156.

57. Hahn, C., Spiegler, M., Herdtweck, E. and Taube, R., *Eur. J. Chem.*, 1999, 435.
58. Saunders, D. R. and Mawby, R. J., *J. Chem. Soc., Dalton, Trans.*, 1984, 2133.

University of Cape Town

CHAPTER 6

CONCLUSIONS

A series of iminophosphine ligands were synthesized and fully characterized using spectroscopic and analytical techniques. These ligands were reacted with suitable palladium and platinum precursors to prepare desired palladium(II) and platinum(II) complexes.

All compounds in this dissertation were characterized by ^1H and ^{31}P NMR spectroscopy, infrared spectroscopy, mass spectrometry and elemental analysis. In addition, all ligands, chloromethyl palladium complexes, bromoalkyl platinum complexes as well as platinacycloalkanes, were further characterized by ^{13}C NMR spectroscopy. Due to their low solubility in common laboratory solvents, palladium and platinum dichloride complexes were not characterized by ^{13}C NMR spectroscopy. X-ray crystal structures of the chloromethyl palladium complex, **3.26**, bromoalkyl platinum complex, **3.14**, and platinacyclopentane, **5.1**, were determined. These complexes display a distorted square planar geometry around the metal centre.

The palladium complexes were prepared by reaction of $[\text{Pd}(\text{COD})\text{Cl}_2]$ or $[\text{Pd}(\text{COD})(\text{Me})\text{Cl}]$ with appropriate iminophosphine ligands. A selected number of these complexes were tested for activity in Suzuki-Miyaura coupling reactions and were found to be highly active. The complexes were found to be tolerant of a wide variety of reaction conditions as well as functional groups on both phenylboronic acids as well as aryl halide substrates. Low catalyst loadings were required while maintaining high conversions and short reaction times. Finally, it was observed that having a pendant group bearing a donor atom on the imine moiety of the iminophosphine ligand enhanced catalytic activity.

Platinum dichloride complexes were prepared by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ with appropriate iminophosphine ligands. These complexes were intended to be precursors for the preparation of platinacycloalkanes. However, reaction of $[\text{Pt}(\text{P}^{\wedge}\text{N})\text{Cl}_2]$ with di-Grignard reagents led to formation of bromoalkyl platinum complexes instead. The unexpected result was attributed to monoalkylation of precursor platinum dichloride complexes, followed by halide metathesis.

Platinacycloalkane complexes were successfully synthesized by reacting $[\text{Pt}(\text{COD})\text{Cl}_2]$ with $\text{BrMg}(\text{CH}_2)_n\text{MgBr}$ ($n = 4, 6$); followed by ligand displacement with appropriate iminophosphine ligands. Platinacycloalkanes were obtained in moderate to good yields. Thermal decomposition behaviour of the complexes was investigated. The results revealed

that: 1) The decomposition reaction follows first order reaction kinetics over the first 30% of the decomposition reaction. Beyond this point, significant deviation from first order behaviour is observed, indicating the increasing involvement of reaction products, most likely the metal containing fragment. 2) α -olefins are the major products of the decomposition reaction. 3) Reaction temperature and duration have a significant effect on the organic distribution.

DTF studies were carried out on the β -elimination/reductive elimination reaction of a model platinacyclopentane complex, **5.13B**. Results from these calculations revealed that the energy barrier for the β -hydride elimination reaction is extremely high, in agreement with the experimentally observed stability of platinacyclopentane complexes toward thermal decomposition. This indicates that the β -elimination/reductive elimination sequence for the decomposition of platinacyclopentane complexes is not likely to occur under laboratory conditions, as has been previously proposed by other researchers. The energy barrier for the reductive elimination step was found to be relatively low, indicating that this step would be likely to occur under the experimental conditions described in Chapter 5. Moreover, Ligand hemilability was found to play a role only in the reductive elimination of 1-butene from the hydridoalkenyl platinum complexes. Imine dissociation was calculated to stabilize the product thereof. In contrast, ligand dissociation was calculated to be energetically disfavoured for β -hydride elimination reactions. In this reaction, the ligand was found to interact more strongly with the metal centre in the transition state structures than in the starting material and the products. Since the formation of α -olefins from the thermal decomposition of platinacycloalkanes suggests that formation of a metal hydride intermediate is an important step in this reaction, alternative mechanisms for the generation of metal hydride species need to be explored.

CHAPTER 7

EXPERIMENTAL PROCEDURES

7.1 CHEMICALS AND PURIFICATION OF SOLVENTS

All reactions were carried out under nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques unless otherwise stated. Solvents were dried and purified by refluxing under argon in the presence of a suitable drying agent. After purification, the solvents were transferred under vacuum into a Teflon-valve storage vessel.

All commercially available chemicals were purchased from either Sigma-Aldrich or Merck and used without further purification. K_2PtCl_4 and $PdCl_2$ were obtained from Johnson Matthey. 2-Diphenylphosphinobenzaldehyde,¹ $Pd(COD)Cl_2$,² $Pd(COD)MeCl$,³ $Pt(COD)Cl_2$ ⁴ were all prepared using literature procedures.

7.2 PHYSICAL AND SPECTROSCOPIC INFORMATION (CHAPTERS 3 & 5)

NMR spectra were recorded on a Varian Mercury-300 MHz (1H : 300 MHz; ^{13}C : 75.5 MHz; ^{31}P : 121 MHz) or Varian Unity-400 MHz (1H : 400 MHz; ^{13}C : 100.6 MHz; ^{31}P : 161.9 MHz) spectrometer. 1H NMR spectra were referenced internally using the residual protons in deuterated solvents ($CDCl_3$: δ 7.27; DMSO: δ 2.50) and values reported relative to the internal standard tetramethylsilane (δ 0.00). ^{13}C NMR spectra were referenced internally to the deuterated solvent resonance ($CDCl_3$: δ 77.0; DMSO: δ 39.4) and the values are reported relative to tetramethylsilane (δ 0.00). All chemical shifts are quoted in δ (ppm) and coupling constants, J , in Hertz (Hz).

Melting points were determined on a Reichert-Jung Thermoar hotstage microscope and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument in the 4000–300 cm^{-1} range using KBr discs or CH_2Cl_2 solutions. Microanalyses were determined using a Fisons EA 1108 CHNO-S instrument. Mass spectra were recorded on a Waters API Quatro Micro triple quadrupole mass spectrometer (ESI, 70 eV), University of Stellenbosch. GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 50 m x 0.20 mm HP-PONA column (0.50 μm film thickness). The carrier gas was helium at 40 psi. The oven was programmed to hold the temperature at 32 °C for 4 min and then to ramp to 200 °C at 10 deg/min and hold for 5 min and then ramp to 250 °C at 10 deg/min and hold for 5 min.

7.3 CATALYTIC SUZUKI-MIYaura COUPLING REACTIONS (CHAPTER 4)

A 100 ml round bottom flask was fitted with a reflux condenser and a magnetic stirring bar. The flask was charged with toluene (15 ml) and the appropriate amount of catalyst reagents and the internal standard (*n*-decane: 2.59 mmol). The contents were thoroughly mixed and an initial sample (t_0) was then taken. The reaction flask was placed in an oil bath at the desired temperature and the reaction mixture allowed to heat or reflux with stirring. A sample was taken and analyzed every 10 min for the first hour and every 30 min thereafter until t_{3h} . In cases where conversion was not complete after 3 h, the reaction mixture was then allowed to stir for a total of 24 h then the final sample was analyzed. The reaction at 140 °C was performed in a sealed tube. All catalytic reactions were done under aerobic conditions.⁵ The products were characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. Retention times were measured by gas chromatography. GC analyses were performed using a Varian 3900 gas chromatography equipped with an FID and a 30 m x 0.32 mm CP-Wax 52 CB column (0.25µm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 30 °C for 4 min and then to ramp to 200 °C at 10 deg/min and hold for 5 min.

7.4 THERMAL DECOMPOSITION REACTIONS (CHAPTER 5)

Thermolysis reactions were carried out in clean, dry, sealed evacuated vertical Schlenk tubes of 1-cm o.d. and 10-cm lengths. Decomposition was accomplished by immersion of the tube in stirred oil bath set at the desired temperature. Before use, the tubes were washed with acetone and distilled water, and dried in an oven at 120 °C for at least 24 h, then cooled under dry nitrogen.

Two procedures were used when the thermal decomposition experiments were carried out under solvent free conditions. For solid complexes, a 20 mg-sample was added to the tube directly, dried under vacuum for at least 3 h before the tube was sealed for themolysis. For the oils, a 20-mg sample was dissolved in dichloromethane and transferred into the tube. Solvent was removed under vacuum, and the sample was dried for at least 3 h before sealing the tube for themolysis. In the case of thermal decomposition in solvent, the sample solutions (0.02 M) were prepared in toluene. The solution to be thermolyzed (0.5 ml) was added to the tube by syringe. The tubes were connected to a vacuum line and degassed through three freeze-thaw cycles. The sample was refrozen and the tube sealed under vacuum. The samples were then immersed in a heated oil bath held constant at the desired temperature. After the appropriate reaction time, the reaction was quenched by immersion in liquid nitrogen. For the thermolysis under solvent free conditions, the decomposition products were extracted by adding cold toluene (0.5 ml) containing *n*-decane (20 µl) as the

internal standard. For the thermolysis in solvent, the decomposition solutions were transferred to a liquid nitrogen-cooled sample vial containing n-decane (20 μ l) and marked at 0.5 ml.

Decomposition products were analyzed by GC or GC-MS. Products were identified by comparison of retention times to those of authentic commercial samples. Yields were determined by response relative to an internal standard (n-decane). Response factors were obtained from authentic samples. GC analyses were performed using a Varian 3800 gas chromatography equipped with an FID and a 30 m x 0.32 mm CP-Wax 52 CB column (0.25 μ m film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 $^{\circ}$ C for 4 min and then to ramp to 200 $^{\circ}$ C at 10 deg/min and hold 5 min. GC-MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60m x 0.25 mm Rtx-1 column (0.5 μ m film thicknesses). The carrier gas was helium at 0.9 ml/min. The oven was programmed to hold at 50 $^{\circ}$ C for 2 min and then ramp to 250 $^{\circ}$ C at 10 deg/min and hold for 8 min.

Solutions for the NMR study were prepared as follows: 0.02 M solution of complex **5.1** in toluene- d_8 was prepared. 0.85 ml aliquots of the solution were transferred to NMR tubes fitted with J. Young valves and degassed using three freeze-thaw cycles. The tubes were sealed under vacuum and allowed to warm to room temperature. The NMR tubes were then transferred to oil baths set at the required temperature for each reaction. At appropriate intervals the reaction was quenched by immersion in liquid nitrogen and 31 P NMR spectra were measured.

7.5 COMPUTATIONAL DETAILS (CHAPTER 5)

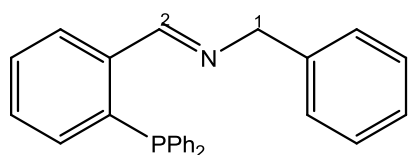
All calculations were carried out with the Gaussian 09 program. The calculations were carried out with the B3LYP density functional level of theory combined with two different basis sets: the LANL2DZ basis set for Pt and 6-31+G (d,p) basis set was used for all other atoms. Full geometry optimizations were carried out for the starting structure, all intermediates and products. All transition structures possessed only one imaginary frequency, and they were further characterized by following the corresponding normal mode toward each product and reactant.⁶

7.6 EXPERIMENTAL DETAILS FOR CHAPTERS 3 & 5

7.6.1 General Procedure for the Synthesis of Primary imine ligands 3.1 – 3.6 (Chapter 3)

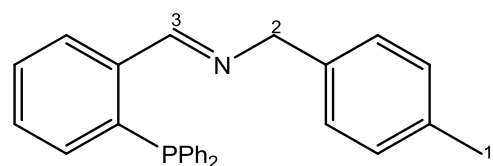
In a round-bottom flask, 2-(diphenylphosphino)benzaldehyde (1.16 g, 4.0 mmol) was dissolved in dry DCM (60 ml) followed by addition of excess anhydrous magnesium sulphate and a molar equivalent of the appropriate amine. The reaction mixture was stirred at room temperature for 24 h, after which magnesium sulphate was filtered off and the solution concentrated under vacuum. The resulting solution was treated with hot hexane, filtered and cooled to -16 °C overnight. During this time either a precipitate (for ligands **3.1**, **3.3** – **3.5**) or an oily residue (for ligands **3.4** and **3.6**) formed. The supernatant was removed and the residue washed with cold hexane, and then dried *in vacuo*. The products were obtained as either off-white solids or yellow-orange oils.⁷⁻¹⁰

Preparation of Benzyl-(2-diphenylphosphanyl-benzylidene)-amine (3.1)



Compound **3.1** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (0.59 g, 2.04 mmol) and benzylamine (0.22 g, 0.22 ml, 2.0 mmol), and was obtained as an off-white crystalline solid (0.74 g, 96 %). M.p. 96 – 97 °C. IR (KBr): 1636 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 4.65 (s, 2H; **H1**), 6.86 (dd, 1H, $^3J_{\text{HH}} = 5.4$ Hz, 7.0 Hz; Ar-**H**), 7.02 (d, 2H, $^3J_{\text{HH}} = 6.8$ Hz; Ar-**H**), 7.18 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz; Ar-**H**), 7.25 (m, 6H; Ar-**H**), 7.32 (t, 6H, $^3J_{\text{HH}} = 5.6$ Hz; Ar-**H**), 8.02 (dd, 1H, $^3J_{\text{HH}} = 3.9$ Hz, 7.6 Hz; Ar-**H**), 8.99 (d, 1H, $^4J_{\text{HH}} = 5.0$ Hz; **H2**). ^{13}C NMR (100.6 MHz, CDCl_3): 65.2 (s; **C1**), 126.6 (s; Ar-**C**), 127.5 (d, $^3J_{\text{CP}} = 4.0$ Hz; Ar-**C**), 128.0 (s; Ar-**C**), 128.4 (s; Ar-**C**), 128.6 (d, $^2J_{\text{CP}} = 7.2$ Hz; Ar-**C**), 129.0 (s; Ar-**C**), 130.4 (s; Ar-**C**), 133.1 (s; Ar-**C**), 134.2 (d, $^1J_{\text{CP}} = 19.9$ Hz; Ar-**C**), 136.1 (d, $^2J_{\text{CP}} = 10.0$ Hz; Ar-**C**), 137.5 (d, $^1J_{\text{CP}} = 19.6$ Hz; Ar-**C**), 139.5 (d, $^1J_{\text{CP}} = 17.3$ Hz; Ar-**C**), 139.0 (s; Ar-**C**), 160.6 (d, $^3J_{\text{CP}} = 22.3$ Hz; **C2**). ^{31}P NMR (161.9 MHz, CDCl_3): -13.8 (s). ESI-MS: m/z 379.18 $[\text{M}]^+$. Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{NP}$ (379.43): C, 82.33; H, 5.90; N, 3.91. Found: C, 82.56; H, 6.11; N, 3.82.

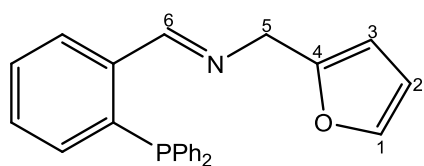
Preparation of (2-Diphenylphosphanyl-benzylidene)-(4-methyl-benzyl)-amine (3.2)



Compound **3.2** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (1.16 g, 4.0 mmol) and 4-Methyl-benzylamine (0.49 g, 0.51 ml, 4.0 mmol), and was obtained as an orange oil (1.28 g, 81%). IR (CH_2Cl_2): 1635 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 1.46 (s, 3H; **H1**), 4.55 (s, 2H; **H2**), 6.05 (d, 1H, $^3J_{\text{HH}} = 5.8$ Hz; Ar-**H**), 6.78 – 7.32 (m, 15H, Ar-**H**), 7.68 (ddd, 1H, $^3J_{\text{HH}} = 0.9$ Hz, 3.9 Hz, 7.7 Hz; Ar-**H**),

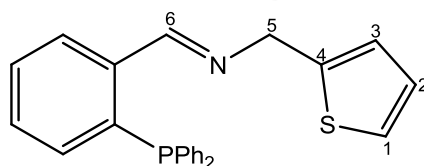
7.97 (ddd, 1H, $^3J_{\text{HH}} = 1.0$ Hz, 4.0 Hz, 7.7 Hz; Ar-**H**), 8.92 (d, 1H, $^4J_{\text{HH}} = 5.1$ Hz; **H3**). ^{13}C NMR (100.6 MHz, CDCl_3): 21.1 (s; **C1**), 64.8 (s; **C2**), 127.0 (s; Ar-**C**), 127.5 (d, $^3J_{\text{CP}} = 4.3$ Hz; Ar-**C**), 127.9 (s, Ar-**C**), 128.6 (d, $^2J_{\text{CP}} = 7.2$ Hz; Ar-**C**), 128.8 (d, $^3J_{\text{CP}} = 1.9$ Hz; Ar-**C**), 129.0 (s; Ar-**C**), 129.1 (s; Ar-**C**), 131.9 (d, $^2J_{\text{CP}} = 10.0$ Hz; Ar-**C**), 133.1 (s; Ar-**C**), 134.0 (d, $^1J_{\text{CP}} = 20.0$ Hz; Ar-**C**), 136.2 (d, $^3J_{\text{CP}} = 2.5$ Hz; Ar-**C**), 137.4 (d, $^1J_{\text{CP}} = 19.0$ Hz; Ar-**C**), 139.3 (d, $^2J_{\text{CP}} = 17.2$ Hz; Ar-**C**), 160.2 (d, $^3J_{\text{CP}} = 22.6$ Hz; **C3**). ^{31}P NMR (161.9 MHz, CDCl_3): -13.9. ESI-MS: m/z 394.17 $[\text{M}+\text{H}]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{NP}$ (393.46): C, 82.42; H, 6.15; N, 3.56. Found: C, 81.97; H, 6.61; N, 3.35.

Preparation of (2-Diphenylphosphanyl-benzylidene)-furan-2-ylmethyl-amine (3.3)



Compound **3.3** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (1.16 g, 4.0 mmol) and furfurylamine (0.39 g, 0.37 ml, 4.0 mmol), and was obtained as an off-white powder (1.02 g, 69%). M.p. 75 – 77 °C. IR (KBr): 1635 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 4.64 (s, 2H; **H5**), 6.03 (dd, 1H, $^4J_{\text{HH}} = 0.8$ Hz, $^3J_{\text{HH}} = 3.2$ Hz; **H3**), 6.27 (dd, 1H, $^4J_{\text{HH}} = 1.2$ Hz, $^3J_{\text{HH}} = 3.2$ Hz; **H2**), 6.89 (dd, 1H, $^4J_{\text{HH}} = 1.2$ Hz, $^3J_{\text{HH}} = 4.8$ Hz; **H1**), 7.32 (m, 13H; Ar-**H**), 8.07 (dd, 1H, $^5J_{\text{HH(m)}} = 1.2$ Hz, $^4J_{\text{HH}} = 4.0$ Hz, $^3J_{\text{HH(o)}} = 7.7$ Hz; Ar-**H**), 8.98 (d, 1H, $^4J_{\text{HH}} = 5.2$; **H6**). ^{13}C NMR (75 MHz, CDCl_3): 57.1 (s; **C5**), 107.4 (s; **C3**), 110.4 (s; **C2**), 127.6 (d, $^3J_{\text{CP}} = 4.2$ Hz; Ar-**C**), 128.5 (d, $^2J_{\text{CP}} = 7.2$ Hz; Ar-**C**), 128.9 (s; Ar-**C**), 129.1 (s; Ar-**C**), 130.5 (s; Ar-**C**), 133.3 (s; Ar-**C**), 134.2 (d, $^1J_{\text{CP}} = 19.9$ Hz; Ar-**C**), 136.3 (d, $^2J_{\text{CP}} = 9.8$ Hz; Ar-**C**), 137.6 (d, $^1J_{\text{CP}} = 19.8$ Hz; Ar-**C**), 139.3 (d, $^1J_{\text{CP}} = 17.4$ Hz; Ar-**C**), 142.2 (s; **C1**), 152.1 (s; **C4**), 161.4 (d, $^3J_{\text{CP}} = 23.1$ Hz; **C6**), ^{31}P NMR (121 MHz, CDCl_3): -14.5 (s). ESI-MS: m/z 369.81 $[\text{M}+\text{H}]^+$. Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{NOP}$ (369.40): C, 78.03; H, 5.46; N, 3.79. Found: C, 77.81; H, 5.56; N, 3.59.

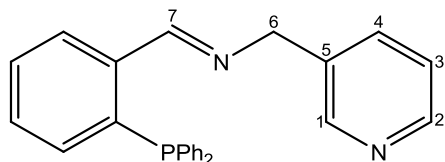
Preparation of (2-Diphenylphosphanyl-benzylidene)-thiophen-2-ylmethyl-amine (3.4)



Compound **3.4** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (1.16 g, 4.0 mmol) and 2-thiophenemethylamine (0.45 g, 0.41 ml, 1.6 mmol), and was obtained as a pale-brown solid (0.99 g, 64%). M.p. 70 – 73 °C. IR (KBr): 1634 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 4.87 (s, 2H; **H5**), 6.78 (d, 1H, $^3J_{\text{HH}} = 2.8$ Hz; **H3**), 6.93 (dd, 2H, $^4J_{\text{HH}} = 4.5$ Hz, $^3J_{\text{HH}} = 8.1$ Hz; **H2**), 7.17 (dd, 1H, $^4J_{\text{HH}} = 1.2$ Hz, $^3J_{\text{HH}} = 5.1$ Hz; **H1**), 7.28 – 7.43 (m, 12H; Ar-**H**), 8.07 (ddd, 1H, $^5J_{\text{HH(p)}} = 1.5$ Hz, $^4J_{\text{HH(m)}} = 4.0$ Hz, $^3J_{\text{HH(o)}} = 7.7$ Hz; Ar-**H**), 9.01 (d, 1H, $^4J_{\text{HH}} = 5.1$ Hz; **H6**). ^{13}C NMR (100.6 MHz, CDCl_3): 60.0 (s; **C5**), 124.5 (s; **C3**), 125.3 (s; **C2**), 126.8 (s; **C1**), 127.9 (d, $^3J_{\text{CP}} = 4.2$ Hz; Ar-**C**), 128.8 (d, $^2J_{\text{CP}} = 7.2$ Hz; Ar-**C**), 129.3 (s; Ar-**C**), 130.0 (s; Ar-**C**), 130.6 (s; Ar-**C**), 133.4 (s; Ar-**C**), 134.0 (d, $^1J_{\text{CP}} = 20.7$ Hz; Ar-**C**), 136.5 (d, $^2J_{\text{CP}} = 9.8$ Hz; Ar-

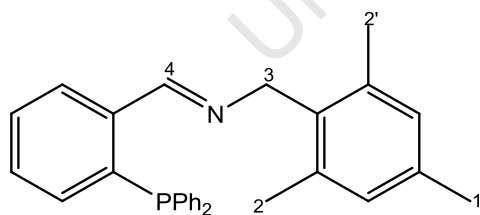
C), 137.8 (d, $^1J_{CP} = 19.4$ Hz; Ar-**C**), 139.2 (d, $^1J_{CP} = 17.2$ Hz; Ar-**C**), 141.8 (s; **C4**), 160.8 (d, $^3J_{CP} = 23.4$ Hz; **C6**), ^{31}P NMR (161.9 MHz, CDCl_3): -14.5 (s). ESI-MS: m/z 386.11 $[\text{M}+\text{H}]^+$. Anal. Calc. for $\text{C}_{24}\text{H}_{20}\text{NPS}$ (385.46): C, 74.78; H, 5.23; N, 3.63; S, 8.32. Found: C, 74.21; H, 5.30; N, 3.35; S, 8.28.

Preparation of (2-Diphenylphosphanyl-benzylidene)-pyridin-3-ylmethyl-amine (3.5)



Compound **3.5** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (1.20 g, 4.1 mmol) and 3-aminomethylpyridine (0.45 g, 0.42 ml, 4.1 mmol), and was obtained as an off-white powder (1.14 g, 74%). M.p. 78 – 81 °C. IR (KBr): 1634 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 4.63 (s, 2H; **H6**), 6.86 (dd, 1H, $^3J_{\text{HH}} = 4.8$ Hz, 7.6 Hz; Ar-**H**), 7.08 (dd, 1H, $^3J_{\text{HH}} = 4.8$ Hz, 7.8 Hz; Ar-**H**), 7.23 (dd, 6H, $^3J_{\text{HH}} = 5.6$ Hz, 7.2 Hz; Ar-**H**), 7.30 (m, 6H; Ar-**H**), 7.36 (t, 1H, $^3J_{\text{HH}} = 7.5$ Hz; **H3**), 7.97 (dd, 1H, $^3J_{\text{HH}} = 3.9$ Hz, 7.6 Hz; **H4**), 8.38 (s, 1H; **H1**) 8.41 (d, 1H, $^3J_{\text{HH}} = 4.7$ Hz; **H2**), 8.98 (d, 1H, $^4J_{\text{HH}} = 5.7$ Hz; **H7**). ^{13}C NMR (100.6 MHz, CDCl_3): 62.4 (s; **C6**), 122.5 (s; **C3**), 123.7 (s; Ar-**C**), 128.0 (d, $^3J_{CP} = 4.0$ Hz; Ar-**C**), 128.6 (d, $^2J_{CP} = 7.0$ Hz; Ar-**C**), 129.1 (s; Ar-**C**), 130.3 (s; Ar-**C**), 133.4 (s; Ar-**C**), 134.4 (d, $^1J_{CP} = 20.2$ Hz; Ar-**C**), 134.6 (s; **C5**), 135.8 (s; **C4**), 136.5 (d, $^2J_{CP} = 9.2$ Hz; Ar-**C**), 137.1 (d, $^1J_{CP} = 16.9$ Hz; Ar-**C**), 137.7 (d, $^2J_{CP} = 19.8$ Hz; Ar-**C**), 148.1 (**C2**), 149.6 (s; **C1**), 161.3 (d, $^3J_{CP} = 21.1$ Hz, **C7**). ^{31}P NMR (161.9 MHz, CDCl_3): -13.4 (s). ESI-MS: m/z 381.15 $[\text{M}+\text{H}]^+$. Anal. Calc. For $\text{C}_{25}\text{H}_{21}\text{N}_2\text{P}$ (380.42): C, 78.93; H, 5.56; N, 7.36. Found: C, 78.95; H, 5.49; N, 7.25.

Preparation of (2-Diphenylphosphanyl-benzylidene)-(2,4,6-trimethyl-benzyl)-amine (3.6)



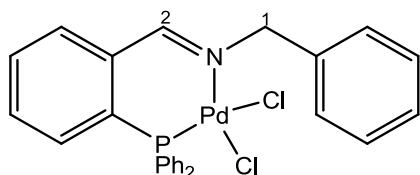
Compound **3.6** was prepared as described in the general procedure using 2-(diphenylphosphino)benzaldehyde (1.16 g, 4.0 mmol) and 2,4,6-Trimethyl-benzylamine (0.72 g, 0.47 ml, 4.8 mmol), and was obtained as a yellow-orange oil (1.30 g, 77%). IR (CH_2Cl_2): 1635 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 2.25 (s, 6H; **H2+H2'**), 2.41 (s, 3H; **H1**), 4.90 (s, 2H; **H3**), 6.95 (br s, 1H; Ar-**H**), 7.00 – 7.02 (m, 1H; Ar-**H**), 7.33 – 7.50 (m, 13H; Ar-**H**), 8.21 (dd, 1H, $^3J_{\text{HH}} = 3.9$ Hz, 6.7 Hz; Ar-**H**), 8.98 (d, 1H, $^4J_{\text{HH}} = 5.1$ Hz; **H4**). ^{13}C NMR (75.5 MHz, CDCl_3): 19.5 (s; **C2+C2'**), 21.0 (s; **C1**), 57.6 (s; **C3**), 127.3 (d, $^3J_{CP} = 4.2$ Hz; Ar-**C**), 128.5 (d, $^2J_{CP} = 7.1$ Hz; Ar-**C**), 128.7 (d, $^2J_{CP} = 6.2$ Hz; Ar-**C**), 128.9 (s; Ar-**C**), 130.1 (s; Ar-**C**), 131.1 (s; Ar-**C**), 131.4 (s; Ar-**C**), 132.9 (s; Ar-**C**), 134.0 (d, $^1J_{CP} = 20.0$ Hz; Ar-**C**), 136.3 (d, $^2J_{CP} = 9.9$ Hz; Ar-**C**), 136.6 (s; Ar-**C**), 137.4 (s; Ar-**C**), 137.6 (s; Ar-**C**),

139.3 (d, $^2J_{\text{CP}} = 16.9$ Hz; Ar-**C**), 158.9 (d, $^3J_{\text{CP}} = 23.0$ Hz; **C4**). ^{31}P NMR (161 MHz, CDCl_3): -13.5. ESI-MS: m/z 422.20 $[\text{M}]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{28}\text{NP}$ (422.36): C, 82.63; H, 6.70; N, 3.32. Found: C, 82.57; H, 6.65; N, 3.29.

7.6.2 General Procedure for the Synthesis of Palladium Dichloride Complexes 3.7 – 3.12 (Chapter 3)

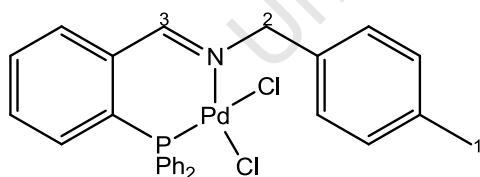
A solution of $[\text{Pd}(\text{COD})\text{Cl}_2]$ in DCM (15 ml) was added to a solution of an appropriate imine ligand (0.50 mmol) in DCM (15 mmol) at ambient temperature. A pale yellow precipitate formed immediately and the reaction was stirred at room temperature for 15 h. The precipitate was filtered, washed with aliquots of DCM and Et_2O and then dried. The products were obtained as pale yellow solids in moderate to good yields.^{9,11,12}

Preparation of $[\text{Pd}(\text{C}_{26}\text{H}_{22}\text{NP})\text{Cl}_2]$ (3.7)

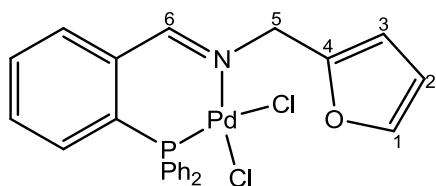


Complex **3.7** was prepared from the reaction of **3.1** (0.28 g, 0.74 mmol) and $[\text{Pd}(\text{COD})\text{Cl}_2]$ (0.21 g, 0.74 mmol). The product was obtained as a yellow powder (0.31 g, 75%). M.p. 199 – 202 °C (decomp.). IR (KBr): 1628 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO-d_6): 5.49 (s, 2H; **H1**), 6.98 – 7.00 (m, 1H; Ar-**H**), 7.12 – 7.13 (m, 5H; Ar-**H**), 7.25 (dd, 4H, $^3J_{\text{HH}} = 1.8, 7.9$ Hz; Ar-**H**), 7.40 (dt, 4H, $^3J_{\text{HH}} = 2.7$ Hz, 7.7 Hz; Ar-**H**), 7.55 – 7.56 (m, 2H; Ar-**H**), 7.73 – 7.75 (m, 1H; Ar-**H**), 7.89 – 7.91 (m, 1H; Ar-**H**), 8.01 – 8.02 (m, 1H; Ar-**H**), 8.84 (s, 1H; **H2**). ^{31}P NMR (161.9 MHz, DMSO-d_6): 34.1 (s). ESI-MS: m/z 521.01 $[\text{M-Cl}]^+$. Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{NPPd}$ (556.76): C, 56.09; H, 3.98; N, 2.54. Found: C, 55.90; H, 3.78; N, 2.50.

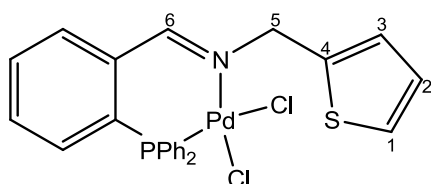
Preparation of $[\text{Pd}(\text{C}_{27}\text{H}_{24}\text{NP})\text{Cl}_2]$ (3.8)



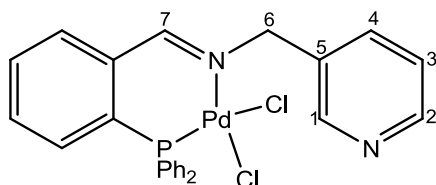
Complex **3.8** was prepared by reacting $[\text{Pd}(\text{COD})\text{Cl}_2]$ (0.21 g, 0.74 mmol) with **3.2** (0.29 g, 0.74 mmol). The product was obtained as a yellow powder (0.21 g, 50%). M.p. 173 – 175 °C (decomp.). IR (KBr): 1628 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO-d_6): 2.26 (s, 3H; **H1**), 5.47 (s, 2H; **H2**), 7.11 – 7.12 (m, 1H; Ar-**H**), 7.19 – 7.20 (m, 4H; Ar-**H**), 7.30 – 7.32 (m, 6H; Ar-**H**), 7.41 – 7.42 (m, 2H; Ar-**H**), 7.60 – 7.61 (m, 2H; Ar-**H**), 7.69 – 7.70 (m, 1H; Ar-**H**), 7.92 – 7.93 (m, 1H; Ar-**H**), 8.17 – 8.19 (m, 1H; Ar-**H**), 8.84 (s, 1H; **H3**). ^{31}P NMR (161 MHz, DMSO-d_6): 30.7 (s). ESI-MS: m/z 535.27 $[\text{M-Cl}]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{NPPd}$ (570.79): C, 56.81; H, 4.24; N, 2.45. Found: C, 55.90; H, 4.31; N, 2.53.

Preparation of [Pd(C₂₄H₂₀NOP)Cl₂] (3.9)

Complex **3.9** was prepared by reacting of [Pd(COD)Cl₂] (0.96 g, 3.36 mmol) with ligand **3.3** (1.24 g, 3.36 mmol). The product was obtained as a yellow powder (1.32 g, 72%). M.p. 198 – 200 °C (decomp.). IR (KBr): 1626 cm⁻¹ (ν_{C=N}, imine). ¹H NMR (400 MHz, DMSO-*d*₆): 5.55 (s, 2H; **H5**), 6.44 (m, 1H; **H3**), 6.61 (d, 1H, ³J_{HH} = 2.7 Hz; **H2**), 7.08 – 7.09 (m, 1H, **H1**), 7.19 (s, 1H; Ar-**H**), 7.24 (dd, 4H, ⁴J_{HH} = 2.9 Hz, 5.0 Hz; Ar-**H**), 7.48 (dt, 4H, ³J_{HH} = 1.9 Hz, 7.9 Hz; Ar-**H**), 7.62 (t, 2H, ³J_{HH} = 7.5 Hz; Ar-**H**), 7.79 (t, 1H, ³J_{HH} = 8.0 Hz; Ar-**H**), 7.93 (t, 1H, ³J_{HH} = 7.4 Hz; Ar-**H**), 8.03 (dd, 1H, ³J_{HH} = 4.0 Hz, 7.1 Hz; **H7**), 8.79 (s, 1H, **H6**). ³¹P NMR (162 MHz, DMSO-*d*₆): 31.3 (s). ESI-MS: *m/z* 511.44 [M-Cl]⁺. Anal. Calc. for C₂₄H₂₀Cl₂NOPPd (546.72): C, 52.72; H, 3.69; N, 2.56. Found: C, 52.42; H, 3.56; N, 2.59.

Preparation of [Pd(C₂₄H₂₀NPS)Cl₂] (3.10)

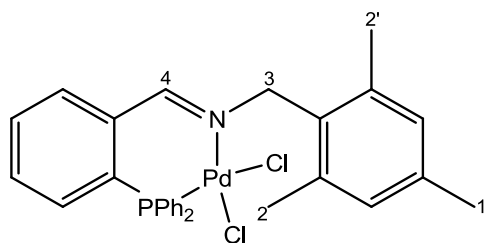
Complex **3.10** was prepared by reacting [Pd(COD)Cl₂] (0.96 g, 3.36 mmol) with ligand **3.4** (1.29 g, 3.36 mmol). The product was obtained as a yellow powder (1.23 g, 65%). M.p. 232 – 234 °C (decomp.). IR (KBr): 1627 cm⁻¹ (ν_{C=N}, imine). ¹H NMR (300 MHz, DMSO-*d*₆): 5.69 (s, 2H; **H5**), 6.53 (dd, 1H, ³J_{HH} = 0.8 Hz, 3.3 Hz; **H3**), 6.79 (dd, 1H, ³J_{HH} = 3.4 Hz, 5.1 Hz; **H2**), 6.99 (dd, 1H, ³J_{HH} = 8.0 Hz, 10.0 Hz; **H1**), 7.23 (dd, 1H, ³J_{HH} = 1.2 Hz, 5.1 Hz; Ar-**H**), 7.44 (ddd, 4H, ³J_{HH} = 1.2 Hz, 8.3 Hz, 12.8 Hz; Ar-**H**), 7.56 (dt, 4H, ³J_{HH} = 3.0 Hz, 7.4 Hz; Ar-**H**), 7.66 – 7.68 (m, 2H; Ar-**H**), 7.74 – 7.75 (m, 1H; Ar-**H**), 7.90 – 7.92 (m, 2H; Ar-**H**), 8.52 (s, 1H; **H6**). ³¹P NMR (121 MHz, DMSO-*d*₆): 35.2 (s). ESI-MS: *m/z* 525.99 [M-Cl]⁺. Anal. Calc. for C₂₄H₂₀Cl₂NPPdS (562.79): C, 51.22; H, 3.58; N, 2.49; S, 5.70. Found: C, 50.98; H, 3.47; N, 2.68; S, 6.00.

Preparation of [Pd(C₂₅H₂₁N₂P)Cl₂] (3.11)

Complex **3.11** was prepared from a reaction of **3.5** (0.28 g, 0.74 mmol) and [Pd(COD)Cl₂] (0.21 g, 0.74 mmol) and the product was obtained as a yellow powder (0.26 g, 63 %). M.p. 209 – 212 °C (decomp.). IR (KBr): 1624 cm⁻¹ (ν_{C=N}, imine). ¹H NMR (400 MHz, DMSO-*d*₆): 5.58 (s, 2H; **H6**), 6.97 – 6.98 (m, 1H; Ar-**H**), 7.15 (dd, 5H, ³J_{HH} = 8.0 Hz, 13.0 Hz; Ar-**H**), 7.41 (t, 4H, ³J_{HH} = 6.8 Hz; Ar-**H**), 7.60 (dd, 3H, ³J_{HH} = 7.8 Hz, 14.7 Hz; Ar-**H**), 7.77 (t, 1H, ³J_{HH} = 7.8 Hz; Ar-**H**), 7.94 (dd, 1H, ³J_{HH} = 4.1 Hz, 7.8 Hz; **H3**), 8.06 (t, 1H, ³J_{HH} = 7.4 Hz; **H4**), 8.49 (d, 1H, ³J_{HH} = 4.6 Hz; **H2**), 8.61 (s, 1H; **H7**), 8.89 (s, 1H; **H1**). ³¹P NMR (161.9 MHz, DMSO-*d*₆):

30.8 (s). ESI-MS: m/z 522.12 $[M-Cl]^+$. Anal. Calc. for $C_{25}H_{21}Cl_2N_2PPd$ (557.75): C, 53.84; H, 3.80; N, 5.02. Found: C, 54.01; H, 3.96; N, 4.96.

Preparation of $[Pd(C_{29}H_{28}NP)Cl_2]$ (3.12)

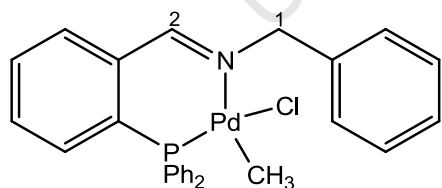


Complex **3.12** was prepared by a reaction of $[Pd(COD)Cl_2]$ (0.21 g, 0.74 mmol) with **3.6** (0.31 g, 0.74 mmol). The product was obtained as a yellow powder (0.30 g, 67%). M.p. 186 - 189 °C (decomp.). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). 1H NMR (400 MHz, DMSO- d_6): 2.23 (s, 6H; **H2+H2'**), 2.45 (s, 3H; **H1**), 5.50 (s, 2H; **H3**), 7.20 – 7.22 (m, 2H; Ar-**H**), 7.26 – 7.28 (m, 4H; Ar-**H**), 7.34 – 7.35 (m, 4H; Ar-**H**), 7.39 – 7.40 (m, 1H; Ar-**H**), 7.64 – 7.65 (m, 2H; Ar-**H**), 7.71 – 7.72 (m, 1H; Ar-**H**), 7.92 – 7.95 (m, 1H; Ar-**H**), 8.15 – 8.16 (m, 1H; Ar-**H**), 8.71 (s, 1H; **H4**). ^{31}P NMR (161 MHz, DMSO- d_6): 31.9 (s). ESI-MS: m/z 564.26 $[M-Cl]^+$. Anal. Calc. for $C_{29}H_{28}Cl_2NPPd$ (598.84): C, 58.16; H, 4.17; N, 2.34. Found: C, 57.97; H, 4.33; N, 2.43.

7.6.3 General Procedure for the Synthesis of Methyl Chloride Palladium Complexes 3.13 – 3.18 (Chapter 3)

To a solution of the appropriate ligand in DCM (15 ml) was added equimolar amount of $[Pd(COD)(CH_3)Cl]$ solution in DCM (15 ml). The reaction was stirred at room temperature for 15 h, after which the solvent was reduced *in vacuo* and hexane was added to the solution to precipitate out the product. The resultant solid was washed with hexane and diethyl ether then dried. The desired products were obtained as pale yellow or off-white solids in moderate to good yields.^{11,13}

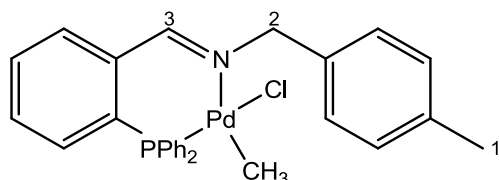
Preparation of $[Pd(C_{26}H_{22}NP)(Me)Cl]$ (3.13)



Complex **3.13** was prepared by a reaction of $[Pd(COD)(CH_3)Cl]$ (0.30 g, 1.13 mmol) with **3.1** (0.42 g, 1.13 mmol) and the product was obtained as a pale yellow powder (0.39 g, 65%). M.p. 169 – 171 °C. IR (KBr): 1638 cm^{-1} ($\nu_{C=N}$, imine). 1H NMR (400 MHz, $CDCl_3$): 0.21 (d, 3H, $^3J_{HP} = 3.2$ Hz; Pd-**CH**₃), 5.09 (s, 2H; **H1**), 7.13 (dd, 1H, $^3J_{HH} = 7.7$, 10.5 Hz; Ar-**H**), 7.18 – 7.23 (m, 8H; Ar-**H**), 7.34 (m, 1H; Ar-**H**), 7.46 (dt, 4H, $^3J_{HH} = 2.3$, 7.6 Hz; Ar-**H**), 7.53 – 7.54 (m, 2H; Ar-**H**), 7.71 (br t, 1H, $^3J_{HH} = 7.5$ Hz; Ar-**H**), 7.82 (br t, 1H, $^3J_{HH} = 7.5$ Hz; Ar-**H**), 7.94 (dd, 1H, $^3J_{HH} = 4.3$, 6.3 Hz; Ar-**H**), 8.80 (s, 1H; **H2**). ^{13}C NMR (100.6 MHz, $CDCl_3$): 0.62 (s; Pd-**CH**₃), 62.5 (s; **C1**), 124.4 (s; Ar-**C**), 124.7 (d, $^2J_{CP} = 7.6$ Hz; Ar-**C**), 127.8 (s; Ar-**C**), 128.3 (s; Ar-**C**), 129.5 (d, $^2J_{CP} = 8.8$ Hz; Ar-**C**), 130.1 (d, $^1J_{CP} = 11.9$ Hz; Ar-**C**), 132.4 (s; Ar-**C**), 134.3 (s; Ar-**C**), 134.8 (d, $^1J_{CP} = 12.1$ Hz; Ar-**C**), 135.5 (s; Ar-**C**), 136.0 (d,

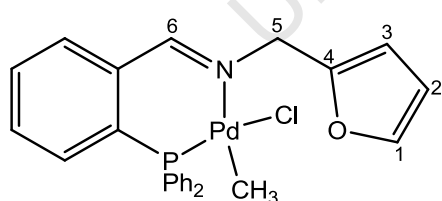
$^1J_{CP} = 13.6$ Hz; Ar-**C**), 137.4 (s; Ar-**C**), 138.0 (s; Ar-**C**), 138.5 (d, $^2J_{CP} = 8.3$ Hz; Ar-**C**), 164.7 (d, $^3J_{CP} = 5.0$ Hz; **C2**). ^{31}P NMR (161.9 MHz, CDCl_3): 38.3 (s). ESI-MS: m/z 501.10 $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{27}\text{H}_{25}\text{ClINOPPd}$ (536.34): C, 60.46; H, 4.70; N, 2.61. Found: C, 60.91; H, 4.43; N, 2.87.

Preparation of $[\text{Pd}(\text{C}_{27}\text{H}_{24}\text{NP})(\text{Me})\text{Cl}]$ (**3.14**)



Complex **3.14** was prepared by the reaction of **3.2** (0.42 g, 1.07 mmol) and $[\text{Pd}(\text{COD})(\text{CH}_3)\text{Cl}]$ (0.28 g, 1.07 mmol) and the product was obtained as a pale yellow solid (0.47 g, 79%). M.p. 122 - 124 °C (decomp.). IR (KBr): 1638 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.56 (d, 3H, $^3J_{\text{HP}} = 2.9$ Hz; Pd-**CH**₃), 2.36 (s, 3H; **H1**), 5.40 (s, 2H; **H2**), 6.91 (d, 2H, $^3J_{\text{HH}} = 7.7$ Hz; Ar-**H**), 7.02 (m, 1H; Ar-**H**), 7.08 (br s, 1H; Ar-**H**), 7.10 (d, 2H, $^4J_{\text{HH}} = 5.9$ Hz; Ar-**H**), 7.14 (d, 3H, $^4J_{\text{HH}} = 5.1$ Hz; Ar-**H**), 7.26 (t, 4H, $^3J_{\text{HH}} = 7.2$ Hz; Ar-**H**), 7.40 (t, 3H, $^3J_{\text{HH}} = 7.2$ Hz; Ar-**H**), 7.47 (dd, 1H, $^3J_{\text{HH}} = 4.1$ Hz; 7.5 Hz, Ar-**H**), 7.55 (t, 1H, $^3J_{\text{HH}} = 7.4$ Hz; Ar-**H**), 8.16 (s, 1H; **H3**). ^{13}C NMR (100.6 MHz, CDCl_3): 2.3 (s; Pd-**CH**₃), 21.2 (s; **C1**), 66.6 (s; **C2**), 126.8 (s; Ar-**C**), 127.2 (s; Ar-**C**), 127.3 (s; Ar-**C**), 127.5 (s; Ar-**C**), 127.8 (d, $^2J_{CP} = 5.9$ Hz; Ar-**C**), 128.0 (s; Ar-**C**), 128.1 (s; Ar-**C**), 128.2 (s; Ar-**C**), 128.6 (d, $^1J_{CP} = 11.1$, Ar-**C**), 128.8 (s; Ar-**C**), 129.4 (d, $^1J_{CP} = 13.6$ Hz; Ar-**C**), 129.7 (s; Ar-**C**), 129.9 (s; Ar-**C**), 130.7 (s; Ar-**C**), 130.8 (d, $^3J_{CP} = 2.0$ Hz; Ar-**C**), 131.3 (d, $^3J_{CP} = 1.3$ Hz; Ar-**C**), 131.8 (s; Ar-**C**), 131.9 (d, $^2J_{CP} = 6.8$ Hz; Ar-**C**), 132.2 (s; Ar-**C**), 132.3 (s; Ar-**C**), 133.6 (d, $^2J_{CP} = 5.5$ Hz; Ar-**C**), 133.9 (d, $^1J_{CP} = 12.4$ Hz; Ar-**C**), 137.0 (s; Ar-**C**), 137.4 (d, $^2J_{CP} = 14.3$ Hz; Ar-**C**), 162.4 (d, $^3J_{CP} = 5.0$ Hz; **C3**). ^{31}P NMR (161.9 MHz, CDCl_3): 37.4 (s). ESI-MS: m/z 514.10 $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{28}\text{H}_{27}\text{ClINPPd}$ (550.37): C, 61.10; H, 4.94; N, 2.54. Found: C, 61.54; H, 4.61; N, 2.49.

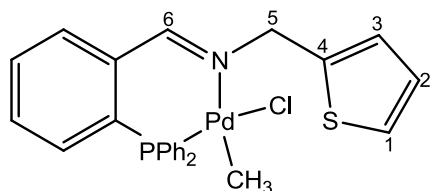
Preparation of $[\text{Pd}(\text{C}_{24}\text{H}_{20}\text{NOP})(\text{Me})\text{Cl}]$ (**3.15**)



Complex **3.15** was prepared by the reaction of **3.3** (0.39 g, 1.07 mmol) and $[\text{Pd}(\text{COD})(\text{CH}_3)\text{Cl}]$ (0.28 g, 1.07 mmol) and the product was obtained as a pale yellow solid (0.40 g, 71%). M.p. 193 - 195 °C. IR (KBr): 1637 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.56 (d, 3H, $^3J_{\text{HP}} = 2.4$ Hz; Pd-**CH**₃), 5.47 (s, 2H; **H5**), 6.35 (m, 1H; **H3**), 6.72 (d, 1H, $^3J_{\text{HH}} = 2.6$ Hz; **H2**), 7.06 (m, 1H; **H1**), 7.15 (t, 1H, $^3J_{\text{HH}} = 8.7$ Hz; Ar-**H**), 7.26 - 7.29 (m, 4H; Ar-**H**), 7.38 (t, 4H, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 7.48 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz; Ar-**H**), 7.56 - 7.58 (m, 1H; Ar-**H**), 7.62 (t, 1H, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 8.24 (br s, 1H; **H-imine**). ^{13}C NMR (100.6 MHz, CDCl_3): 2.9 (s; Pd-**CH**₃), 59.1 (s; **C5**), 110.6 (s; **C3**), 111.3 (s; **C2**), 126.9 (d, $^2J_{CP} = 7.5$ Hz; Ar-**C**), 128.2 (s; Ar-**C**), 128.7 (d, $^1J_{CP} = 11.2$ Hz; Ar-**C**), 130.9 (d, $^3J_{CP} = 2.0$ Hz; Ar-**C**), 131.4 (d, $^3J_{CP} = 1.7$ Hz; Ar-**C**), 132.2 (d, $^2J_{CP} = 6.8$ Hz; Ar-**C**), 133.5 (s; Ar-**C**), 134.1 (d, $^1J_{CP} = 12.6$ Hz; Ar-**C**), 135.9

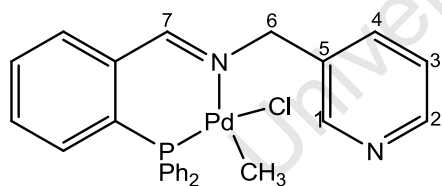
(d, $^2J_{CP} = 8.7$ Hz; Ar-**C**), 136.0 (s; Ar-**C**), 142.8 (s; **C1**), 149.5 (s; **C4**), 163.7 (d, $^3J_{CP} = 5.1$ Hz; **C6**). ^{31}P NMR (161.9 MHz, CDCl_3): 37.4 (s). ESI-MS: m/z 490.21 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{25}\text{H}_{23}\text{ClNOPPd}$ (526.30): C, 57.05; H, 4.40; N, 2.66. Found: C, 57.56; H, 4.39; N, 2.98.

Preparation of $[\text{Pd}(\text{C}_{24}\text{H}_{20}\text{NPS})(\text{Me})\text{Cl}]$ (**3.16**)



Complex **3.16** was prepared by the reaction of **3.4** (0.41 g, 1.07 mmol) and $[\text{Pd}(\text{COD})(\text{CH}_3\text{Cl})]$ (0.28 g, 1.07 mmol) and the product was obtained as a pale yellow solid (0.42 g, 73%). M.p. 188 – 190 °C. IR (KBr): 1637 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.56 (d, 3H, $^3J_{\text{HP}} = 2.9$ Hz; Pd- CH_3), 5.48 (s, 2H; **H5**), 6.36 (m, 1H; **H3**), 6.73 (d, 1H, $^3J_{\text{HH}} = 2.6$ Hz; **H2**), 7.10 (m, 1H; **H1**), 7.16 (t, 1H, $^3J_{\text{HH}} = 8.8$ Hz; Ar-**H**), 7.29 (t, 4H, $^4J_{\text{HH}} = 5.8$ Hz; Ar-**H**), 7.39 (t, 4H, $^3J_{\text{HH}} = 7.6$ Hz; Ar-**H**), 7.48 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz; Ar-**H**), 7.54 – 7.55 (m, 1H; Ar-**H**), 7.64 (t, 1H, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 8.24 (br s, 1H; **H6**). ^{13}C NMR (100.6 MHz, CDCl_3): 2.3 (s; Pd- CH_3), 61.5 (s; **C5**), 123.9 (**C3**), 127.0 (**C2**), 127.7 (d, $^1J_{\text{CP}} = 12.0$ Hz; Ar-**C**), 128.3 (s; Ar-**C**), 128.8 (s; Ar-**C**), 130.0 (d, $^1J_{\text{CP}} = 11.3$ Hz; Ar-**C**), 130.9 (d, $^3J_{\text{CP}} = 2.1$ Hz; Ar-**C**), 131.2 (d, $^3J_{\text{CP}} = 1.5$ Hz; Ar-**C**), 132.4 (d, $^2J_{\text{CP}} = 6.8$ Hz; Ar-**C**), 133.7 (s; **C1**), 134.2 (d, $^1J_{\text{CP}} = 12.4$ Hz; Ar-**C**), 135.9 (d, $^2J_{\text{CP}} = 8.5$ Hz; Ar-**C**), 137.3 (d, $^2J_{\text{CP}} = 14.4$ Hz; Ar-**C**), 138.6 (s; **C4**), 163.4 (d, $^3J_{\text{CP}} = 5.1$ Hz; **C6**). ^{31}P NMR (161.9 MHz, CDCl_3): 37.5 (s). ESI-MS: m/z 506.83 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{25}\text{H}_{23}\text{ClNPPdS}$ (542.37): C, 55.36; H, 4.27; N, 2.58; S, 5.91. Found: C, 55.42; H, 4.25; N, 2.31; S, 5.87.

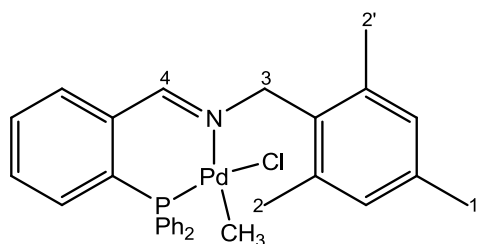
Preparation of $[\text{Pd}(\text{C}_{25}\text{H}_{21}\text{N}_2\text{P})(\text{Me})\text{Cl}]$ (**3.17**)



Compound **3.17** was prepared by the reaction of $[\text{Pd}(\text{COD})(\text{CH}_3\text{Cl})]$ (0.13 g, 0.50 mmol) and **3.5** (0.19 g, 0.5 mmol) and the product was obtained as a pale yellow powder (0.19 g, 72%). M.p. 180 – 182 °C. IR (KBr): 1635 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.61 (d, 3H, $^3J_{\text{HP}} = 3.0$ Hz; Pd- CH_3), 5.49 (s, 2H; **H6**), 7.09 (dd, 1H, $^3J_{\text{HH}} = 7.4$ Hz, 9.8 Hz; Ar-**H**), 7.14 – 7.17 (m, 4H; Ar-**H**), 7.39 – 7.41 (m, 4H; Ar-**H**), 7.46 – 7.49 (m, 3H; Ar-**H**), 7.60 – 7.62 (m, 1H; Ar-**H**), 7.65 – 7.66 (m, 1H; **H3**), 8.00 (td, 1H, $^3J_{\text{HH}} = 1.8$ Hz; 7.8 Hz, Ar-**H**), 8.28 (1H, s; **H4**) 8.32 (d, 1H, $^4J_{\text{HH}} = 2.2$, Hz; **H1**), 8.40 (s, 1H; **H7**), 8.51 (dd, 1H, $^3J_{\text{HH}} = 1.6$ Hz, 4.8 Hz; **H2**). ^{13}C NMR (100.6 MHz, CDCl_3): 2.6 (s; Pd- CH_3), 64.4 (s; **C6**), 123.3 (s; Ar-**C**), 126.5 (s; Ar-**C**), 128.7 (d, $^1J_{\text{CP}} = 11.2$ Hz; Ar-**C**), 130.4 (d, $^3J_{\text{CP}} = 1.7$ Hz; Ar-**C**), 131.1 (d, $^3J_{\text{CP}} = 2.3$ Hz; Ar-**C**), 132.3 (d, $^2J_{\text{CP}} = 6.7$ Hz; Ar-**C**), 132.5 (s; Ar-**C**), 133.1 (d, $^1J_{\text{CP}} = 12.4$ Hz; Ar-**C**), 133.8 (s; Ar-**C**), 133.9 (s; Ar-**C**), 134.1 (s; **C3**), 136.1 (d, $^1J_{\text{CP}} = 8.7$ Hz; Ar-**C**), 137.4 (s; **C4**), 138.1 (s; **C**-pyridyl), 149.0 (s; **C2**), 150.4 (s; **C1**), 163.6 (d, $^3J_{\text{CP}} = 4.8$ Hz; **C7**).

^{31}P NMR (161.9 MHz, CDCl_3): 37.6 (s). ESI-MS: m/z 501.11 $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{26}\text{H}_{24}\text{ClN}_2\text{PPd}$ (537.33): C, 58.12; H, 4.50; N, 5.21. Found: C, 58.52; H, 4.56; N, 5.13.

Preparation of $[\text{Pd}(\text{C}_{29}\text{H}_{28}\text{NP})(\text{Me})\text{Cl}]$ (3.18)



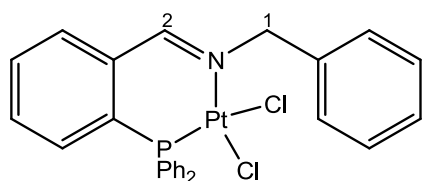
Complex **3.18** was prepared by the reaction of **3.6** (0.50 g, 1.18 mmol) and $[\text{Pd}(\text{COD})(\text{CH}_3)\text{Cl}]$ (0.31 g, 1.18 mmol) and the product was obtained as a pale yellow solid (0.54 g, 79%). M.p. 135 - 138 °C (decomp). IR (KBr): 1638 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.51 (d, 3H, $^3J_{\text{HP}} = 3.1\text{ Hz}$; Pd- CH_3), 2.27 (s, 6H; $\text{H}_2+\text{H}_2'$) 2.33 (s, 3H; H_1), 5.32 (s, 2H; H_3), 6.95 (d, 2H, $^3J_{\text{HH}} = 7.1\text{ Hz}$; Ar- H), 7.06 – 7.07 (m, 1H; Ar- H), 7.11 (d, 2H, $^3J_{\text{HH}} = 7.6\text{ Hz}$; Ar- H), 7.21 (d, 3H, $^3J_{\text{HH}} = 7.1\text{ Hz}$; Ar- H), 7.31 (m, 3H; Ar- H), 7.49 (t, 4H, $^3J_{\text{HH}} = 7.8\text{ Hz}$; Ar- H), 7.81 (t, 1H, $^3J_{\text{HH}} = 7.1\text{ Hz}$; Ar- H), 8.36 (s, 1H; H_4). ^{13}C NMR (100.6 MHz, CDCl_3): 2.1 (s; Pd- CH_3), 21.5 (s; $\text{C}_2+\text{C}_2'$), 23.7 (s; C_1) 64.7 (s; C_3), 126.1 (s; Ar- C), 127.2 (s; Ar- C), 127.4 (s; Ar- C), 127.5 (s; Ar- C), 127.9 (d, $^2J_{\text{CP}} = 6.0\text{ Hz}$; Ar- C), 128.0 (s; Ar- C), 128.1 (s; Ar- C), 128.3 (s; Ar- C), 128.7 (d, $^1J_{\text{CP}} = 10.2$, Ar- C), 129.0 (s; Ar- C), 129.6 (d, $^1J_{\text{CP}} = 13.1\text{ Hz}$; Ar- C), 129.7 (s; Ar- C), 130.0 (s; Ar- C), 130.4 (s; Ar- C), 130.8 (s; Ar- C), 131.5 (d, $^3J_{\text{CP}} = 2.0\text{ Hz}$; Ar- C), 131.8 (d, $^1J_{\text{CP}} = 11.9\text{ Hz}$; Ar- C), 132.0 (d, $^2J_{\text{CP}} = 7.1\text{ Hz}$; Ar- C), 132.2 (s; Ar- C), 132.3 (s; Ar- C), 133.6 (d, $^2J_{\text{CP}} = 6.4\text{ Hz}$; Ar- C), 134.1 (s; Ar- C), 138.1 (s; Ar- C), 142.3 (d, $^2J_{\text{CP}} = 14.1\text{ Hz}$; Ar- C), 162.8 (d, $^3J_{\text{CP}} = 5.0\text{ Hz}$; C_4).

^{31}P NMR (161.9 MHz, CDCl_3): 38.1 (s). ESI-MS: m/z 543.69 $[\text{M}-\text{Cl}]^+$. Anal. Calc. for $\text{C}_{30}\text{H}_{31}\text{ClNPPd}$ (578.42): C, 62.29; H, 5.40; N, 2.42. Found: C, 62.33; H, 5.42; N, 2.39.

7.6.4 General Procedure for the Synthesis of Platinum Dichloride Complexes 3.19 – 3.24 (Chapter 3)

To a solution of the appropriate ligand in DCM (15 ml) was added equimolar amount of $[\text{Pt}(\text{COD})\text{Cl}_2]$ solution in DCM (15 ml). A pale yellow precipitate formed immediately and the reaction was further stirred at room temperature for 15 h, after which the solvent was reduced *in vacuo* and the precipitate filtered. The yellow solid obtained was washed with aliquots of DCM followed by Et_2O and then dried. The desired products were obtained as pale yellow solids in moderate to good yields.¹⁴

Preparation of $[\text{Pt}(\text{C}_{26}\text{H}_{22}\text{NP})\text{Cl}_2]$ (3.19)

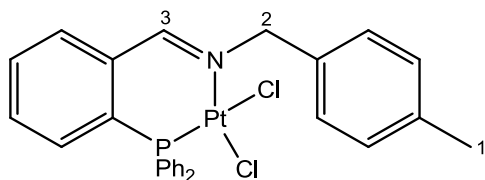


Compound **3.19** was prepared by reacting $[\text{Pt}(\text{COD})\text{Cl}_2]$ (0.22 g, 0.61 mmol) with **3.1** (0.23 g, 0.61 mmol) and the product was obtained as a pale yellow solid (0.27 g, 69%).

M.p. 181 – 183 °C. IR (KBr): 1631 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 5.78 (s, 2H; H_1), 7.06 (dd, 1H, $^3J_{\text{HH}} = 7.1\text{ Hz}$, 10.7 Hz; Ar- H), 7.14 (m, 4H; Ar- H), 7.26 (d, 2H, $^3J_{\text{HH}} = 7.7\text{ Hz}$; Ar- H), 7.38 (dt, 4H, $^3J_{\text{HH}} = 2.8\text{ Hz}$, 7.7 Hz; Ar- H).

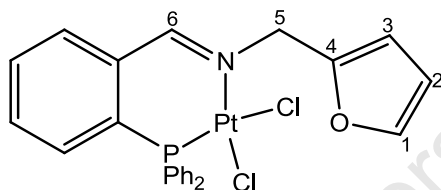
H), 7.54 (dt, 4H, $^3J_{\text{HH}} = 1.9$ Hz, 7.4 Hz; Ar-**H**), 7.84 (td, 3H, $^3J_{\text{HH}} = 7.6$ Hz, $^3J_{\text{HP}} = 23.0$ Hz; Ar-**H**), 8.00 (dd, 1H, $^4J_{\text{HH}} = 4.4$ Hz, 5.1 Hz; Ar-**H**), 9.09 (s, 1H, $^3J_{\text{HPt}} = 108.8$ Hz; **H2**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 4.29 (s, $J_{\text{PPt}} = 3764$ Hz). ESI-MS: m/z 609.43 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{NPt}$ (645.42): C, 48.38; H, 3.44; N, 2.17. Found: C, 48.01; H, 3.57; N, 2.41.

Preparation of $[\text{Pt}(\text{C}_{27}\text{H}_{24}\text{NP})\text{Cl}_2]$ (**3.20**)



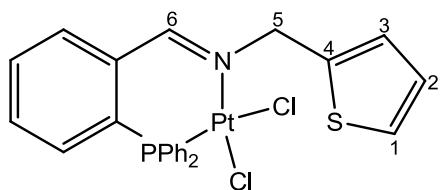
Compound **3.20** was prepared by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (0.40 g, 1.08 mmol) with **3.2** (0.43 g, 1.08 mmol). The product was obtained as a pale yellow solid (0.41 g, 58%). M.p. 275 – 280 °C (decomposes without melting). IR (KBr): 1632 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO- d_6): 2.26 (s, 3H; **H1**), 5.67 (s, 2H; **H2**), 6.88 (m, 1H; Ar-**H**), 7.10 (m, 4H; Ar-**H**), 7.32 (d, 2H, $^3J_{\text{HH}} = 7.7$; Ar-**H**), 7.50 (d, 4H, $^3J_{\text{HH}} = 7.8$ Hz; Ar-**H**), 7.73 (m, 4H; Ar-**H**), 7.82 (td, 2H, $^3J_{\text{HH}} = 7.8$ Hz, $^3J_{\text{HP}} = 21.2$ Hz; Ar-**H**), 7.96 (m, 1H; Ar-**H**), 9.01 (s, 1H, $^3J_{\text{PH}} = 109.1$ Hz; **H3**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 4.44 (s, $J_{\text{PPt}} = 3890$ Hz). ESI-MS: m/z 624.13 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{27}\text{H}_{24}\text{Cl}_2\text{NPt}$ (659.44): C, 49.18; H, 3.67; N, 2.12. Found: C, 48.93; H, 3.51; N, 2.49.

Preparation of $[\text{Pt}(\text{C}_{24}\text{H}_{20}\text{NOP})\text{Cl}_2]$ (**3.21**)



Compound **3.21** was prepared by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (0.41 g, 1.10 mmol) with **3.3** (0.40 g, 1.10 mmol). The product was obtained as a pale yellow solid (0.55 g, 79%). M.p. 198 – 200 °C. IR (KBr): 1633 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO- d_6): 5.78 (2H, s; **H5**), 6.30 (1H, m; **H3**), 6.43 (1H, d, $^4J_{\text{HH}} = 2.5$ Hz; **H2**), 7.03 (1H, dd, $^3J_{\text{HH}} = 8.3$ Hz, 9.5 Hz; **H1**), 7.16 (4H, dd, $^3J_{\text{HH}} = 7.6$ Hz, 12.7 Hz; Ar-**H**), 7.36 (4H, t, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 7.47 (2H, t, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 7.74 (2H, td, $^3J_{\text{HH}} = 7.4$ Hz, $^3J_{\text{HP}} = 19.6$ Hz; Ar-**H**), 7.90 (1H, dd, $^3J_{\text{HH}} = 4.7$ Hz, 6.3 Hz; Ar-**H**), 8.90 (s, 1H, $^3J_{\text{HPt}} = 106.2$ Hz; **H6**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 5.87 (s, $J_{\text{PPt}} = 3760$ Hz). ESI-MS: m/z 500.06 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NOPt}$ (635.38): C, 45.37; H, 3.17; N, 2.20. Found: C, 45.83; H, 3.90; N, 2.17.

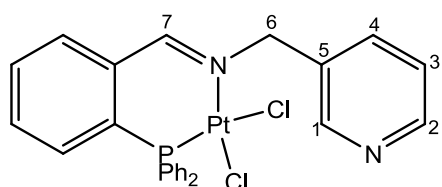
Preparation of $[\text{Pt}(\text{C}_{24}\text{H}_{20}\text{NPS})\text{Cl}_2]$ (**3.22**)



Compound **3.22** was prepared by the reaction of $\text{PtCl}_2(\text{COD})$ (0.25 g, 0.67 mmol) with **3.4** (0.26 g, 0.67 mmol). The product was obtained as a pale yellow solid (0.38 g, 87%). M.p. 201 – 202 °C. IR (KBr): 1630 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO- d_6): 5.89 (2H, s; **H5**), 6.85 (1H, d, $^4J_{\text{HH}} = 3.4$ Hz; **H3**), 6.78 (1H, dd, $^4J_{\text{HH}} = 3.4$ Hz, 5.1 Hz; **H2**), 7.06 (1H, dd,

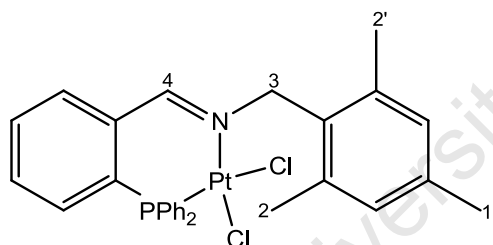
$^3J_{\text{HH}} = 7.2$ Hz, 10.6 Hz; **H1**), 7.15 (4H, dd, $^4J_{\text{HH}} = 1.2$ Hz, 5.1 Hz; Ar-**H**), 7.34 (4H; m, Ar-**H**), 7.48 (2H, m; Ar-**H**), 7.76 (2H, m; Ar-**H**), 7.91 (1H, d, $^4J_{\text{HH}} = 5.2$ Hz; Ar-**H**), 8.98 (1H, s, $^3J_{\text{HPt}} = 100.0$ Hz; **H6**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 4.41 (s, $J_{\text{PPt}} = 3763$ Hz). ESI-MS: m/z 615.37 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{NPtS}$ (651.45): C, 44.25; H, 3.09; N, 2.15; S, 4.92. Found: C, 44.36; H, 3.10; N, 2.71; S, 5.14.

Preparation of $[\text{Pt}(\text{C}_{25}\text{H}_{21}\text{N}_2\text{P})\text{Cl}_2]$ (**3.23**)



Compound **3.23** was prepared by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (0.51 g, 1.36 mmol) with **3.5** (0.52 g, 1.36 mmol). The product was obtained as a pale yellow solid (0.61 g, 70%). M.p. 168 – 170 °C. IR (KBr): 1629 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO- d_6): 5.81 (s, 2H; **H6**), 7.09 (m, 1H; Ar-**H**), 7.39 (m; 4H, Ar-**H**), 7.60 (m, 4H; Ar-**H**), 7.85 (m, 4H; Ar-**H**), 7.92 (m, 2H; 1 x Ar-**H** + 1 x **H3**), 8.10 (dt, 1H, $^3J_{\text{HH}} = 2.0$ Hz, 7.5 Hz; **H4**), 8.53 (dd, 1H, $^4J_{\text{HH}} = 1.6$ Hz, $^3J_{\text{HH}} = 4.4$ Hz; **H2**), 8.63 (m, 1H; **H1**), 9.20 (s, 1H, $^3J_{\text{HPt}} = 107.6$ Hz; **H7**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 4.72 (s, $J_{\text{PPt}} = 3726$ Hz). ESI-MS: m/z 611.03 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{25}\text{H}_{21}\text{Cl}_2\text{N}_2\text{P}$ (646.40): C, 46.45; H, 3.27; N, 4.33. Found: C, 46.13; H, 3.61; N, 4.41.

Preparation of $[\text{Pt}(\text{C}_{29}\text{H}_{28}\text{NP})\text{Cl}_2]$ (**3.24**)



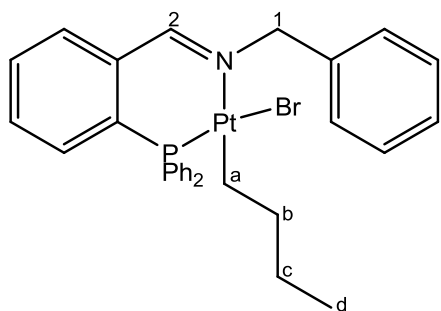
Compound **3.24** was prepared by the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (0.40 g, 1.07 mmol) with **3.6** (0.45 g, 1.11 mmol). The product was obtained as a pale yellow solid (0.50 g, 68%). M.p. 265 – 267 °C (decomposes without melting). IR (KBr): 1631 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, DMSO- d_6): 2.21 (6H, s; **H2+H2'**), 2.35 (3H, s; **H1**), 5.74 (2H, s; **H3**), 7.00 (1H, m; Ar-**H**), 7.21 (3H, d, $^3J_{\text{HH}} = 7.1$; Ar-**H**), 7.36 (2H, m; Ar-**H**), 7.67 (4H, d, $^3J_{\text{HH}} = 8.0$ Hz; Ar-**H**), 7.71 (4H, m; Ar-**H**), 7.79 (2H, td, $^3J_{\text{HH}} = 7.5$ Hz; $^3J_{\text{HPt}} = 20.9$ Hz, Ar-**H**), 9.17 (1H, s, $^3J_{\text{HPt}} = 105.8$ Hz; **H4**). ^{31}P NMR (161.9 MHz, DMSO- d_6): 5.71 (s; $J_{\text{PPt}} = 3684$ Hz). ESI-MS: m/z 652.96 $[\text{M}-\text{Cl}]^+$. Anal. Calc. For $\text{C}_{29}\text{H}_{28}\text{Cl}_2\text{NP}$ (687.50): C, 50.66; H, 4.11; N, 2.04. Found: C, 50.79; H, 4.47; N, 2.00.

7.6.5 General Procedure for the Synthesis of Platinum Alkyl Bromide Complexes **3.25 – 3.26** (Chapter 3)

A suspension of an appropriate $[\text{Pt}(\text{iminophos})\text{Cl}_2]$ complex in dry THF (20 ml) under a nitrogen atmosphere was cooled to - 80 °C. Excess (1.5 – 2.0 molar equivalents) $\text{BrMg}(\text{C}_4\text{H}_8)\text{MgBr}$, was added dropwise and the resulting reaction mixture was allowed to warm to room temperature and stirred for 18 h. During this time an orange solution was observed. After stirring for 18 h, the solution was cooled to 0 °C and a saturated ammonium

chloride solution (2 ml) and de-ionized water (5 ml) were added to hydrolyze the excess Grignard reagent. DCM (10 ml) was added to the mixture and the organic layer was then collected and dried over anhydrous MgSO_4 . After filtration and removal of excess solvent an orange oily residue was obtained. This residue was dissolved in DCM (1–2 ml) and upon addition of hexane the products precipitated out as yellow-orange solids. The solids were dried under vacuum and characterized.

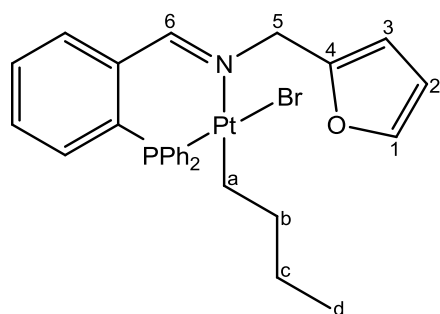
Preparation of $[\text{Pt}(\text{C}_{26}\text{H}_{22}\text{NP})(\text{C}_4\text{H}_9)\text{Br}]$ (3.25)



Complex **3.25** was prepared by the reaction of complex **3.19** (0.20 g, 0.31 mmol) with excess $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$. After workup and recrystallization the product was obtained as a bright yellow crystalline solid (0.17 g, 87%). M.p. 204 – 203 °C (with decomposition). IR (CH_2Cl_2): 1628 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.58, (t, 3H, $^3J_{\text{HH}} = 7.3\text{ Hz}$; **Hd**), 0.95 (dd, 2H,

$^3J_{\text{HH}} = 7.2\text{ Hz}$, 14.6 Hz; **Ha**), 1.22 (td, 2H, $^3J_{\text{HH}} = 7.8\text{ Hz}$, 15.7 Hz; **Hb**), 1.37 (2H, m, **Hc**), 5.79 (br s, 2H; **H1**), 7.20 – 7.25 (m, 8H, Ar-**H**), 7.28 – 7.32 (m, 2H; Ar-**H**), 7.33 – 7.35 (m, 3H; Ar-**H**), 7.45 (dt, 2H, $^3J_{\text{HH}} = 1.7\text{ Hz}$, 7.2; Ar-**H**), 7.51 (dd, 2H, $^3J_{\text{HH}} = 5.5\text{ Hz}$, 7.1 Hz; Ar-**H**), 7.59 (t, 1H, $^3J_{\text{HH}} = 7.4\text{ Hz}$; Ar-**H**), 8.39 (s, 1H, $J_{\text{HPt}} = 34.8\text{ Hz}$, **H2**). ^{13}C NMR (100.6 MHz, CDCl_3): 7.4 (d, $^2J_{\text{CP}} = 3.5\text{ Hz}$, **Ca**), 13.8 (s; **Cd**), 26.3 (s; **Cb**), 35.1 (s; **Cc**), 69.0 (s; **C1**), 127.0 (s; Ar-**C**), 127.6 (s; Ar-**C**), 127.8 (s; Ar-**C**), 128.3 (d, $^1J_{\text{CP}} = 11.3\text{ Hz}$; Ar-**C**), 128.5 (s; Ar-**C**), 128.6 (s; Ar-**C**), 129.9 (s; Ar-**C**), 130.0 (s; Ar-**C**), 130.9 (d, $^3J_{\text{CP}} = 2.5\text{ Hz}$; Ar-**C**), 131.2 (d, $^3J_{\text{CP}} = 4.2\text{ Hz}$; Ar-**C**), 132.0 (d, $^2J_{\text{CP}} = 7.7\text{ Hz}$; Ar-**C**), 132.7 (d, $^3J_{\text{CP}} = 3.3\text{ Hz}$; Ar-**C**), 134.0 (d, $^1J_{\text{CP}} = 11.6\text{ Hz}$; Ar-**C**), 135.4 (d, $^2J_{\text{CP}} = 12.9\text{ Hz}$; Ar-**C**), 161.4 (d, $^3J_{\text{CP}} = 4.7\text{ Hz}$; **C2**). ^{31}P NMR (161 MHz, CDCl_3): 16.1 (s, $J_{\text{PPt}} = 5000\text{ Hz}$). ESI-MS; m/z 632.56 $[\text{M-Br}]^+$, 575.48 $[\text{M-C}_4\text{H}_9\text{Br}]^+$. Anal. Calc. For $\text{C}_{30}\text{H}_{31}\text{BrNPt}$ (711.53): C, 50.64; H, 4.39; N, 1.97. Found: C, 50.71; H, 4.41; N, 1.96.

Preparation of $[\text{Pt}(\text{C}_{24}\text{H}_{20}\text{NOP})(\text{C}_4\text{H}_9)\text{Br}]$ (3.26)



Complex **3.26** was prepared by the reaction of complex **3.21** (0.30 g, 0.47 mmol) with excess $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$. After workup and recrystallization the product was obtained as an orange crystalline solid (0.26 g, 78%). M.p. 193 – 194 °C (melts with decomposition). IR (CH_2Cl_2): 1630 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.44, (t, 3H, $^3J_{\text{HH}} = 7.3\text{ Hz}$; **Hd**), 0.80 (dd, 2H,

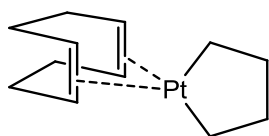
$^3J_{\text{HH}} = 7.6\text{ Hz}$, 14.5 Hz; **Ha**), 1.07, (dd, 2H, $^3J_{\text{HH}} = 7.7\text{ Hz}$, 15.1 Hz; **Hb**), 1.33 (m, 2H; **Hc**),

5.67 (br s, 2H, **H5**), 6.27 (dd, 1H, $^3J_{\text{HH}} = 1.9 \text{ Hz}$, 3.2 Hz; **H3**), 6.65 (dd, 1H, $^3J_{\text{HH}} = 0.4 \text{ Hz}$, 3.2 Hz; **H2**), 6.98 (dd, 1H, $^3J_{\text{HH}} = 0.8 \text{ Hz}$, 1.8 Hz; **H1**), 7.17 - 7.23 (m, 8H; Ar-**H**), 7.34 (t, 2H, $^3J_{\text{HH}} = \text{Ar-**H**}$), 7.41 (d, 3H, $^3J_{\text{HH}} = 6.7 \text{ Hz}$; Ar-**H**), 7.46 (d, 1H, $^3J_{\text{HH}} = 7.2 \text{ Hz}$; Ar-**H**), 8.27 (s, 1H, $^3J_{\text{HPt}} = 33.1 \text{ Hz}$, **H6**). ^{13}C NMR (100.6 MHz, CDCl_3): 7.6 (d, $^2J_{\text{CP}} = 3.7 \text{ Hz}$, **Ca**), 13.7 (s; **Cd**), 29.7 (s; **Cb**), 34.9 (s; **Cc**), 61.3 (s; **C5**), 110.6 (s; **C3**), 111.7 (s; **C2**), 128.4 (d, $^1J_{\text{CP}} = 11.4 \text{ Hz}$; Ar-**C**), 130.9 (s; Ar-**C**), 131.2 (s; Ar-**C**), 132.1 (d, $J_{\text{CP}} = 7.7 \text{ Hz}$; Ar-**C**), 132.5 (d, $J_{\text{CP}} = 3.1 \text{ Hz}$; Ar-**C**), 134.2 (d, $^1J_{\text{CP}} = 13.3 \text{ Hz}$; Ar-**C**), 135.5 (d, $^2J_{\text{C-P}} = 8.7 \text{ Hz}$; Ar-**C**), 142.8 (s; **C1**), 149.9 (s; **C4**), 162.2 (d, $^3J_{\text{CP}} = 4.6 \text{ Hz}$; **C6**). ^{31}P NMR (121 MHz, CDCl_3): 16.2 (s, $J_{\text{Pt-P}} = 5018 \text{ Hz}$). ESI-MS; m/z 622.32 $[\text{M-Br}]^+$, 565.19 $[\text{M-C}_4\text{H}_9\text{Br}]^+$. Anal. Calc. For $\text{C}_{28}\text{H}_{29}\text{BrNOPt}$ (701.49): C, 47.94; H, 4.17; N, 2.00. Found: C, 47.99; H, 4.20; N, 1.98.

7.6.6 General Procedure for the Synthesis of Platinacycloalkanes 5.1 – 5.12 (Chapter 5)

The metallacycloalkanes were prepared from the reaction of $[\text{Pt}(\text{COD})\text{Cl}_2]$ with appropriate di-Grignard reagents to give $[\text{Pt}(\text{COD})(\text{CH}_2)_n]$, where $n = 4$ or 6. After work-up, the 1,5-cyclooctadienyl ligand was displaced by the P^N ligands previously described.

Preparation of $[\text{Pt}(\text{COD})(\text{C}_4\text{H}_8)]^{15}$



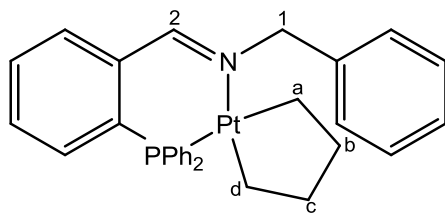
A suspension of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (2.0 g, 5.34 mmol) in dry THF (20 ml) under a nitrogen atmosphere was cooled to -80°C . Excess (1.5 – 2.0 molar equivalents) $\text{BrMg}(\text{C}_4\text{H}_8)\text{MgBr}$ was added dropwise and the resulting reaction mixture allowed to stir until dissolution of $[\text{Pt}(\text{COD})\text{Cl}_2]$ was observed and a clear solution was obtained. The solution was then cooled to 0°C and a saturated ammonium chloride solution (2 ml) and de-ionized water (5 ml) were added to hydrolyze the excess Grignard reagent. DCM (10 ml) was added to the mixture and the organic layer was collected and dried over anhydrous MgSO_4 . After filtration and removal of excess solvent a pale yellow solid was obtained and this solid was dried under vacuum then characterized. The product was obtained as a pale yellow solid (1.81 g, 94%). ^1H NMR (400 MHz, CDCl_3): 1.28 – 1.63 (m, 4H; Pt-**CH**₂-), 1.84 – 2.26 (m, 4H; Pt-**CH**₂-**CH**₂-), 2.27 (m, 8H; -**CH**₂- (COD)), 4.84 (s, 4H, $J_{\text{H-Pt}} = 40.4 \text{ Hz}$, =**CH**- (COD)).

7.6.6.1 Preparation of Platinacyclopentanes (5.1 – 5.12) (Chapter 5)

To a solution of $[\text{Pt}(\text{COD})(\text{C}_4\text{H}_8)]$ (0.29 g, 0.75 mmol) in THF (20 ml) was added a solution of an equimolar amount of the appropriate ligand in THF. The resulting orange solution was stirred at room temperature overnight. Removal of solvent gave an orange oily residue which was then dissolved in minimal DCM (1 – 2 ml). Addition of hexane to this solution resulted in precipitation of an orange solid. The supernatant was decanted and the solid was

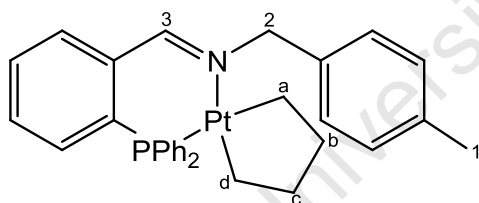
extensively washed with hexane then dried under vacuum. The products were obtained as orange solids in good yields.¹⁵

Preparation of [Pt(C₂₆H₂₂NP)(C₄H₈)] (5.1)



Complex **5.1** was prepared by the reaction of [Pt(COD)(C₄H₈)] (0.18 g, 0.50 mmol) and **3.1** (0.19 g, 0.50 mmol), and the product was obtained as an orange solid (0.26 g, 83%). M.p. 164 – 167 °C (decomp). IR (KBr): 1631 cm⁻¹ (ν_{C=N}, imine). ¹H NMR (400 MHz, CDCl₃): 0.79 – 0.84 (m, 4H; **Ha+Hd**), 1.76 – 1.79 (m, 4H; **Hb+Hc**), 5.50 (s, 2H, ³J_{H-Pt} = 16.4 Hz; **H1**), 6.88 (d, 2H, ³J_{HH} = 7.8 Hz; Ar-**H**), 7.00 (d, 2H, ³J_{HH} = 7.1 Hz; Ar-**H**), 7.11 – 7.35 (m, 15H; Ar-**H**), 8.18 (s, 1H, ³J_{HPt} = 35.1 Hz; **H2**). ¹³C NMR (100.6 MHz, CDCl₃): 15.8 (d, ²J_{CP} = 2.9 Hz; **Cd**), 28.0 (s; **Cc**), 29.7 (s; **Cb**), 33.9 (d; ²J_{CP} = 5.7 Hz; **Ca**), 68.8 (s; **C1**), 127.3 (s; Ar-**C**), 128.1 (d, ¹J_{CP} = 9.0 Hz; Ar-**C**), 128.4 (s; Ar-**C**), 128.7 (s; Ar-**C**), 129.4 (s; Ar-**C**), 129.8 (s; Ar-**C**), 130.3 (s; Ar-**C**), 131.5 (s; Ar-**C**), 131.8 (s; Ar-**C**), 131.9 (d, ³J_{CP} = 4.9 Hz; Ar-**C**), 133.6 (s; Ar-**C**), 133.9 (d, ¹J_{CP} = 12.6 Hz; Ar-**C**), 135.3 (d, ¹J_{CP} = 8.3 Hz; Ar-**C**), 137.7 (s; Ar-**C**), 138.9 (d, ²J_{CP} = 16.7 Hz; Ar-**C**), 162.0 (d, ³J_{CP} = 5.5 Hz; **C2**). ³¹P NMR (161.9 MHz, CDCl₃): 25.0 (s, J_{Pt} = 1894 Hz). ESI-MS: *m/z* 631.18 [M+H]⁺, 575.12 [M-C₄H₈]⁺. Anal. Calc. For C₃₀H₃₀NPt (630.62): C, 57.14; H, 4.80; N, 2.22. Found: C, 56.91; H, 4.83; N, 2.12.

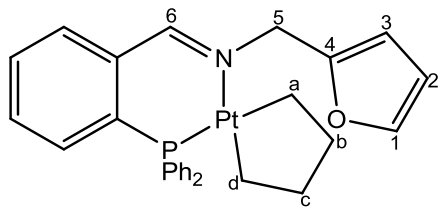
Preparation of [Pt(C₂₇H₂₄NP)(C₄H₈)] (5.2)



Complex **5.2** was prepared by the reaction of [Pt(COD)(C₄H₈)] (0.18 g, 0.50 mmol) and **3.2** (0.20 g, 0.50 mmol), and the product was obtained as an orange solid (0.24 g, 76%). M.p. 142 – 143 °C (decomp). IR (KBr): 1634 cm⁻¹ (ν_{C=N}, imine). ¹H NMR (400 MHz, CDCl₃): 0.87 – 1.01 (m, 4H; **Ha+Hd**), 1.74 – 1.79 (m, 4H; **Hb+Hc**), 2.31 (s, 3H; **H1**), 5.25 (s, 2H, ³J_{HPt} = 15.8 Hz; **H2**), 6.99 (d, 2H, ³J_{HH} = 7.1 Hz; Ar-**H**), 7.05 (d, 2H, ³J_{HH} = 6.8 Hz; Ar-**H**), 7.17 – 7.34 (m, 14H; Ar-**H**), 8.17 (s, 1H, ³J_{HPt} = 34.8 Hz; **H3**). ¹³C NMR (100.6 MHz, CDCl₃): 16.1 (d, ²J_{CP} = 3.1 Hz; **Cd**), 22.1 (s; **C1**), 28.0 (s; **Cc**), 30.3 (s; **Cd**), 33.1 (d; ²J_{CP} = 6.0 Hz; **Ca**), 67.9 (s; **C2**), 125.5 (s; Ar-**C**), 127.2 (s; Ar-**C**), 128.0 (d, ¹J_{CP} = 8.8 Hz; Ar-**C**), 128.5 (s; Ar-**C**), 128.9 (d, ¹J_{CP} = 9.3 Hz; Ar-**C**), 129.4 (s; Ar-**C**), 129.6 (s; Ar-**C**), 129.7 (d, ³J_{CP} = 1.7 Hz; Ar-**C**), 130.3 (d, ³J_{CP} = 1.2 Hz; Ar-**C**), 131.5 (s; Ar-**C**), 131.8 (s; Ar-**C**), 131.9 (d, ²J_{CP} = 5.1 Hz; Ar-**C**), 132.2 (d, ³J_{CP} = 2.6 Hz; Ar-**C**), 133.6 (d, ²J_{CP} = 5.0 Hz; Ar-**C**), 134.1 (d, ²J_{CP} = 7.9 Hz; Ar-**C**), 135.0 (d, ¹J_{CP} = 11.9 Hz; Ar-**C**), 138.1 (s; Ar-**C**), 140.1 (d, ²J_{CP} = 16.9 Hz; Ar-**C**), 162.2 (d, ³J_{CP} = 5.1 Hz; **C3**). ³¹P NMR (161.9 MHz, CDCl₃): 26.2 (s, J_{Pt} = 1920 Hz).

Hz). ESI-MS: m/z 645.20 $[M+H]^+$, 589.44 $[M-C_4H_8]^+$. Anal. Calc. For $C_{31}H_{32}NPt$ (644.64): C, 57.76; H, 5.00; N, 2.17. Found: C, 57.79; H, 5.03; N, 2.15.

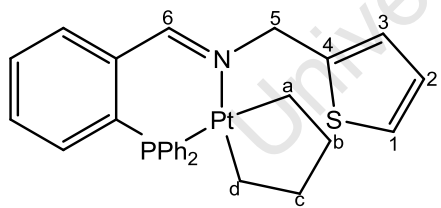
Preparation of $[Pt(C_{24}H_{20}NOP)(C_4H_8)]$ (5.3)



Complex **5.3** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (0.14 g, 0.40 mmol) and **3.3** (0.15 g, 0.40 mmol). The product was obtained as an orange solid. (0.22 g, 87%). M.p. 146 – 148 °C (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). 1H NMR (400 MHz,

$CDCl_3$): 0.86 – 0.88 (m, 4H; **Ha+Hd**), 1.45 – 1.48 (m, 4H; **Hb+Hc**), 5.49 (s, 2H, $^3J_{H-Pt} = 15.1$ Hz; **H5**), 6.22 (dd, 1H, $^3J_{HH} = 1.9$ Hz, 3.2 Hz; **H3**), 6.27 (d, 1H, $^3J_{HH} = 3.2$ Hz; **H2**), 7.08 (dd, 1H, $^3J_{HH} = 0.8$ Hz, 1.8 Hz; **H1**), 7.24 – 7.41 (m, 14H; Ar-**H**), 8.15 (s, 1H, $J_{H-Pt} = 35.0$ Hz; **H6**). ^{13}C NMR (100.6 MHz, $CDCl_3$): 15.8 (d, $^2J_{CP} = 2.8$ Hz; **Cd**), 26.3 (s; **Cc**), 28.0 (s; **Cb**), 33.9 (d, $^2J_{CP} = 5.8$ Hz; **Ca**), 60.9 (s; **C5**), 110.2 (s; **C3**), 111.7 (s; **C2**), 128.1 (d, $^1J_{C-P} = 9.7$ Hz; Ar-**C**), 128.3 (d, $^1J_{CP} = 11.0$ Hz; Ar-**C**), 128.6 (d, $^2J_{CP} = 5.4$ Hz; Ar-**C**), 129.7 (d, $^3J_{CP} = 1.8$ Hz; Ar-**C**), 130.2 (d, $^3J_{CP} = 1.4$ Hz; Ar-**C**), 131.4 (s; Ar-**C**), 131.7 (s; Ar-**C**), 131.9 (d, $^3J_{CP} = 4.9$ Hz; Ar-**C**), 132.0 (s; Ar-**C**), 132.3 (d, $^3J_{CP} = 2.7$ Hz; Ar-**C**), 133.9 (d, $^1J_{CP} = 12.6$ Hz; Ar-**C**), 134.1 (s; Ar-**C**), 135.2 (d, $^2J_{CP} = 8.3$ Hz; Ar-**C**), 138.7 (d, $^2J_{CP} = 16.4$ Hz; Ar-**C**), 142.7 (s; **C1**), 150.4 (s; **C4**), 161.6 (d, $^3J_{CP} = 5.2$ Hz; **C6**). ^{31}P NMR (121 MHz, $CDCl_3$): 25.3 (s, $J_{PPt} = 1904$ Hz). ESI-MS: m/z 621.17 $[M+H]^+$, 564.50 $[M-C_4H_8]^+$. Anal. Calc. For $C_{28}H_{28}NOPPt$ (620.58): C, 54.19; H, 4.55; N, 2.26. Found: C, 54.41; H, 4.82; N, 2.36.

Preparation of $[Pt(C_{24}H_{20}NPS)(C_4H_8)]$ (5.4)

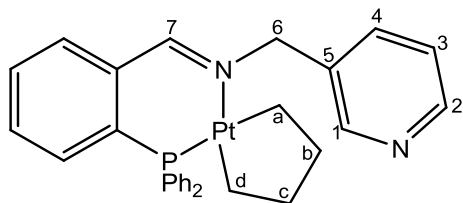


Complex **5.4** was prepared by the reaction of $[Pt(COD)(C_4H_8)]$ (0.13 g, 0.36 mmol) and **3.4** (0.14 g, 0.36 mmol). The product was obtained as an orange solid (0.19 g, 81%). M.p. 127 – 129 °C (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$, imine). 1H NMR (400 MHz,

$CDCl_3$): 0.80 – 0.83 (m, 4H; **Ha+Hd**), 1.69 – 1.72 (m, 4H; **Hb+Hc**), 5.70 (s, 2H, $^3J_{HPt} = 16.4$ Hz; **H5**), 6.38 (dd, 1H, $^3J_{HH} = 1.8$ Hz, 3.0 Hz; **H3**), 6.45 (d, 1H, $^3J_{HH} = 3.2$ Hz; **H2**), 7.14 (dd, 1H, $^3J_{HH} = 1.0$ Hz, 1.8 Hz; **H1**), 7.28 – 7.47 (m, 14H; Ar-**H**), 8.21 (s, 1H, $^3J_{HPt} = 36.4$ Hz; **H6**). ^{13}C NMR (100.6 MHz, $CDCl_3$): 15.9 (d, $^2J_{CP} = 3.0$ Hz; **Cd**), 25.9 (s; **Cc**), 27.8 (s; **Cb**), 36.1 (d, $^2J_{CP} = 5.9$ Hz; **Ca**), 61.4 (s; **C5**), 123.5 (s; **C3**), 125.0 (s; **C2**), 128.0 (d, $^1J_{CP} = 10.1$ Hz; Ar-**C**), 128.5 (d, $^1J_{CP} = 11.4$ Hz; Ar-**C**), 128.9 (d, $^2J_{CP} = 4.8$ Hz; Ar-**C**), 129.5 (d, $^3J_{CP} = 2.0$ Hz; Ar-**C**), 130.9 (d, $^3J_{CP} = 1.8$ Hz; Ar-**C**), 131.5 (s; Ar-**C**), 131.6 (s; Ar-**C**), 131.8 (d, $^3J_{CP} = 5.1$ Hz; Ar-**C**), 132.1 (s; Ar-**C**), 132.5 (d, $^3J_{CP} = 2.9$ Hz; Ar-**C**), 134.2 (d, $^1J_{CP} = 11.6$ Hz; Ar-**C**), 134.4 (s; Ar-**C**), 135.5 (d, $^2J_{CP} = 8.8$ Hz; Ar-**C**), 137.9 (d, $^2J_{CP} = 16.0$ Hz; Ar-**C**), 143.3 (s; **C1**), 151.6

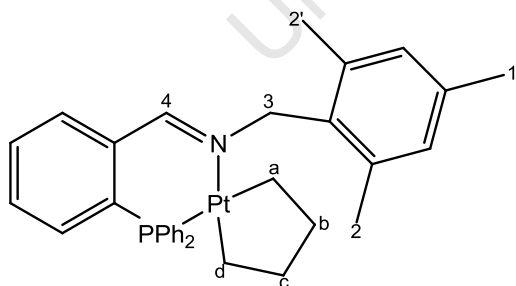
(s; **C4**), 162.4 (d, $^3J_{CP} = 4.3$ Hz; **C6**). ^{31}P NMR (161.9 MHz, CDCl_3): 25.7 (s, $J_{\text{PPt}} = 2066$ Hz). ESI-MS: m/z 637.13 $[\text{M}+\text{H}]^+$, 581.08 $[\text{M}-\text{C}_4\text{H}_8]^+$. Anal. Calc. For $\text{C}_{28}\text{H}_{28}\text{NPSPt}$ (636.65): C, 52.82; H, 4.43; N, 2.20; S, 5.04. Found: C, 53.01; H, 4.31; N, 2.17; S, 5.00.

Preparation of $[\text{Pt}(\text{C}_{25}\text{H}_{21}\text{N}_2\text{P})(\text{C}_4\text{H}_8)]$ (**5.5**)



Complex **5.5** was prepared by reacting $[\text{Pt}(\text{COD})(\text{C}_4\text{H}_8)]$ (0.13 g, 0.36 mmol) and **3.5** (0.14 g, 0.36 mmol). The product was obtained as an orange solid. (0.17 g, 76%). M.p. 139 - 142 °C (decomp). IR (KBr): 1630 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.89 – 0.93 (m, 4H; **Ha+Hd**), 1.41 - 1.46 (m, 4H; **Hb+Hc**), 5.69 (s, 2H, $^3J_{\text{H-Pt}} = 16.0$ Hz; **H6**), 7.12 (1H, d, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 7.18 – 7.21 (5H, m; Ar-**H**), 7.39 – 7.41 (4H, m; Ar-**H**), 7.51 – 7.53 (2H, m; Ar-**H**), 7.60 – 7.62 (1H, m; Ar-**H**), 7.65 – 7.66 (1H, m; **H3**), 8.03 (1H, td, $^3J_{\text{HH}} = 2.0$ Hz; 7.4 Hz, Ar-**H**), 8.30 (s, 1H; **H4**) 8.35 (1H, d, $^4J_{\text{HH}} = 2.1$, Hz; **H2**), 8.43 (1H, s, $^3J_{\text{HPt}} = 35.7$ Hz; **H7**), 8.56 (1H, dd, $^3J_{\text{HH}} = 1.4$ Hz, 5.0 Hz; **H1**). ^{13}C NMR (100.6 MHz, CDCl_3): 16.0 (d, $^2J_{\text{CP}} = 2.8$ Hz; **Cd**), 26.3 (s; **Cc**), 28.5 (s; **Cb**), 34.1 (d, $^2J_{\text{CP}} = 5.7$ Hz; **Ca**), 64.4 (s; **C6**), 125.9 (s; **C3**), 126.5 (s; **C**), 129.1 (d, $^1J_{\text{CP}} = 12.3$ Hz; Ar-**C**), 130.4 (d, $^3J_{\text{CP}} = 1.6$ Hz; Ar-**C**), 131.6 (d, $^3J_{\text{CP}} = 1.6$ Hz; Ar-**C**), 132.0 (d, $^2J_{\text{CP}} = 6.7$ Hz; Ar-**C**), 132.8 (s; **C5**), 133.1 (d, $^1J_{\text{CP}} = 12.4$ Hz; Ar-**C**), 134.0 (s; Ar-**C**), 134.1 (s; Ar-**C**), 134.3 (s; **C4**), 136.9 (d, $^2J_{\text{CP}} = 17.4$ Hz; Ar-**C**), 137.2 (s; Ar-**C**), 139.4 (s; Ar-**C**), 149.7 (s; **C2**), 151.0 (s; **C1**), 162.1 (d, $^3J_{\text{CP}} = 5.3$ Hz; **C7**). ^{31}P NMR (161.9 MHz, CDCl_3): 25.7 (s, $J_{\text{PPt}} = 1886$). ESI-MS: m/z 632.27 $[\text{M}+\text{H}]^+$, 575.36 $[\text{M}-\text{C}_4\text{H}_8]$. Anal. Calc. for $\text{C}_{29}\text{H}_{29}\text{N}_2\text{PPd}$ (631.61): C, 55.15; H, 4.63; N, 4.44. Found: C, 55.20; H, 4.77; N, 4.39.

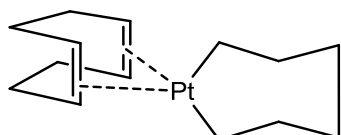
Preparation of $[\text{Pt}(\text{C}_{29}\text{H}_{28}\text{NP})(\text{C}_4\text{H}_8)]$ (**5.6**)



Complex **5.6** was prepared using $[\text{Pt}(\text{COD})(\text{C}_4\text{H}_8)]$ (0.17 g, 0.48 mmol) and **3.6** (0.17 g, 0.40 mmol). The product was obtained as an orange solid (0.27 g, 85%). M.p. 172 – 175 °C (decomp). IR (KBr): 1635 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.81 – 0.92 (m, 4H, **Ha+Hd**), 1.76 – 1.80 (m, 4H, **Hb+Hc**), 2.21 (s, 6H; **H2+H2'**), 2.40 (s, 3H; **H1**), 5.27 (2H, s, $^3J_{\text{H-Pt}} = 17.0$ Hz; **H3**), 7.01 (d, 2H, $^3J_{\text{HH}} = 7.6$ Hz; Ar-**H**), 7.10 (d, 2H, $^3J_{\text{HH}} = 7.0$ Hz; Ar-**H**), 7.21 – 7.30 (m, 12H, Ar-**H**), 8.20 (s, 1H, $^3J_{\text{H-Pt}} = 35.4$ Hz; **H4**). ^{13}C NMR (126 MHz, CDCl_3): 15.8 (d, $^2J_{\text{CP}} = 3.0$ Hz; **Cd**), 22.1 (s; **C2+C2'**), 24.0 (s; **C1**), 27.6 (s; **Cc**), 29.9 (s; **Cb**), 32.7 (d; $^2J_{\text{CP}} = 5.9$ Hz; **Ca**), 66.7 (s; **C3**), 126.3 (s; Ar-**C**), 128.0 (s; Ar-**C**), 128.8 (d, $^1J_{\text{CP}} = 9.0$ Hz; Ar-**C**), 129.0 (s; Ar-**C**), 129.5 (d, $^1J_{\text{CP}} = 9.1$ Hz; Ar-**C**), 129.6 (s; Ar-**C**), 129.9 (s;

Ar-C), 130.0 (d, $^3J_{CP} = 1.4$ Hz; Ar-C), 130.3 (d, $^3J_{CP} = 1.5$ Hz; Ar-C), 131.7 (s; Ar-C), 131.8 (s; Ar-C), 132.0 (d, $^2J_{CP} = 5.3$ Hz; Ar-C), 132.9 (d, $^3J_{CP} = 2.4$ Hz; Ar-C), 133.8 (d, $^2J_{CP} = 5.4$ Hz; Ar-C), 134.4 (d, $^2J_{CP} = 9.3$ Hz; Ar-C), 134.8 (d, $^1J_{CP} = 12.1$ Hz; Ar-C), 137.9 (s; Ar-C), 139.4 (s, Ar-C), 142.2 (d, $^2J_{CP} = 16.5$ Hz; Ar-C), 161.9 (d, $^3J_{CP} = 5.3$ Hz; C4). ^{31}P NMR (161.9 MHz, CDCl_3): 26.7 (s, $J_{\text{PPt}} = 1843$ Hz). ESI-MS: m/z 672.23 $[\text{M}+\text{H}]^+$, 617.16 $[\text{M}-\text{C}_4\text{H}_8]^+$. Anal. Calc. For $\text{C}_{31}\text{H}_{32}\text{NPt}$ (672.70): C, 58.92; H, 5.39; N, 2.08. Found: C, 58.97; H, 5.00; N, 2.01.

Preparation of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]^{15\text{a}}$

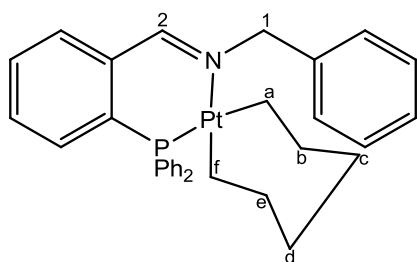


A suspension of $[\text{Pt}(\text{COD})\text{Cl}_2]$ (3.0 g, 8.0 mmol) in dry THF (20 ml) under a nitrogen atmosphere was cooled to -80 °C. Excess (1.5 – 2.0 molar equivalents) $\text{BrMg}(\text{C}_6\text{H}_{12})\text{MgBr}$ was added dropwise and the resulting reaction mixture was allowed to stir until dissolution of $[\text{Pt}(\text{COD})\text{Cl}_2]$ was observed and the solution started turning brown. The solution was then cooled to 0 °C and a saturated ammonium chloride solution (2 ml) and deionized water (5 ml) were added to hydrolyze the excess Grignard reagent. DCM (10 ml) was added to the mixture and the organic layer was collected and dried over anhydrous MgSO_4 . After filtration and removal of excess solvent a brown oil was obtained and dried under vacuum. The product was obtained as a brown oil (1.74 g, 56%). ^1H NMR (400 MHz, CDCl_3): 1.30 – 1.60 (m, 4H; Pt- CH_2 -), 1.87 – 2.22 (m, 8H; Pt- CH_2 - CH_2 -), 2.27 (m, 8H; - CH_2 - (COD)), 4.87 (s, 4H, $J_{\text{HPt}} = 40.6$ Hz, = CH - (COD)).

7.6.6.2 Preparation of Platinacycloheptanes 5.7 – 5.12 (Chapter 5)

To a solution of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) in THF (20 ml) was added a solution of an equimolar amount of the appropriate ligand in THF. The resulting orange solution was stirred at room temperature overnight. The solution was concentrated and hexane was added. An orange oily residue separated from the solution and the supernatant was decanted. The oily residue was washed with hexane then dried under vacuum. The products were obtained as sticky orange oils in good yields.^{18a}

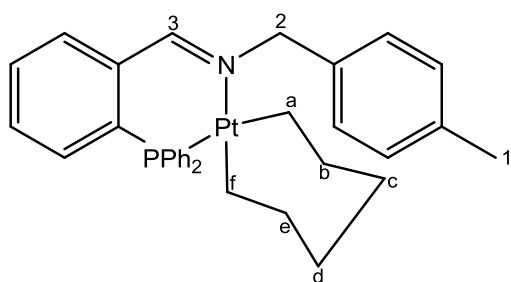
Preparation of $[\text{Pt}(\text{C}_{26}\text{H}_{22}\text{NP})(\text{C}_6\text{H}_{12})]$ (5.7)



Complex **5.7** was prepared by the reaction of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) with ligand **3.1** (0.24 g, 0.64 mmol). The product was obtained as a brown oil. (0.32 g, 73%). IR (KBr): 1635 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.74 – 0.76 (m, 4H; $\text{Ha}+\text{Hf}$), 1.42 – 1.45 (8H, m; ($\text{Hb}-\text{He}$)), 5.38 (2H, s, $^3J_{\text{HPt}} = 16.8$ Hz; H1), 7.08 (dd, 1H, $^3J_{\text{HH}} = 1.2$ Hz, 8.3 Hz; Ar- H), 7.11 (d, 1H, $^4J_{\text{HH}} = 1.8$ Hz; Ar- H), 7.13 (dd, 2H, $^5J_{\text{HH}}$

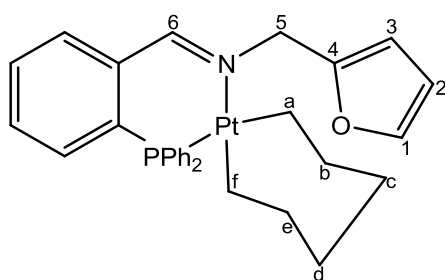
= 1.6 Hz, $^3J_{\text{HH}} = 7.8$ Hz; Ar-**H**), 7.21 (m, 1H; Ar-**H**), 7.39 – 7.51 (m, 14H; Ar-**H**), 8.33 (s, 1H, $^3J_{\text{HPt}} = 34.7$ Hz; **H2**). ^{13}C NMR (75.5 MHz, CDCl_3): 14.9 (d, $^2J_{\text{CP}} = 3.0$ Hz; **Cf**), 26.2 (s; **Ce**), 28.1 (s; **Cb**), 32.3 (s; **Cd**), 32.4 (s; **Cc**), 34.2 (d; $^2J_{\text{CP}} = 5.0$ Hz; **Ca**), 65.4 (s; **C1**), 125.9 (s; Ar-**C**), 127.6 (d, $^1J_{\text{CP}} = 9.3$ Hz; Ar-**C**), 127.9 (s; Ar-**C**), 128.4 (s; Ar-**C**), 128.6 (s; Ar-**C**), 129.0 (s; Ar-**C**), 129.4 (s; Ar-**C**), 129.9 (s; Ar-**C**), 130.7 (s; Ar-**C**), 131.3 (s; Ar-**C**), 132.0 (d, $^2J_{\text{CP}} = 5.1$ Hz; Ar-**C**), 133.6 (s; Ar-**C**), 134.6 (d, $^1J_{\text{CP}} = 12.2$ Hz; Ar-**C**), 135.5 (d, $^1J_{\text{CP}} = 9.1$ Hz; Ar-**C**), 137.9 (s; Ar-**C**), 138.6 (d, $^2J_{\text{CP}} = 17.0$ Hz; Ar-**C**), 162.7 (d, $^3J_{\text{CP}} = 5.5$ Hz; **C2**). ^{31}P NMR (121 MHz, CDCl_3): 26.8 (s, $J_{\text{Pt}} = 1802$ Hz). ESI-MS: m/z 659.34 $[\text{M}+\text{H}]^+$, 575.20 $[\text{M}-\text{C}_4\text{H}_8]^+$.

Preparation of $[\text{Pt}(\text{C}_{27}\text{H}_{24}\text{NP})(\text{C}_6\text{H}_{12})]$ (**5.8**)



Complex **5.8** was prepared by the reaction of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) with ligand **3.2**. The product was obtained as a brown oil (0.29 g, 68%). IR (KBr): 1635 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.76 – 0.89 (m, 4H; **Ha+Hf**), 0.95 – 1.37 (m, 8H; **Hb-He**), 2.30 (s, 3H; **H1**), 5.45 (s, 2H, $^3J_{\text{HPt}} = 16.0$ Hz; **H2**), 7.01 (dd, 1H, $^3J_{\text{HH}} = 1.2$ Hz, 8.3 Hz; Ar-**H**), 7.11 (d, 1H; $^4J_{\text{HH}} = 1.7$ Hz, Ar-**H**), 7.14 (dd, 2H, $^3J_{\text{HH}} = 1.4$ Hz, 7.2 Hz; Ar-**H**), 7.18 (m, 2H; Ar-**H**), 7.30 – 7.44 (m, 12H; Ar-**H**), 8.13 (s, 1H, $^3J_{\text{PtH}} = 33.0$ Hz; **H3**). ^{13}C NMR (75.5 MHz, CDCl_3): 17.3 (d, $^2J_{\text{CP}} = 3.1$ Hz; **Cf**), 21.7 (s; **C1**), 25.3 (s; **Ce**), 27.2 (s; **Cb**), 31.9 (s; **Cd**), 32.0 (s; **Cc**), 34.7 (d, $^2J_{\text{CP}} = 6.0$ Hz; **Ca**), 64.9 (s; **C2**), 125.5 (s; Ar-**C**), 127.2 (s; Ar-**C**), 128.0 (d, $^1J_{\text{CP}} = 8.8$ Hz; Ar-**C**), 128.5 (s; Ar-**C**), 128.9 (d, $^1J_{\text{CP}} = 9.3$ Hz; Ar-**C**), 129.4 (s; Ar-**C**), 129.6 (s; Ar-**C**), 129.7 (d, $^3J_{\text{CP}} = 1.7$ Hz; Ar-**C**), 130.3 (d, $^3J_{\text{CP}} = 1.2$ Hz; Ar-**C**), 131.5 (s; Ar-**C**), 131.8 (s; Ar-**C**), 131.9 (d, $^2J_{\text{CP}} = 5.1$ Hz; Ar-**C**), 132.2 (d, $^3J_{\text{CP}} = 2.6$ Hz; Ar-**C**), 133.6 (d, $^2J_{\text{CP}} = 5.0$ Hz; Ar-**C**), 134.1 (d, $^2J_{\text{CP}} = 7.9$ Hz; Ar-**C**), 135.0 (d, $^1J_{\text{CP}} = 11.9$ Hz; Ar-**C**), 138.1 (s; Ar-**C**), 140.1 (d, $^2J_{\text{CP}} = 15.9$ Hz; Ar-**C**), 162.2 (d, $^3J_{\text{CP}} = 5.1$ Hz; **C3**). ^{31}P NMR (121 MHz, CDCl_3): 25.9 (s, $J_{\text{Pt}} = 1954$ Hz). ESI-MS: m/z 671.63 $[\text{M}+\text{H}]^+$, 589.50 $[\text{M}-\text{C}_4\text{H}_8]$.

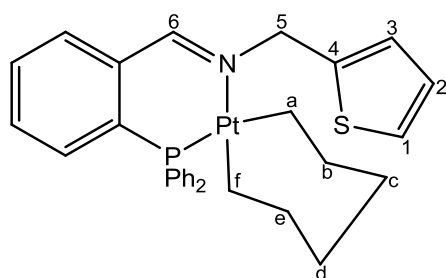
Preparation of $[\text{Pt}(\text{C}_{24}\text{H}_{20}\text{NOP})(\text{C}_6\text{H}_{12})]$ (**5.9**)



Complex **5.9** was prepared by the reaction of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) with ligand **3.3** (0.24 g, 0.64 mmol). The product was obtained as a dark-orange oil (0.31 g, 77%). IR (KBr): 1632 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.72 – 0.75 (m, 4H; **Ha+Hf**), 1.31 – 1.39 (m, 8H; **Hb-He**), 5.77 (s, 2H, $^3J_{\text{HPt}} = 15.7$ Hz; **C5**), 6.29 (dd, 1H, $^3J_{\text{HH}} = 2.0$ Hz, 3.1 Hz; **H3**), 6.34 (1H, d, $^3J_{\text{HH}} = 3.2$ Hz; **H2**), 7.06 (1H, dd, $^3J_{\text{HH}} = 0.9$ Hz, 2.0 Hz; **H1**), 7.24 – 7.42 (m, 14H; Ar-**H**), 8.16 (s, 2H, $^3J_{\text{HPt}} = 31.8$ Hz;

H6). ^{13}C NMR (75.5 MHz, CDCl_3): 15.1 (d, $^2J_{\text{CP}} = 2.8$ Hz; **Cf**), 24.3 (s; **Ce**), 24.9 (s; **Cb**), 31.4 (s; **Cd**), 31.5 (s; **Cc**), 33.7 (d, $^2J_{\text{CP}} = 4.9$ Hz; **Ca**), 63.5 (s; **C5**), 109.6 (s; **C3**), 110.3 (s; **C2**), 127.7 (d, $^1J_{\text{CP}} = 10.0$ Hz; Ar-**C**), 127.9 (d, $^1J_{\text{CP}} = 11.6$ Hz; Ar-**C**), 128.8 (d, $^2J_{\text{CP}} = 5.0$ Hz; Ar-**C**), 129.5 (d, $^3J_{\text{CP}} = 1.4$ Hz; Ar-**C**), 130.7 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 131.1 (s; Ar-**C**), 131.5 (s; Ar-**C**), 131.7 (s; Ar-**C**), 131.9 (d, $^3J_{\text{CP}} = 5.1$ Hz; Ar-**C**), 132.0 (s; Ar-**C**), 132.8 (d, $^3J_{\text{CP}} = 2.4$ Hz, Ar-**C**), 134.0 (d, $^1J_{\text{CP}} = 12.3$ Hz; Ar-**C**), 134.7 (s; Ar-**C**), 135.6 (d, $^2J_{\text{CP}} = 8.1$ Hz; Ar-**C**), 138.3 (d, $^2J_{\text{CP}} = 17.1$ Hz, Ar-**C**), 143.1 (s; **C1**), 149.7 (s; **C4**), 162.6 (d, $^3J_{\text{CP}} = 5.4$ Hz; **C6**). ^{31}P NMR (121 MHz, CDCl_3): 26.4 (s, $J_{\text{Ppt}} = 1860$ Hz). ESI-MS: m/z 649.69 $[\text{M}+\text{H}]^+$, 565.41 $[\text{M}-\text{C}_4\text{H}_8]$.

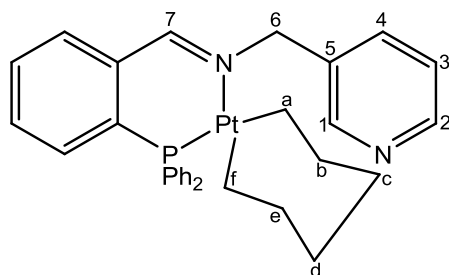
Preparation of $[\text{Pt}(\text{C}_{24}\text{H}_{20}\text{NPS})(\text{C}_6\text{H}_{12})]$ (**5.10**)



Complex **5.10** was prepared by the reaction of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) with ligand **3.4** (0.25 g, 0.64 mmol). The product was obtained as a dark-orange oil (0.30 g, 71%). IR (KBr): 1631 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.76 – 0.80 (m, 4H; **Ha+Hf**), 1.26 – 1.43 (8H, m; **Hb-He**), 5.50 (2H, s, $^3J_{\text{HPt}} =$

16.1 Hz; **C5**), 6.17 (1H, dd, $^4J_{\text{HH}} = 2.0$ Hz, $^3J_{\text{HH}} = 3.2$ Hz, **H3**), 6.23 (1H, d, $^3J_{\text{HH}} = 3.0$ Hz, **H2**), 7.11 (1H, dd, $^4J_{\text{HH}} = 0.8$ Hz, $^3J_{\text{HH}} = 1.8$ Hz; **H1**), 7.30 – 7.39 (m, 14H; Ar-**H**), 8.17 (1H, s, $^3J_{\text{HPt}} = 33.8$ Hz; **H6**). ^{13}C NMR (75.5 MHz, CDCl_3): 17.1 (d, $^2J_{\text{CP}} = 2.9$ Hz; **Cf**), 22.9 (s; **Ce**), 23.3 (s; **Cb**), 30.4 (s; **Cd**), 30.7 (**Cc**), 34.1 (d, $^2J_{\text{CP}} = 6.0$ Hz; **Ca**), 63.9 (s; **C5**), 122.7 (s; **C3**), 124.0 (s; **C2**), 128.3 (d, $^1J_{\text{CP}} = 10.7$ Hz; Ar-**C**), 128.6 (d, $^1J_{\text{CP}} = 11.7$ Hz; Ar-**C**), 129.1 (d, $^2J_{\text{CP}} = 4.8$ Hz; Ar-**C**), 129.5 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 130.7 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 131.3 (s; Ar-**C**), 131.6 (s; Ar-**C**), 131.8 (d, $^3J_{\text{CP}} = 5.4$ Hz; Ar-**C**), 132.3 (s; Ar-**C**), 132.9 (d, $^3J_{\text{CP}} = 3.1$ Hz, Ar-**C**), 134.2 (d, $^1J_{\text{CP}} = 12.1$ Hz; Ar-**C**), 134.1 (s; Ar-**C**), 135.5 (d, $^2J_{\text{CP}} = 9.7$ Hz; Ar-**C**), 137.9 (d, $^2J_{\text{CP}} = 15.8$ Hz, Ar-**C**), 142.3 (s; **C1**), 151.1 (s; **C4**), 163.0 (d, $^3J_{\text{CP}} = 5.1$ Hz; **C6**). ^{31}P NMR (121 MHz, CDCl_3): 27.1 (s, $J_{\text{Ppt}} = 1830$ Hz). ESI-MS: m/z 665.59 $[\text{M}+\text{H}]^+$, 581.45 $[\text{M}-\text{C}_4\text{H}_8]$.

Preparation of $[\text{Pt}(\text{C}_{25}\text{H}_{21}\text{N}_2\text{P})(\text{C}_6\text{H}_{12})]$ (**5.11**)

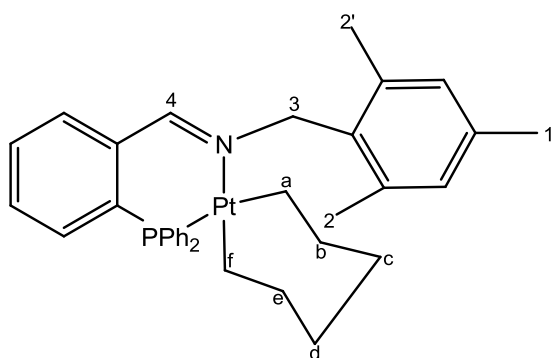


Complex **5.11** was prepared by the reaction of $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.25 g, 0.64 mmol) with ligand **3.5** (0.24 g, 0.64 mmol). The product was obtained as a brown oil (0.27 g, 65%). IR (KBr): 1634 cm^{-1} ($\nu_{\text{C}=\text{N}}$, imine). ^1H NMR (300 MHz, CDCl_3): 0.76 – 0.81 (m, 4H; **Ha+Hf**), 1.37 – 1.63 (m, 8H; **Hb-He**), 5.38 (s, 2H, $^3J_{\text{HPt}} =$

15.9 Hz; **H6**), 7.09 (1H, dd, $^3J_{\text{HH}} = 7.8$ Hz, 9.3 Hz; Ar-**H**), 7.15 – 7.24 (4H, m; Ar-**H**), 7.36 – 7.40 (4H, m; Ar-**H**), 7.53 – 7.57 (3H, m; Ar-**H**), 7.64 – 7.64 (1H, m; Ar-**H**), 7.70 – 7.72 (1H, m; **H3**), 8.09 (1H, td, $^3J_{\text{HH}} = 2.3$ Hz; 7.8 Hz, Ar-**H**), 8.32 – 8.33 (m, 1H; **H4**), 8.36 (1H, $^4J_{\text{HH}} = 1.6$

Hz, 5.4 Hz; **H2**), 8.41 (1H, s, $^3J_{\text{HPt}} = 37.1$ Hz; **H7**), 8.60 (1H, dd, d, $^4J_{\text{HH}} = 2.0$, Hz; **H1**). ^{13}C NMR (100.6 MHz, CDCl_3): 16.8 (d, $^2J_{\text{CP}} = 3.3$ Hz; **Cf**), 24.7 (s; **Ce**), 25.4 (s; **Cb**), 31.4 (s; **Cd**), 31.7 (**Cc**), 33.5 (d, $^2J_{\text{CP}} = 5.6$ Hz; **Ca**), 67.2 (s; **C6**), 126.1 (s; **C3**), 126.4 (s; Ar-**C**), 129.7 (d, $^1J_{\text{CP}} = 12.2$ Hz; Ar-**C**), 130.9 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 131.6 (d, $^3J_{\text{CP}} = 1.6$ Hz; Ar-**C**), 132.3 (d, $^2J_{\text{CP}} = 7.0$ Hz; Ar-**C**), 132.6 (s; Ar-**C**), 133.5 (d, $^1J_{\text{CP}} = 12.4$ Hz; Ar-**C**), 133.9 (s; **C4**), 134.1 (s; Ar-**C**), 134.8 (s; **C5**), 136.7 (d, $^2J_{\text{CP}} = 16.9$ Hz; Ar-**C**), 137.5 (s; Ar-**C**), 140.1 (s; Ar-**C**), 148.9 (s; **C2**), 150.8 (s; **C1**), 161.9 (d, $^3J_{\text{CP}} = 6.0$ Hz; **C7**). ^{31}P NMR (121 MHz, CDCl_3): 26.6 (s, $J_{\text{PPt}} = 1835$ Hz). ESI-MS: m/z 660.61 $[\text{M}+\text{H}]^+$, 576.47 $[\text{M}-\text{C}_4\text{H}_8]$.

Preparation of $[\text{Pt}(\text{C}_{29}\text{H}_{28}\text{NP})(\text{C}_6\text{H}_{12})]$ (**5.12**)



Complex **5.12** was prepared using $[\text{Pt}(\text{COD})(\text{C}_6\text{H}_{12})]$ (0.21 g, 0.54 mmol) and **3.6** (0.23 g, 0.54 mmol). The product was obtained as a brown oil (0.23 g, 60%). IR (KBr): 1634 cm^{-1} ($\nu_{\text{C=N}}$, imine). ^1H NMR (400 MHz, CDCl_3): 0.79 – 0.93 (m, 4H; **Ha+Hf**), 1.80 – 1.91 (m, 8H; **Hb+He**), 2.26 (s, 6H; **H2+H2'**), 2.43 (s, 3H; **H1**), 5.53 (2H, s, $^3J_{\text{HPt}} = 16.4$ Hz; **H3**), 7.07 (d, 2H,

$^3J_{\text{HH}} = 7.8$ Hz; Ar-**H**), 7.13 (d, 2H, $^3J_{\text{HH}} = 7.3$ Hz; Ar-**H**), 7.33 – 7.42 (m, 12H; Ar-**H**), 8.17 (s, 1H, $^3J_{\text{HPt}} = 35.0$ Hz; **H4**). ^{13}C NMR (100.6 MHz, CDCl_3): 16.7 (d, $^2J_{\text{CP}} = 2.6$ Hz; **Cf**), 24.3 (s; **C2+C2'**), 24.9 (s; **C1**), 26.2 (s; **Ce**), 26.9 (s; **Cb**), 29.1 (s; **Cd**), 29.4 (s; **Cc**), 33.3 (d, $^2J_{\text{CP}} = 6.2$ Hz; **Ca**), 65.9 (s; **C3**), 127.3 (s; Ar-**C**), 128.2 (s; Ar-**C**), 128.4 (d, $^1J_{\text{CP}} = 9.3$ Hz; Ar-**C**), 129.2 (s; Ar-**C**), 129.5 (d, $^1J_{\text{CP}} = 9.1$ Hz; Ar-**C**), 129.7 (s; Ar-**C**), 129.9 (s; Ar-**C**), 130.1 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 130.5 (d, $^3J_{\text{CP}} = 1.8$ Hz; Ar-**C**), 131.7 (s; Ar-**C**), 131.8 (s; Ar-**C**), 131.9 (d, $^2J_{\text{CP}} = 5.0$ Hz; Ar-**C**), 133.1 (d, $^3J_{\text{CP}} = 2.6$ Hz; Ar-**C**), 134.0 (d, $^2J_{\text{CP}} = 5.1$ Hz; Ar-**C**), 134.3 (d, $^2J_{\text{CP}} = 10.0$ Hz; Ar-**C**), 134.6 (d, $^1J_{\text{CP}} = 11.9$ Hz; Ar-**C**), 138.3 (s; Ar-**C**), 139.6 (s; Ar-**C**), 141.9 (d, $^2J_{\text{CP}} = 17.7$ Hz; Ar-**C**), 163.4 (d, $^3J_{\text{CP}} = 5.1$ Hz; **C4**). ^{31}P NMR (121 MHz, CDCl_3): 26.7 (s, $J_{\text{PPt}} = 1863$ Hz). ESI-MS: m/z 701.53 $[\text{M}+\text{H}]^+$, 617.49 $[\text{M}-\text{C}_4\text{H}_8]$.

7.7 CRYSTALLOGRAPHIC DATA FOR **3.14**, **3.25** and **5.1**

Single-crystal X-ray diffraction data for complexes **3.14**, **3.25** and **5.1** were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection was carried out at 173(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.¹⁶ The data were scaled and absorption corrections were performed using SADABS.¹⁷ The structure was solved by direct methods using SHELXS-97¹⁷ and refined by full-matrix least-squares methods based on F^2 using

SHELXL-97¹⁷ and using the graphics interface program X-Seed.¹⁸ The programs X-Seed and POV-Ray¹⁹ were both used to prepare molecular graphic images. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically with C-H distances ranging from 0.95 Å to 0.98 Å and refined as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2 - 1.5 U_{\text{eq}}(\text{C})$. The structure was successfully refined to the R factor 0.0238. The parameters for crystal data collection and structure refinements are in Table 6.1.

University of Cape Town

Table 7.1: Crystal and Refinement Data for **3.14**, **3.25** and **5.1**

	3.14	3.25	5.1
Empirical formula	C ₂₈ H ₂₇ ClNPd	C ₂₈ H ₂₉ BrNOPt	C ₃₀ H ₃₀ NPt
Formula weight	550.33	701.49	630.61
T, K	173(2)	173(2)	173(2)
λ , Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/n	P2(1)/c	P-1
a, Å	10.0673(8)	15.7405(6)	9.7744(13)
b, Å	21.8872(18)	13.8347(6)	11.3517(15)
c, Å	11.0593(9)	11.7993(5)	12.6780(16)
α , deg	90	90	72.898(3)
β , deg	92.3710(10)	95.4740(10)	67.960(3)
γ , deg	90	90	82.749(3)
V, Å ³	2434.8(3)	2557.76(18)	1246.0(3)
Z	4	4	2
Density _{calc} , mg/mL	1.501	1.822	1.681
Absorption coefficient, mm ⁻¹	0.954	7.132	5.713
F(000)	1120	1360	620
Crystal size, mm	0.24 x 0.23 x 0.12	0.20 x 0.18 x 0.14	0.09 x 0.07 x 0.06
θ range for data collection, deg	1.86 to 27.14	1.96 to 30.56	1.80 to 28.34
Limiting indices	-12 \leq h \leq 12, -28 \leq k \leq 28, -14 \leq l \leq 14	-22 \leq h \leq 22, -19 \leq k \leq 19, -16 \leq l \leq 16	-13 \leq h \leq 13, -15 \leq k \leq 15, -16 \leq l \leq 16
Reflections collected / unique	38460 / 5380 [R(int) = 0.0444]	53170 / 7844 [R(int) = 0.0465]	27034 / 6180 [R(int) = 0.0549]
Completeness to θ	27.14 (99.9%)	30.56 (99.9 %)	28.34 (99.4 %)
Max. and min. transmission	0.8941 and 0.8034	0.7461 and 0.6162	0.7980 and 0.6776

CHAPTER 7: Experimental Details

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5380 / 0 / 291	7844 / 0 / 298	6180 / 0 / 298
Goodness-of-fit on F^2	1.025	1.023	1.043
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0238, wR2 = 0.0546	R1 = 0.0216, wR2 = 0.0533	R1 = 0.0350, wR2 = 0.0746
R indices (all data)	R1 = 0.0321, wR2 = 0.0584	R1 = 0.0292, wR2 = 0.0562	R1 = 0.0448, wR2 = 0.0786
Largest diff. peak and hole	0.370 and -0.405 e.A ⁻³	1.680 and -0.872 e.A ⁻³	2.829 and -1.044 e.A ⁻³

University of Cape Town

7.8 REFERENCES

1. (a) Ravindar, V., Hemling, H. and Blum, J., *Synth. Commun.*, 1992, **22**, 1453. (b) Chatt, J., Vallarino, L. M. and Venanzi, L. M., *J. Chem. Soc.*, 1957, 3413.
2. Bailey, C. T. and Linsesky, G. C., *J. Chem. Edu.*, 1985, 896.
3. Rülke, R. E., Ernsting, J. M., Spek, A. L., Elsevier, C. J., van Leeuwen, P. W. N. M., and Vrieze, K., *Inorg. Chem.*, 1993, **32**, 5769.
4. (a) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6521. (b) Drew, D. and Doyle, J. R., *Inorg. Synth.*, 1990, **28**, 346.
5. Olsson, D. and Wendt, O. F., *J. Organomet. Chem.*, 2009, **694**, 3112.
6. (a) Becke, A. D., *J. Chem. Phys.*, 1993, **98**, 5648. (b) Lee, C., Yang, W., Parr, R. G., *Phys. Rev.*, 1988, **37**, 785. (c) Miehlich, B., Savin, A., Stoll, H., *Chem. Phys. Lett.*, 1989, **157**, 200. (d) Hay, P. J., Wadt, W. R., *J. Chem. Phys.*, 1985, **82**, 299. (e) Hehre, W. J., Ditchfield, R., Pople, J. A., *J. Chem. Phys.*, 1972, **56**, 2257. (f) Hariharan, P. C., Pople, J. A., *Theor. Chim. Acta*, 1973, **28**, 213. (g) Spitznagel, G. W., Clark, T., Chandrasekhar, J., Schleyer, P. v. R., *J. Comput. Chem.*, 1982, **3**, 3633. (h) Clark, T., Chandrasekhar, J., Spitznagel, G. W., Schleyer, P. v. R., *J. Comput. Chem.*, 1983, **4**, 294.
7. (a) Del Zotto, A., Baratta, W., Ballico M., Herdtweck, E. and Rigo, P., *Organometallics*, 2007, **26**, 5636. (b) Masson, J. P., Bahsoun, A. A., Youinou, M. and Osborn, J. A. C. R. *Chimie*, 2002, **5**, 305. (c) Crossetti, G. L., Filgueiras, C. A., Howie, R. A., Wardell, J. L. and Ziglo, C. M., *Acta Cryst.*, 2001, **C57**, 1279. (d) Bhagwart, U. A., Mukhedkar, V. A. and Mukhedkar, A. J. *J. Chem. Soc. Dalton Trans.*, 1980, 2319. (e) del Campo, O., Carbayo, A., Cuevas, J. V., Garcia-Herbaso, G. and Munoz, A., *Eur. J. Inorg. Chem.*, 2009, 2254. (f) Thibault, M-H., Lucier, B. E. G., Schurko, R. W. and Fontaine, F-G., *Dalton Trans.*, 2009, 7701.
8. Liek, C., Machnitzki, P., Mickel, T., Schenk, S., Tepper, M. and Stelzer, O., *Zeit. Nat. B: Chem. Sci.*, 1999, **54**, 1532.
9. Mogorosi, M. M., Mahamo, T., Moss, J. R., Mapolie, S. F., Sloomweg, J. C., Lammertsma, K., and Smith, G. S., *J. Organomet. Chem.*, 2011, **696**, 3585.
10. (a) Gao, J.-X., Ikayira, T. and Noyori, R., *Organometallics*, 1996, **15**, 1087. (b) Shirakawa, E., Nakao, Y., Murota Y. and Hiyama T., *J. Organomet. Chem.*, 2003, **670**, 132. (c) Rülke, R.E., Kaasjager, V.E., Wehman, P., Elsevier, C.J., van Leeuwen, P.W.N.M., and Vrieze, K., *Organometallics*, 1996, **15**, 3022. (d) Wang, C., Friedrich, S., Youkin, T.R., Li, R.T., Grubbs, R.H., Bansleben, D.A., and Day, M.W., *Organometallics*, 1998, **17**, 3149. (e) Lavery, A., and Nelson, S.M., *J. Chem. Soc.*

- Dalton., Trans.*, 1984, 615. (f) Williams, D.B.G., and Pretorius, M., *J. Mol. Cat. A: Che.*, 2008, **284**, 77.
11. Mahamo, T., Mogorosi, M. M., Moss, J. R., Mapolie, S. F., Smith, G. S, Sloomweg, J. C., and Lammertsma, K., *J. Organomet. Chem.*, 2012, **703**, 34.
 12. Sanchez, G., Momlona, F., Peres, J. and Lopez, G., *Transition Met. Chem.*, 2001, **26**, 10.
 13. (a) Reddy, K. R., Tsai, W-W., Surekha, K., Lee, G-H., Peng, S-M., Chen, J-T., and Liu, S-T., *J. Chem. Soc., Dalton, Trans.*, 2002, 1776. (b) Flapper, J., Kooijman, H., Lutz, M., Spek, A. L., van Leeuwen, P. W. N. M., Elsevier, C. J. and Kamer, P. C. J., *Organometallics*, 2009, **28**,1180. (c) Ankersmit, H. A., Loken, B. H., Kooijman, H., Spek, A. L., Vrieze, K. and van Koten, G., *Inorg. Chim. Acta.*, 1996, **252**, 141. (d) Brinkmann, P. H. P., Luinstra G. A., *J. Organomet. Chem.*, 1999, **572**, 193.
 14. Song, H-B., Zheng-Zhi Zhang, Z-Z. and Mak, T. C., W., *Polyhedron*, 2002, **21**, 1043.
 15. (a) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1973, **95**, 4451. (b) Miller, T. M. and Whitesides, G. M., *Organometallics*, 1986, **5**, 1473.
 16. SAINT Version 7.60a, Bruker AXS Inc., Madison, WI, USA, 2006.
 17. Sheldrick, G. M., SHELXS-97, SHELXL-97 and SADABS version 2.05, University of Göttingen, Germany, 1997.
 18. (a) Barbour, L. J., *J. Supramol. Chem.*, 2001, **1**, 189. (b) Atwood, J. L. and Barbour, L. J., *Cryst. Growth Des.*, 2003, **3**, 3.
 19. <http://www.povray.org>.