Nitrogen-donor Nickel and Palladium Complexes as Olefin Transformation Catalysts

By

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Thesis

Submitted in fulfillment of the requirement for the degree

Philosophiae Doctor

in

Chemistry

in the

Faculty of Science

at the

University of Johannesburg

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January 2008
DECLARATION

I declare that the thesis, Nitrogen-donor nickel and palladium complexes as olefin transformation catalysts, is my original work and has never been presented for the award of any degree at any other university before and that all the information, references and sources I have used and or quoted have been indicated and acknowledged by means of complete physical reference.

Name: Stephen Otieno Ojwach

Signature: ……………………… Date…………………………..
DEDICATION

Dedicated to my late father William Ojwach
**Preface**

It is now accepted that in recent years homogeneous transition metal olefin oligomerisation and polymerisation catalysis has had a major impact in the modern chemical industry. Academic and industrial research in this field is currently vibrant, and the output in research papers and books attests to this. However design of desirable catalysts that would perform these oligomerisation and polymerisation catalytic reactions as required in the chemical industry still remains a challenge to researchers. This is mainly with respect to catalysts’ activity, selectivity and stability. The balance between these three factors therefore underlies the rationale of the development of suitable transition metal olefin oligomerisation and polymerisation catalysts and forms the fundamental problems that every researcher in this field seeks to solve. In this thesis attempts to achieve the balance between catalyst stability, activity and selectivity of some nitrogen-donor nickel and palladium complexes is systematically investigated.

This thesis is organised in seven chapters. **Chapter 1** covers the introduction of olefin catalysis; the section emphasises on the economic and industrial significance of the alpha olefin products and the role of late transition metals in these catalytic processes. **Chapter 2** reviews the relevant literature on the design of late transition metal catalysts based on nitrogen donor ligands towards olefin oligomerisation and polymerisation reactions. The current efforts directed towards achieving the delicate balance between catalysts’ activity, selectivity and stability is reviewed.
Chapter 3 describes the coordination behaviour of potential tridentate 2,6-bis(pyrazol-1-ylmethyl)pyridine ligands to palladium. The synthesis of these palladium complexes and their chemistry when reacted with a chloride abstractor and attempts to use the palladium complexes as ethylene and phenylacetylene polymerisation catalysts are described in this chapter. Density Functional Studies (DFT) using Gaussian03 on the energetic of the formation of tridentate cationic complexes and ethylene coordination barriers have been performed to gain insight into the reactions of these systems with ethylene upon chloride abstraction.

In Chapter 4 attempts to circumvent the tridentate coordination behaviour of the complexes in Chapter 3 by using bidentate unsymmetrical (pyrazolylmethyl)pyridine ligands is reported. In this chapter, the synthesis and molecular structures of the palladium complexes and generation of active catalysts for olefin oligomerisation and polymerisation in the presence of weakly coordinating solvents is described. The synthesis of hemi-labile pyrazolyl ligands containing a phenoxy or weakly coordinating pyrazolyl unit, their palladium complexes and reactions with ethylene is also described. DFT studies on the stability of the cationic species and the relative binding affinities of ethylene and weakly coordinating solvents have also been performed.

The synthesis of nickel complexes of bis(pyrazolylmethyl)pyridine and (pyrazolylmethyl)pyridine ligands and their molecular structures is reported in Chapter 5. The nickel complexes have been found to give highly active catalysts for the
oligomerisation of ethylene and higher \( \alpha \)-olefins when activated with \( \text{EtAlCl}_2 \) as a co-catalyst. These oligomerisation reactions are also discussed in this chapter.

In Chapter 6 is reported a convenient synthetic route to substituted (pyridinyl)benzothiazole compounds. The synthesis and characterisation of ligands and their palladium complexes is also discussed in this chapter. The complexes have been found to catalyse Heck coupling reactions of iodobenzene with butylacrylates at mild conditions and at low catalyst loadings. These Heck coupling reactions are also discussed in this chapter.

The final part, Chapter 7, gives a summary and some of the significant outcomes and findings of this research work. The chapter also outlines the challenges and future prospects that arose from the work in this thesis.

**List of original publication**

This thesis is based on the following publications and manuscripts:


II. Palladium complexes of multidentate pyrazolylmethyl pyridine ligands: Synthesis, Structures and phenylacetylene polymerisation, **Stephen O. Ojwach**,
III. Positional disorder manifested as compositional in a pseudo-\(C_2\)-symmetrical Pd complex, Ilia A. Guzei, Lara C. Spencer, Stephen O. Ojwach, James Darkwa


V. Nickel complexes of bis(pyrazolylmethyl)pyridine ligands; synthesis, characterization and ethylene oligomerisation catalysis, Stephen O. Ojwach, James Darkwa, Selwyn F. Mapolie, (Manuscript to be submitted to *Journal of Molecular Catalysis, A. Chemical*).

VI. Cationic palladium complexes based on unsymmetrical and hemi-labile (pyrazolylmethyl)pyridine ligands: Synthesis, molecular structures, stability and ethylene polymerisation studies, Stephen O. Ojwach, Ilia A. Guzei, James Darkwa, Selwyn F. Mapolie, (Manuscript under preparation to be submitted to *Journal of Organometallic Chemistry*).
VII. Nickel complexes based on (pyazolylmethyl)pyridine ligands as highly active catalysts for ethylene oligomerisation, Stephen O. Ojwach, Ilia A. Guzei, James Darkwa, Selwyn F. Mapolie, (Manuscript under preparation to be submitted to Organometallics).

VIII. Nickel complexes of multidentate (pyazolylmethyl)pyridine ligands as catalysts for the oligomerisation and co-oligomerisation of alpha olefins with ethylene, Stephen O. Ojwach, James Darkwa, Selwyn F. Mapolie, (Manuscript under preparation to be submitted to Journal of Molecular Catalysis, A. Chemical).
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Compounds, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L1) and 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (L2) were prepared by phase transfer alkylation of 2,6-bis(bromomethyl)pyridine with two mole equivalents of the appropriate pyrazole. Ligands L1 and L2 reacted with either [PdCl2(NCMe)2] or [PdClMe(COD)] to form mononuclear palladium complexes [(PdCl2(L1)] (1), [(PdClMe(L1)] (2), [(PdCl2(L2)] (3), [(PdClMe(L2)] (4). All new compounds prepared were characterised by a combination of 1H NMR, 13C NMR spectroscopy and microanalyses. The coordination of L2 in a bidentate fashion through the pyridine nitrogen atom and one pyrazolyl nitrogen atom has been confirmed by single crystal X-ray crystallography of complex 3.

Reactions of 1, 2 and 3 with the halide abstractor NaBAr4 (Ar = 3,5-(CF3)2C6H3) led to the formation of the stable tridentate cationic species [(PdCl(L1)]BAr4 (5), [(PdMe(L1)]BAr4 (6) and [(PdCl(L2)]BAr4 (7) respectively. Tridentate coordination of L1 and L2 in the cationic complexes has also been confirmed by single X-ray crystallography of complexes 5 and 6. The analogous carbonyl linker cationic species, [Pd{(3,5-Me2pz-CO)2-py}Cl+] (9) and [Pd{(3,5-tBu2pz-CO)2-py}Cl+] (10), prepared by halide abstraction from [Pd{(3,5-Me2pz-CO)2-py}Cl2] and [Pd{(3,5-tBu2pz-CO)2-py}Cl2] with NaBAr4, were however less stable. While cationic complexes 5-7 showed indefinite stability in solution, 9 and 10 had t1/2 of 14 and 2 days respectively. Attempts to crystallise 1 and 3 from the mother liquor resulted in the isolation of the salts [PdCl(L1)]2[Pd2Cl6] (11) and [PdCl(L2)]2[Pd2Cl6] (12). Although when complexes 1-4
were reacted with modified methylaluminoxane (MMAO) or NaBAR₄, no active catalysts for ethylene oligomerisation or polymerisation were formed, activation with silver triflate (AgOTf) produced active catalysts that oligomerised and polymerised phenylacetylene to a mixture of cis-transoidal and trans-cisoidal polyphenylacetylene.

Compounds 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L₃) and 2-(3,5-di-tert-butylpyrazol-1-ylmethyl)pyridine (L₄) were prepared by phase transfer alkylation of 2-picoly chloride hydrochloride with one mole equivalent of the appropriate pyrazole. Compounds 2-(3,5-bis-trifluoromethyl-pyrazol-1-ylmethyl)-6-(3,5-dimethyl-pyrazol-1-ylmethyl)-pyridine (L₅) and 2-(3,5-dimethyl-pyrazol-1-ylmethyl)-6-phenoxymethylpyridine (L₆) were isolated in good yields by reacting (2-chloromethyl-6-3,5-dimethylpyrazol-1-ylmethyl)pyridine with an equivalent amount of potassium salt of 3,5-bis(trifluoromethyl)pyrazolate and potassium phenolate respectively. L₃-L₆ react with either [Pd(NCMe)₂Cl₂] or [PdClMe(COD)] to give mononuclear palladium complexes 13-18 of the general formulae [PdCl₂(L)] or [PdClMe(L)] where L = is the bidentate ligands L₃, L₄, L₅ and L₆ respectively. Single crystal X-ray crystallography of complexes 13, 15 and 16 has been used to confirm the solid state geometry of the complexes.

In attempts to generate active olefin oligomerisation catalysts, the chloromethyl Pd(II) complexes 14 and 16 were reacted with the halide abstractor NaBAR₄ in the presence of stabilising solvents (i.e Et₂O or NCMe) but no catalytic activities were observed. Decomposition was evident as observed from the deposition of palladium black in
experiments using Et$_2$O. In experiments where NCMe was used as the stabilising solvent, the formation of cationic species stabilised by NCMe was evident from $^1$H NMR analyses. Reaction of complex 14 with NaBAr$_4$ on a preparative scale in a mixture of CH$_2$Cl$_2$ and NCMe solvent gave the cationic complex [[PdMeNCMe(L3)]BAr$_4$ (19) in good yields. Complex 17 reacted with NABAr$_4$ to give tridentate cationic species [[PdMe(L5)]BAr$_4$ (20) which is inactive towards ethylene oligomerisation or polymerisation reactions. The tridentate coordination of L5 in 20 has also been established by single crystal X-ray structure of 20. Catalysts generated from 18 and 19 catalysed ethylene polymerisation at high pressures to branched polyethylene; albeit with very low activity. The Choromethyl palladium complex 14 reacted with sulfur dioxide to form complex 21. The nature of the product has been established by $^1$H NMR, $^{13}$C NMR and mass spectrometry to be an insertion product of SO$_2$ into the Pd-Me bond of 14.

Compounds L1-L4 reacted with the nickel salts NiCl$_2$ or NiBr$_2$ in a 1:1 mole ratio to give the nickel complexes [NiCl$_2$(L1)] (22), [NiBr$_2$(L1)] (23), [NiCl$_2$(L2)] (24), and [NiBr$_2$(L2)] (25), [Ni$_2$(μ$_2$-Cl)$_2$Cl$_2$(L3)$_2$] (26), [Ni$_2$(μ$_2$-Br)$_2$Br$_2$(L3)$_2$] (27), [NiCl$_2$(L4)] (29) and [NiBr$_2$(L4)] (30) in good yields. Reaction of L3 with NiBr$_2$ in a 2:1 mole gave the octahedral complex [NiBr$_2$(L4)$_2$] (28) in good yields. Complexes 22-30 were characterised by a combination micro-analyses, mass spectrometry and single crystal X-ray analyses for 27 and 30. No NMR data were acquired because of the paramagnetic nature of the complexes.

When complexes 22-30 were activated with EtAlCl$_2$, highly active olefin oligomerisation catalysts were formed. In the ethylene oligomerisation reactions, three oligomers: C$_{11}$, C$_{14}$
and C\textsubscript{16} were identified as the major products. Selectivity of 40% towards \(\alpha\)-olefins were generally obtained. In general catalysts that contain the bidentate ligands L\textsubscript{3} and L\textsubscript{4} were more active than those that contain the tridentate ligands L\textsubscript{1} and L\textsubscript{2}. Dichloride complexes exhibited relatively higher catalytic activities than their dibromide analogues.

Turn over numbers (TON) for oligomer formation showed high dependence on ethylene concentration. A Lineweaver-Burk analysis of reactions catalysed by 22 and 26 showed TON saturation of 28 393 kg oligomer/mol Ni.h and 19 000 kg oligomer/mol Ni.h respectively. Catalysts generated from complexes 22-30 also catalysed oligomerisation of the higher olefins, 1-pentene, 1-hexene and 1-heptene and displayed good catalytic activities. Only two products C\textsubscript{12} and C\textsubscript{15} were obtained in the 1-pentene oligomerisation reactions. The 1-hexene reactions also gave two products, C\textsubscript{12} and C\textsubscript{18}, while 1-heptene oligomerisation reactions gave predominantly C\textsubscript{14} oligomers.

Five benzoazoles were used to prepare a series of palladium complexes that were investigated as Heck coupling catalysts. The compounds 2-pyridin-2-yl-1H-benzoimidazole (L7) and 2-pyridin-2-yl-benothiazole (L8) were prepared following literature procedures. The new ligands 2-(4-tert-butylpyridin-2-yl)-benzooxazole (L9) and 2-(4-tert-butyl-pyridin-2-yl)-benzothiazole (L10) were prepared by ring closure of aminophenol and aminothiophenol with tert-butyl picolinic acid respectively. The ligand 6-tert-Butyl-2-(4-tert-butyl-pyridin-2-yl)-benzothiazole (L11) was prepared by intramolecular cyclisation under basic conditions is described. Reactions of L7-L11 with either [Pd(NCMe)\textsubscript{2}Cl\textsubscript{2}] or [Pd(COD)MeCl] afforded the corresponding mononuclear palladium complexes [PdClMe(L7)] (31), [PdClMe(L8)] (32), [PdCl\textsubscript{2}(L9)] (33), [PdMeCl(L9)] (34), [PdCl\textsubscript{2}(L10)] (5), [PdMeCl(L10)] (36) and [PdMeCl(L11)] (37) as
confirmed by mass spectrometry and micro-analyses. The palladium complexes 31-37 were efficient Heck coupling catalysts for the reaction of iodobenzene with butylacrylate under mild conditions and showed good stability.
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<td>atm</td>
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<tr>
<td>COD</td>
<td>Cyclooctadiene</td>
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<tr>
<td>ESI</td>
<td>Electron spray ionisation</td>
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<tr>
<td>GC</td>
<td>Gas chromatography</td>
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<tr>
<td>GC-MS</td>
<td>Gas chromatography-mass spectrometry</td>
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<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
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<td>HDLPE</td>
<td>High density linear polyethylene</td>
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<td>Infrared spectroscopy</td>
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<td>L</td>
<td>Ligand</td>
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<td>LAO</td>
<td>Linear alpha olefins</td>
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<td>LLDPE</td>
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<td>LHDPE</td>
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<td>MMAO</td>
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ACKNOWLEDGEMENTS

The universal statement ‘All experiments were performed under vacuum’, that appears in this thesis is completely deceptive and its significance does not go beyond the technical aspects. Without the services of the people mentioned here, the work in this thesis would not have been achieved. First I wish to express my sincere gratitude to my supervisor Prof. James Darkwa and co-supervisor Prof. Selwyn Mapolie for their unrelenting and unconditional professional guidance throughout this research work. My gratitude also goes to Prof. Gunnar Westman not only for his warm hospitality during my visit to Sweden but also for his professional input and advice on the work described in Chapter 7. DR. Ilia Guzei is greatly thanked for his services in the X-ray molecular structural elucidation of the compounds described in this work which proved very useful in understanding the coordination chemistry of the compounds. The experience gained during the Organometallic research group seminars and cross-table consultations with my colleagues is highly applauded. I am also very grateful to the Chemistry department and the entire University of Johannesburg community for providing a friendly environment fundamental for this research work. I highly feel indebted to my family for their constant moral support and advice throughout this difficult moment. Lastly but not least, I thank the Almighty Lord for His spiritual protection and guidance up throughout this work.
CHAPTER 1

General introduction to the synthesis and applications of olefins and the role of transition metal catalysts

1.1 Introductory remarks

The industrial applications of transition metal catalysts in various olefin transformations such as olefin oligomerisation and polymerisation has witnessed significant growth over the past decade. Measured by the man-years of research, the number of books, patents and papers, the chemistry of transition metal catalysed olefin transformations is one of the areas that has attracted enormous research interests. The obvious question that arise is why olefins? What is the significance of olefins from an industrial and economic perspective apart from academic interests? And finally what is the role of metal complexes in these transformations? This chapter aims to shed some light on the above questions by looking at a general overview of the synthesis of olefins, some of their industrial applications and the roles of transition metal catalysis as practiced in industry. This chapter mainly reviews ethylene and higher α-olefin oligomerisation and polymerisation reactions and their industrial applications in our daily lives. Special attention is also paid to value addition to the olefin monomers through transition metal-catalysed reactions.

1.2 Synthesis of α-olefins

Linear α-olefins are a range of industrially significant olefins that encompasses 1-butene, 1-hexene, 1-octene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene and higher blends of olefins that contains C_{20}-C_{24}, C_{24}-C_{30} and C_{20}-C_{30} ranges. Industrially, these
alpha olefins are commonly prepared by two main routes: oligomerisation of ethylene and by Fischer Tropsch synthesis.\(^1\) In addition, to these two technologies, there are a number of synthetic protocols that are employed\(^2\) as outlined in the subsequent sections.

**1.2.1 Ethylene oligomerisation and polymerisation**

Catalytic dimerisation or oligomerisation is by far the most widely used in the conversion of moderately cheap, low molecular weight (i.e. C\(_2\)-C\(_4\)) olefin feed stocks into industrially important higher olefins (C\(_8\)-C\(_{30}\)). The use of organometallic complexes in this catalytic process has been widely studied\(^3\) and a number of reviews detailing the synthesis and applications of organometallic complexes as ethylene oligomerisation or polymerisation catalysts have appeared.\(^3\) There are currently six commercial industrial processes that oligomerise ethylene to linear \(\alpha\)-olefins. Four of these processes produce wide distributions of linear \(\alpha\)-olefins. These are: the Ethyl Corporation (Ineos) process, the Gulf (Chevron Phillips Chemical Company), the Shell Higher Olefin Process (SHOP) and the Idemistu Petrochemical process. The other two processes make single \(\alpha\)-olefin carbon number oligomers. These are: the Phillips (CP Chemical Company), ethylene trimerisation process, produces only 1-hexene. The sixth one offered by technology licensor, IFP, dimerises ethylene to high purity 1-butene.

---

Both the Ethyl Corporation (Ineos) and Gulf (Chevron Phillips Chemical Company) processes employ the Ziegler-Natta\textsuperscript{4} type catalytic methods (Scheme 1.1a). In the Gulf process triethylaluminium is used as a catalyst. The reaction is single-step process and is conducted at high pressure (1 000 psig) and high temperature. The product formation follows a Schulz-Flory\textsuperscript{5} (geometric distribution in which greater amounts of lower, C\textsubscript{n}, oligomers are produced than the higher olefins, C\textsubscript{n+2}) distribution typical of catalytic process. The Ethyl linear olefin process (Scheme 1.1b) is a two-step process which uses stoichiometric quantity of Et\textsubscript{3}Al with ethylene at high pressure (usually above 1 000 psig) and low temperature (below 400 F). Typically 9 moles of ethylene are added per mole of Et\textsubscript{3}Al resulting in a tri-octyl aluminium.

![Scheme 1.1](image)


On the other hand, the Shell Higher Olefin Process (SHOP) uses phosphine-donor nickel catalysts and operates in three catalytic stages: (i) oligomerisation, (ii) isomerisation and (iii) metathesis reactions. The oligomerisation reaction can be carried out in polar solvents such as ethylene glycol that are largely miscible with α-olefins. At temperatures of 80-120 °C and at ethylene pressure of 70-140 bar, a mixture of mainly C₄-C₂₀ α-olefins is formed. Distillation yields the desired α-olefins in the C₁₂-C₁₈ range and both lower (C₄-C₁₀) and higher cut (C₂₀+) olefins. The lower and higher cuts can be distilled off or taken to the isomerisation chamber. Under moderate conditions, the C₄-C₁₀ and C₁₈+ are isomerised to internal olefins. The internal olefins then pass to the metathesis step which employs Re₂O₇ supported on aluminium oxide as a catalyst. The major advantage of this process is the combination of different stages that results in high flexibility to produce a wide variety of olefins which are all in the molecular weight range desired commercially.

Other commercial processes for the oligmerisation of ethylene to higher alpha olefins include Phillips Process (CP Chemical Company) which employs a chromium complex prepared from Cr(III) 2-ethylhexanoate, 2,5-dimethylpyrrole, diethylaluminium chloride and triethylamine in toluene at 115 °C and 100 bar. This is a trimerisation process and produces oligomers containing ca 94% hexenes which are about 99% 1-hexenes. The aromatic solvent presumably stabilizes the Cr complex through coordination.⁷a

---

There exist two other alpha-olefin processes that are yet to be commercialized. One is an ethylene oligomerisation process to a wide range of linear alpha olefins technology being offered by a technology licensor UOP. The most recent non-commercial α-olefin process is the Sabic-Linde “α-Sablin” process being commercialized by a Saudi Arabian Basic Industries Company in Saudi Arabia. The “α-Sablin process is a low pressure ethylene oligomerisation process conducted over heterogeneous catalyst in a slurry bed. It also makes C₄-C₂₀+ α-olefins.

1.2.2 Other significant non-commercial ethylene oligomerisation and polymerisation transition metal catalysts

Following the work of Ziegler and Natta, a lot of research efforts have been spent on the design of homogeneous systems that could allow for the modification of both the steric and electronic properties of the catalysts as well control of product distribution and microstructure. The first homogeneous α-olefin polymerisation catalysts utilising Group 4 metalloccenes was first reported in 1957.⁸ Since then, single-site metalloccene catalysts have been the subject of enormous interests and have witnessed their modification to enhance catalyst activity, stability and selectivity. Metalloccene

---

catalysts capable of copolymerisations of ethylene and higher α-olefins have also been discovered by Bercaw and his group.\textsuperscript{9} These copolymerisation reactions produce polymers with short branches known as linear low density polyethylene (LLDPE).

In 1995, Brookhart\textsuperscript{10} and coworkers discovered a new ethylene polymerisation homogeneous catalyst based on α-diimine nickel and palladium metal complexes. Depending on the steric bulk of the aryl substituents on the ligand backbone, either high density linear polyethylene or low density polyethylene are obtained (Figure 1.1). To date a number of nitrogen-donor late transition metal catalysts have been developed that oligomerise or polymerize ethylene and higher α-olefins depending on catalyst structure.

![Figure 1.1: Dependence of ethylene polymerisation products on the structure of Brookhart type catalysts.\textsuperscript{10b}](image)

The electrophilicity of the nickel and palladium metal centres also results in rapid rates of olefin insertion, while bulky ligands favor chain propagation over termination resulting in the formation of high molecular weight polymers. In 1998, Brookhart and Gibson discovered that five coordinate 2,6-bis(arylimino)pyridyl Fe(II) and Co(II) dihalides when activated with MAO form active catalysts for the oligomerisation or polymerisation of ethylene and higher α-olefins (Scheme 1.2).11

![Scheme 1.2](image)

The size, nature and regiochemistry of the substituents are crucial in controlling the polymerisation and oligomerisation of α-olefins.12 For example Fe(II) catalysts with only...

one methyl substituent on the aryl ring have significant selectivity for ethylene oligomerisation to linear $\alpha$-olefins with Schulz-Flory distribution. However, commercialisation of these homogeneous transition metal catalysts have been hindered due to difficulty in separation of products from the catalyst traces and also their high activity requires heavy engineering works to alleviate reactor fouling and mass transport problems.

1.3 Applications of $\alpha$-olefins

The $\alpha$-olefins have found a wide range of end uses encompassing both direct and indirect industrial applications. As such the significant efforts being directed towards the synthesis of olefins both in academic and industrial laboratories is not a hollow exercise. These include the use of ethylene to form polyethylene, $\text{C}_4$-$\text{C}_8$ as co-monomers in the production of Low Density Polyethylene (LDPE) and linear aldehydes among other uses. The higher oligomers ($\text{C}_{10}$-$\text{C}_{30}$) find an important application in the detergent industry as lubricants and surfactants as well as fuel additives.\(^4\)\(^1\)\(^3\) Figure 1.2 gives the distribution of the end uses of olefins.

1.3.1 Application of α-olefins as detergents, lubricants and fuel additives

The linear α-olefins (C_{10}-C_{30}) have a wide range of applications in the detergent and fuel industries. For example, the predominant application of 1-decene is in the synthesis of lubricant feedstock and as a blend with higher linear α-olefins (C_{10}-C_{20}) to produce surfactants for aqueous detergent formulations. The olefins are reacted with benzene to make linear alkyl benzene (LAB), which is then sulfonated to a biodegradable linear alkyl benzene sulfonate (LABS), a popular low cost surfactant for industrial and household detergent applications.

Another example of an $\alpha$-olefin that is used in making detergents is C$_{14}$. Although some of the C$_{14}$ produced commercially are converted into aqueous detergents, C$_{14}$ has other important applications such as conversion into chloroparaffins. A recent application of C$_{14}$ is as on-land drilling fluid lubricant, replacing diesel or kerosene. Despite its high cost, C$_{14}$ has significant advantage environmentally over the middle range (C$_{10}$-C$_{12}$) olefins, in that it is biodegradable, and in handling, the material it is less irritating to skin and less toxic. Higher range linear $\alpha$-olefins (C$_{16}$-C$_{18}$) find their primary use as hydrophobes in oil-soluble surfactants and as lubricating fluids themselves. C$_{16}$-C$_{18}$, alpha or internal olefins, are used as synthetic drilling fluid base for high value off-shore synthetic drilling fluids.

Another significant application of C$_{16}$-C$_{18}$ olefins is in paper sizing. Linear $\alpha$-C$_{16}$-C$_{18}$ olefins are isomerised to linear internal olefins, which are then reacted with maleic acid anhydride to make an alkyl succinic anhydride; a popular paper sizing chemical.$^{15}$

The production capacity of linear $\alpha$-C$_{20}$-C$_{30}$ olefins is only about 5-10% of the total production of linear $\alpha$-olefin plants. They are mainly used in reactive and non-reactive applications, including as feed stocks for heavy linear alkyl benzene (LAB) and low molecular weight polymers to enhance the properties of waxes.

1.3.2 Polyethylene production and end uses

Polyolefin materials are being applied in everyday life. Polymerisation of ethylene results in the formation of either linear high density polyethylene (LHDPE) or branched low density polyethylene (LLDPE) depending on the catalyst structure (Figure 1.1).\textsuperscript{16} LHDPE and LLDPE use approximately 2-4% and 8-10% of the lower oligomers C\textsubscript{4}-C\textsubscript{8} comonomers respectively.\textsuperscript{10b} The end uses of the polymers depend on the polymers microcrystalline structure, mechanical and physical properties. While HDPE are used as films for cooking, storage tanks, building and construction pipes, LLDPE are mainly used for food packaging, and waste disposal bags (Figure 1.3).\textsuperscript{10b}

![Figure 1.3: Uses of different types of polyethylene](image)

- **HDPE Tarps**
- **HDPE Bottles**
- **LDPE Garbage Bags**
- **LDPE Films**
1.4 Conversion of alpha olefins to fine chemicals and pharmaceutical products

Industrial applications of linear \( \alpha \)-olefins go beyond their direct use of conversion into various significant fine chemicals and pharmaceutical products. The versatility of the double bond in the olefin molecule could be chemically exploited to synthesize new molecules and improve the value of the olefin products to a greater extent. To date, both homogeneous and heterogeneous catalysts have played a major role in the conversion of olefins to more industrial useful products.\(^{17}\) These involve reactions of \( \alpha \)-olefins with carbon monoxide to give commercially useful products like aldehydes, alcohols and ketones. Oxidation of \( \alpha \)-olefins using molecular oxygen to give epoxides is another useful reaction practiced in industry. Other transformations that convert \( \alpha \)-olefins to more useful chemical and or products include metathesis which is currently to produce a wide range of fine chemicals. In this section, a brief overview of selected transformations of olefins to more useful fine chemicals and pharmaceutical products catalysed by transition metals is described.

1.4.1 Reactions with carbon monoxide

The industrial chemistry of carbon monoxide with olefins embraces one of the most versatile applications of homogeneous catalysis. The reactions of carbon monoxide with olefins fall into two main categories: carbonylation, the insertion of carbon monoxide into an olefin molecule and hydroformylation which is a transition metal catalysed reaction of carbon monoxide and hydrogen resulting in the addition of a hydrogen atom and a formyl group to the olefin double bond. From linear α-olefins, carboxylic acids can be produced by addition of water and carbon monoxide to an olefin, a reaction termed as hydrocarbonylation (Eq. 1.1).\textsuperscript{18} This reaction is catalysed by a variety of transition metal complexes including Ni(CO)\textsubscript{4}, Co\textsubscript{2}(CO)\textsubscript{8} and HPtCl\textsubscript{6}.\textsuperscript{19}

\[ \text{R} + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Ni(CO)}_4} \text{RCOOH} + \text{RCHOH} \]

\textsuperscript{(1.1)}


The synthesis of esters by addition of carbon monoxide and an alcohol to an olefin known as hydroesterification can also be achieved using transition metal catalysts as in the synthesis of carboxylic acids (eq. 1.2). Hydroesterification of alpha olefins at 80 °C and 200 bar in the presence of a bimetallic catalyst based on Sn(II) chloride and either Pt or Pd complexes affords linear esters with up to 99% selectivity. With Pt-based catalysts, selectivity to linear esters increases with olefin chain length, though the reaction rate reaches maximum at around C7 and such catalysts are relatively inactive for carbonylation of substituted or internal olefins.19a

Another useful reaction utilizing CO and α-olefins is the hydroformylation reaction. This constitutes one of the largest homogeneous catalysis employed in industry to convert α-olefins to aldehydes, acids and alcohols (Scheme 1.3). Since its discovery

by Roelen\textsuperscript{21} in 1938, hydroformylation has developed into an extremely important industrial process. All the early work on hydroformylation have been carried out using cobalt catalyst, HCo(CO)\textsubscript{4}, under relatively vigorous conditions (200-400 bar, 150-200 °C). However, disadvantages of Co catalysts include low selectivity towards desired linear isomers, low catalyst stability and substantial formation of byproducts such as ketones and alkanes.

Co-polymerisation of \(\alpha\)-olefins with carbon monoxide is another area that has witnessed enormous growth with the discovery of the less oxophilic late transition metal olefin polymerisation catalyst.\textsuperscript{22} Most notable catalysts are the Brookhart \(\alpha\)-diimine palladium


catalysts which efficiently incorporate CO monomers in the backbone of polyolefins.\textsuperscript{23a,b} Palladium complexes containing fused aromatic N-N ligands have been reported to efficiently catalyse the copolymerisation of CO and alpha olefins.\textsuperscript{23a} Exposure of an acidified methanol of solution of Pd(II) diphosphine chelate to an olefin-CO mixture, leads to the formation of polymers of containing CO monomer inserted in an alternating fashion.\textsuperscript{23b} The resulting polyketone, which has remarkable mechanical strength and thermal strength, has been commercialised as a valuable engineering plastic, but general applications have so far been hindered by its sensitivity to photo-oxidation.

1.4.2 Oxidation of olefins

Oxidation of \(\alpha\)-olefins to give oxygen-containing compounds (alcohols, aldehydes, epoxides) is an extremely important reaction in the chemical industry.\textsuperscript{24} Currently the world production capacity of ethylene oxide is about 17.1 Mt/a. Approximately 75\% is consumed for the production of glycols, i.e. ethylene glycol used in making polyesters and antifreeze, triethyl glycol (solvent, plasticizer, gas dehydration) and higher glycols.\textsuperscript{25}


Originally these oxidations were carried out based on chlorohydrin process, but due to environmental hazards, this process could not be sustained.\textsuperscript{26a} The use of a number of organometallic complexes saw complete phasing out of the chlorine technology. For example, silver based catalyst, Ag/Al\textsubscript{2}O\textsubscript{3}, discovered in the 1940s proved very affordable and environmentally friendly (Scheme 1.4).\textsuperscript{26b}

![Scheme 1.4](image)

The other oxidation process commonly known as the Wacker process uses Pd(II) salts in the oxidation of ethylene to acetaldehyde (eq. 1.4) This process can also be extended to higher olefins, e.g propene to acetone.\textsuperscript{27}

\[
\text{R=CH}_2\text{CH=CH}_2 + [\text{PdCl}_4]^{2-} \xrightarrow{\text{H}_2\text{O}} \text{R-CH}(_2\text{CH}_3)\text{CHO} \\
(1.4)
\]

\begin{itemize}
\end{itemize}
1.4.3 Metathesis of olefins

Olefin metathesis, also known as olefin disproportionation, discovered in the 1950s by Phillips and pioneered by the work of Chauvin, Schrock and Grubbs is one of the most valuable technologies in producing olefins and in further conversions. Depending on the nature of substrate, several specific types of metathesis are possible: Cross Metathesis (CM) for bulk chemicals (Scheme 1.5), Ring Opening Metathesis Polymerisation (ROMP) for specialty plastics and Ring Closing Metathesis (RCM) for fine chemicals. A number of metathesis processes have been implemented industrially on large scale, and research into catalyst and process development is gaining much impetus in both academic and chemical laboratories.

Scheme 1.5

The industrial applications of olefin metathesis are diverse. ROMP processes are unique in that they offer specialty polymer products between those of saturated polyethylene and highly unsaturated polybutadienes. These polymers are used as elastomers and possible replacement for rubber due to their good strength and ageing properties.\textsuperscript{30} RCM and CM offer convenient routes to the synthesis of a wide range of intricate products of relevance to the pharmaceutical, agrochemical and fragrance industries. Companies including Shell and Phillips have developed and operated several metathesis processes based on heterogeneous catalysts for the production of higher value olefin based fine chemical products. For example, 5-decenyl acetate, the major component of the peach twig borer pheromone can be effectively produced from 5-decene and 1,10-diacetoxy-5-decene (eq.1.5) under low temperatures of 5 °C to maintain selectivity using Grubb’s type Ruthenium catalyst.\textsuperscript{31}

\begin{equation}
\begin{array}{c}
\text{AcO} \\
\text{OAc} \\
\text{OAc}
\end{array}
\begin{array}{c}
+ \\
\text{AcO} \\
\text{OAc} \\
\text{OAc}
\end{array}
\end{equation}

(eq.1.5)


From this chapter, the significance of $\alpha$-olefins both from the academic and industrial point of view is enormous. This therefore justifies current research efforts being spent in the design of transition metal catalysts active for the oligomerisation and polymerisation of ethylene and lower molecular weight $\alpha$-olefins ($C_3$-$C_8$) to produce higher $\alpha$-olefins and polymers. This is mainly aimed at designing and developing active, stable and selective catalysts. In the next chapter, a review of nitrogen-donor transition metal complexes as $\alpha$-olefin oligomerisation and polymerisation catalysts is described.
CHAPTER 2

Review of nitrogen-donor transition metal complexes as α-olefin oligomerisation and polymerisation catalysts

2.1 Background information

Transition metal α-olefin oligomerisation and polymerisation catalysts form one of the main classes of present day industrial catalytic processes. The secret behind this development lies in better understanding of how these catalysts work especially homogeneous based systems. This has seen research on the design of homogeneous catalysts both in academic and industrial domains take centre stage with respect to improvement on catalyst activity, selectivity and stability. Numerous reviews on catalyst design based on structure-activity relationships have appeared and the amount of resources currently being spent on this field outlines its usefulness.1

This chapter is a review of the relevant literature to the synthesis of catalyst precursors and α-olefin oligomerisation and polymerisation catalysis. The review of the catalysis is divided into two main parts. The first part covers early transition metal catalysts and the second part reviews late transition metal catalysts.

2.2 Early transition metal olefin polymerisation catalysts

The first highly active \( \alpha \)-olefin polymerisation catalysts were developed by Karl Ziegler and Giulio Natta in 1950. These catalysts are now known as Ziegler-Natta type catalysts and operate under heterogeneous conditions. To date major industrial \( \alpha \)-olefin polymerisation processes are built on this discovery.\(^2\) These catalysts facilitate the production of cheap polyethylene and polypropylene which have greatly revolutionized the polyolefin industry. However, the Ziegler-Natta type catalysts are not without drawbacks. Their ill-defined nature renders them not to be easily amenable to steric and electronic tuning; hence the extent to which product distribution and properties could be modified is severely limited. In addition, the heterogeneous nature of the catalysts makes any significant mechanistic studies essentially impossible.

To circumvent these problems associated with Ziegler-Natta catalysts, a lot of research efforts have been spent on the design of Ziegler-Natta type homogeneous catalysts that allow for the modification of both steric and electronic properties of the catalysts as well as control of product distribution and microstructure. Although the first homogeneous olefin polymerisation catalysts utilizing Group 4 metalloccenes was first reported in 1957,\(^{2c}\) it was not until two decades later that the activity was dramatically increased with

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the discovery of methylaluminoxane (MAO) as an activator. Since then, single-site metallocene catalysts have been the subject of enormous interests and have witnessed their modification to enhance catalyst activity, stability and selectivity. Metallocene catalysts capable of co-polymerisations of ethylene and higher α-olefins have also been discovered by Bercaw and his group. Examples of metallocene catalysts are shown in Figure 2.1a.

The Metallocene catalysts (Figure 2.1a) however do not result in proper control of polymer morphology due to their flexible nature. As a result constraint geometry catalysts (ansa-metallocenes), Figure 2.1c, to allow for control of polymer microstructure due to the rigid backbone hence give uniform active species have been developed. Such examples include catalysts developed by Bercaw and the C2, C5 and C1 symmetric catalysts developed by Waymouth. These catalysts produce polymers with

![Figure 2.1: Group 4 metallocene and constrained geometry catalysts (half-sandwich).](image)

short branches known as linear low density polyethylene (LLDPE).

Majority of the understanding with respect to the performance, basic functioning and limitations of polymerisation catalysts is derived from studies of soluble catalysts. To date a large body of mechanistic work for the homogeneous transition metal catalyzed olefin polymerisation has led to a general mechanism for the polymerisation process as shown in Scheme 2.1. The overall mechanism is broken into three major steps: initiation, chain propagation and chain termination. Initiation involves generation of an active catalyst species through halide abstraction and formation of metal-carbon bond by a co-catalyst usually aluminium alkylating agents (e.g. EtAlCl₂ or MAO) that creates a vacant coordinating site on the metal centre of the active catalyst. Co-catalysts play a

**Initiation**

\[ L_nM-X \xrightarrow{\text{co-catalyst}} L_nM-R \]

**Propagation**

\[ L_nM-R \xrightarrow{\text{migratory insertion}} L_nM-R^+ \xrightarrow{\text{migration}} L_nM-\overbrace{\text{polyethylene}}^\text{propagation} \]

**Chain termination**

\[ L_nM-\overbrace{\text{polyethylene}}^\text{termination} \]

Scheme 2.1: General mechanism of transition metal-catalyzed olefin polymerisation
crucial role in single-site Ziegler-Natta type olefin oligomerisation or polymerisation catalysis. Their role in metal-catalysed oligomerisation or polymerisation reactions can be listed as follows. First is to transform the catalyst precursor into an active catalyst (initiation), Eq. 2.1. Second, an effective activation requires favourable co-catalyst to catalyst precursor interactions and also kinetic/thermodynamic considerations. Finally, the co-catalyst which becomes an anion after activation forms a vital part of a catalytically active cation-anion pair and may significantly influence the activity and nature of products produced.\textsuperscript{1f}

\begin{equation}
\text{activation pathway} \\
\text{Lewis acidity, thermodynamics kinetics, structural match} \\
\text{catalyst activity} \\
\text{catalyst stability} \\
\text{catalyst solubility} \\
\text{product properties}
\end{equation}

(2.1)

To date a number of co-catalysts have been used and they display different activities and determine the nature of the products formed. The first to be used are aluminium alkyls and alkylaluminium dichlorides (Me\textsubscript{3}Al, EtAlCl\textsubscript{2}) in the classical homogeneous Ziegler-Natta catalysts.\textsuperscript{1b} However, the inability of metallocenes activated by alkylaluminium halides to polymerise higher $\alpha$-olefins has limited their applications. A number of attempts have been made to improve the performance of these catalysts. One such attempt led to the discovery of methylaluminoxane (MAO).\textsuperscript{3} Activation using MAO affords highly active catalysts for the polymerisation of ethylene and higher $\alpha$-olefins.
Despite MAO’s excellent activity, its exact nature and activation remains a “black box” and its poor storage stability has also hindered its application. Attempts to enhance the stability of MAO saw the development of modified MAO (MMAO) which contains other alky groups such triisobutyl and triethylaluminium. However, MMAOs are less active compared to MAO. Another group of co-catalysts tested so far include perfluoroaryl boranes and fluoroarylamines, B(C₆F₅)₃ and Al(C₆F₅)₃ respectively discovered by Massey and Park.⁵c-d In combination with group 4 metallocenes alkyls, these co-catalysts promotes highly efficient olefin polymerisation reactions. The major advantage of these co-catalysts over MAO is their ability to allow isolation of crysrallographically characterisable cationic metal complexes hence gives insight into the activation processes.

Chain propagation starts by olefin coordination to the vacant metal centre of the active catalyst (Scheme 2.1). The coordinated olefin monomer subsequently undergoes insertion into the metal-carbon bond. This thus creates a new vacant site. Repetition of this process (chain propagation) results in the polymerisation process until chain termination takes place. Chain termination occurs by β-hydride elimination to release the growing polymer chain from the metal centre. The relative rates of chain propagation ($k_p$) and chain termination ($k_t$) determine the polymer chain length. Three situations arise. First is where $k_p$ is much greater than $k_t$; high molecular weight polymers are formed. In the second is when, $k_p$ and $k_t$ are similar; oligomers with a Schulz-Flory distribution (Figure 2.2) are formed. Lastly is when $k_t$ is much larger than $k_p$; this gives exclusively dimers.
High molecular weight polymers are generally formed from early transition metal catalysts (Groups 4, 5 and 6), while catalysts derived from Group 8 metals favor chain termination through $\beta$-hydride elimination and give mostly oligomers. Depending on the metal centre, increasing the oxidation state is reported to decrease chain propagation. For example, Gambarotta has recently established that while Cr(III) catalysts based on 2,6-bis(cyclohexylthiomethyl)pyridine ligand exclusively give ethylene trimers, catalysts

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obtained from Cr(II) favour chain propagation leading to a wide oligomer distribution of C4-C16 oligomers and polymers.\textsuperscript{7}

Early transition metal catalysts, though very active for olefin polymerisation, have limitations due to their sensitivity to impurities in the monomer feed and high oxophilicity to functionalised monomers like CO, methyl acrylates and vinyl acetates. Thus homopolymers of technically important polar monomers and copolymers of these monomers with olefins are currently being produced by radical high temperature-pressure polymerisation that offers little control of polymer microstructure.\textsuperscript{8} The design of new generation of well defined single-site catalysts that are tolerant to polar monomers is thus currently gaining considerable attention in catalyst research.

2.3 Late transition metal olefin oligomerisation and polymerisation catalysts.

2.3.1 Nickel and palladium N\textsuperscript{O} and N\textsuperscript{P} chelate catalysts

The first example of late transition metal catalyzed olefin oligomerisation or polymerisation was developed by Keim and coworkers and forms the basis of the Shell Higher Olefin Process (SHOP).\textsuperscript{9} The catalyst based on Ni(II) P\textsuperscript{O} chelate (2-1) either oligomerises ethylene to higher linear α-olefins with a Schulz-Flory distribution or

\begin{thebibliography}{9}
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\bibitem{8} K. W. Doak, \textit{In Encyclopaedia of Polymer Science and Engineering}, vol 6 Wiley New York, 1986 pp 386.
\end{thebibliography}
polymerises ethylene to linear polyethylene (Figure 2.3). Consistent with low sensitivity of late transition metals to functionalized monomers, the SHOP catalysts are compatible with polar solvents and can co-polymerise ethylene with functionalized monomers as long as the functional group is separated from the olefin group by one or more methylene units.  

![Figure 2.3 SHOP ethylene oligomerisation and polymerisation system](image)

To date numerous efforts have been made to design \(\alpha\)-olefin oligomerisation and polymerisation catalysts based on N\(^\ominus\)O, N\(^\ominus\)P chelates that could rival the SHOP catalysts. Cationic nickel (2-II) and palladium (2-III) catalysts containing phenacyldiarylphosphine ligands have been used to oligomerise or polymerise ethylene. Catalysts with sterically bulky alkyl substituents on the phosphine group produce polymers while those with less bulky substituents produce oligomers.  

In other attempts to design alternative nickel catalysts that could rival the SHOP catalysts, a series of salicylaldiminato complexes of Ni(II) have been found to catalyze ethylene polymerisation and α-olefin dimerisation reactions with moderate activity.\textsuperscript{12a}

The availability of many sites for substitution on both the phenyl and pyridine rings renders these catalysts versatile and are the best studied of the N\textsuperscript{O} chelate systems. Compounds 2-IV to 2-VI illustrates substituent variations on phenyl and pyridine rings that offer different catalytic activities and product microstructure.

\textbf{2-II} \hspace{1cm} \textbf{2-III}

\textbf{2-IV} \hspace{1cm} \textbf{2-V} \hspace{1cm} \textbf{2-VI}

It is well known that bulky aryl groups on salicylaldiminato ligands promote ligand dissociation (2-IV to 2-VI) thus facilitating olefin coordination and enhanced activity.\(^{12b}\)

In addition, increasing the steric bulk of the N-aryl \textit{ortho} substituents results in increased polymer linearity and high molecular weight polymers. Bulky substituents adjacent to the phenoxide moiety also enhances catalyst stability by preventing decomposition.\(^{12a}\)

Introduction of electron-withdrawing groups, such as halogens and particularly nitro groups, on the phenoxide ring have been shown to increase the productivity of these catalysts.\(^ {13a}\)

More recently Chen \textit{et al.}\(^ {14}\) reported that neutral dinuclear Ni(II) catalysts (2-VII) of arene-bridged salicylaldimine ligands polymerise ethylene albeit with low activity (TON of about 300 kg PE/mol Ni.h. Introduction of electron withdrawing groups such as nitro groups on the phenyl rings was observed to increase the activity of the catalysts significantly. In addition to ethylene, these salicylaldiminato based Ni(II) catalysts also promote homo and copolymerisation of higher \(\alpha\)-olefins such as 1-hexene and 1-octene with ethylene.\(^ {13b}\)

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A new family of N^O chelate Ni(II) ethylene oligomerisation and polymerisation catalysts were reported based on anilinoperinaphthenone ligands by Brookhart and coworkers.\textsuperscript{15a} Catalysts of type 2-VIII are highly active (TOF of 60 000 mol C\textsubscript{2}H\textsubscript{4}/mol Ni.h) but are relatively unstable. In a follow up work, Brookhart reported neutral Ni(II) catalysts derived from aniline-substituted enone ligands bearing CF\textsubscript{3} and COCF\textsubscript{3} electron-withdrawing groups (2-IX). Interestingly catalysts 2-IX show very high activities (TON of 10\textsuperscript{6} kg PE/mol Ni.h) with high stability and half lives exceeding 15 h.\textsuperscript{15b}

Braunstein\textsuperscript{16} and Brookhart\textsuperscript{17} discovered ethylene oligomerisation catalysts based on phosphino-pyridine and phosphino-oxazoline ligands respectively. The N^P Ni(II) catalysts (2-X) trimerise ethylene to 1-hexene (TOF of 61 000 mol C\textsubscript{2}H\textsubscript{4}/mol Ni.h). On the other hand, the phosphine-oxazoline palladium complex (2-XI) catalyses ethylene oligomerisation to give C\textsubscript{4}-C\textsubscript{24} oligomers.

Most of the N^O and N^P nickel and palladium complex show very low activities towards higher α-olefin oligomerisation reactions and in most cases only dimerise the α-higher olefins. Another limitation of these catalysts is their low level of tolerance to polar monomers. Attempts to co-polymerise or co-oligomerise ethylene with commercially significant monomers such as methyl acrylate or vinyl acetate have been unsuccessful. As such, there has been continued search for highly active nitrogen-donor late transition metal catalysts that offer better tolerance to polar monomers and more significantly oligomerise or polymerise higher α-olefins.

2.3.2 Cationic α-diimine nickel and palladium α-olefin oligomerisation and polymerisation catalysts

In 1995 Brookhart and coworkers\textsuperscript{18} opened a new page in the research for transition metal olefin oligomerisation and polymerisations catalysts when they discovered highly active...
active Ni(II) and Pd(II) ethylene and \( \alpha \)-olefin polymerisation catalysts based on \( \alpha \)-diimine ligands (Figure 2.4). The nickel catalysts in particular have shown activities that rival the well established metallocenes. Both the nickel and palladium catalysts polymerise ethylene and other \( \alpha \)-olefins to high molecular weight polymers that possess unique microstructures.

Three key features of these \( \alpha \)-diimine catalysts that make them unique include: (i) highly electrophilic cationic nickel and palladium metal centres; (ii) use of sterically bulky ligands and (iii) use of non-coordinating counter ions. The electrophilicity of the nickel and palladium metal centres results in rapid rates of olefin insertion, while bulky ligands favour chain propagation over termination resulting in the formation of high molecular weight polymers. The use of non-coordinating counter ions provides an accessible coordination site for an incoming olefin. As expected for late transition metal catalysts, rapid \( \beta \)-hydride elimination without loss of olefin results to polymers that are highly branched. The nickel catalysts give polyethylene ranging from linear to branched polymers that have \textit{ca.} 100 branches per 1 000 carbon atoms depending on reaction
conditions. On the other hand, palladium catalysts produce polyethylene containing nearly the same number of branches.

Detailed mechanistic studies by Brookhart and his group\textsuperscript{19} has led to the proposed mechanism shown in Scheme 2.2 to explain the branching observed in these polymerisation reactions.\textsuperscript{19} The alkyl ethylene complex \textit{a} is the catalyst resting state. The turn-over limiting step is the migratory 1,2 insertion of the monomer to form a 14 electron system \textit{b} which can be rapidly trapped by ethylene to reform to an alkyl complex \textit{a}. This 1,2 insertion generally results in the formation of linear polyethylene. In the square planar complexes conversion of \textit{c} to \textit{d} must be an associative process due to the low stability of the three co-ordinate system. It has been observed that the rates of associated displacement and chain transfer (\textit{c} to \textit{d}) are greatly reduced by the steric bulk of the \textit{α}-diimine ligands. This is achieved by blocking the axial approach of the olefin monomers. The subsequent result is a much higher rate of chain propagation than chain transfer rate, hence production of higher molecular weight polyethylene. On the other hand complex \textit{b} can undergo β-hydride elimination to yield \textit{c}. This could undergo further 2,1 reinsertion with opposite regiochemistry to produce a branched alkyl group in \textit{f}. Trapping and insertion of \textit{f} produces a methyl branch, while further chain migration, β-hydride elimination and readdition results in the formation of branched polyethylene.

Scheme 2.2: Mechanism for ethylene polymerisation and isomerisation with Brookhart catalysts

For nickel catalysts, the energy barriers to β-hydride elimination or ethylene insertion are very similar. In each case this is about 14 kcal/mol. Therefore small changes in polymerisation conditions can dramatically affect the amount of branching. However, for palladium catalysts the ethylene insertion barrier is only 9 kcal/mol thus changing the reaction conditions does not appreciably affect the degree of polymer branching. In general α-diimine nickel catalysts are more active (TON = 11, 000 kg PE/mol Ni.h) than their palladium catalysts. The Brookhart type catalysts also polymerise higher α-olefins although exhibit lower activity. For example nickel catalysts polymerise 1-hexene to give high molecular weight poly-1-hexene (TON = 176 kg poly-1-hexene/mol Ni.h). The much lower activities observed for higher α-olefins polymerisations relative to
ethylene for the nickel catalysts are as a consequence of the agostic interaction of the catalyst resting state after methyl migration since chain growth is first order in α-olefin.\textsuperscript{1a}

Another important feature of the Brookhart catalysts is their tolerance to polar monomers and their ability to co-polymerise ethylene and methyl acrylate by an insertion mechanism. For example the nickel complexes co-polymerise ethylene with methyl acrylate at 120 °C and 1 000 psi to produce polyethylene with 0.8% mole per cent incorporation of methyl acrylate (TON = 60 000 kg PE/mol Ni.h in 90 h).\textsuperscript{20} The palladium catalysts are less active with activities of TON of about 100 kg PE/mol Pd.h.\textsuperscript{21} Typical methyl acrylate incorporation for palladium catalysts is about 6% but higher values can be achieved at higher methyl acrylate loadings; though this results in reduced activity.

Since this ground breaking discovery by Brookhart, numerous research efforts have been directed towards the design of other α-diimine nickel and palladium catalysts that are meant to rival the Brookhart catalysts but in most cases they are worse.\textsuperscript{1a, 1c} One such example is a report by Kress and his group\textsuperscript{22} of cationic palladium pyridylimine α-olefin oligomerisation catalysts (2-XII). The activity of this palladium catalyst is only 105 kg

\begin{thebibliography}{9}
\end{thebibliography}

oligomer/mol Pd.h at temperatures of 60 °C. The oligomer fraction is between C<sub>10</sub>-C<sub>30</sub> and interestingly has high level of isomerisation. Laine *et al.*<sup>23</sup> have developed nickel (2-XIII) and palladium (2-IV) catalysts that polymerise ethylene when sterically demanding alkyl groups are introduced on the pyridine ring. Interestingly though, the dichloride palladium complexes (2-IV) did not catalyse ethylene polymerisation when activated with MAO.<sup>23b</sup>

![Chemical structures](image)

**2-XII**  
**2-XIII**  
**2-IV**

2.3.3 *Multidentate nitrogen donor late transition catalysts*

The design of the α-olefin polymerisation catalysts have also witnessed the use of multidentate ligands and other metal centres like iron and cobalt other than the bidentate α-diimine nickel and palladium catalysts. In 1998, Brookhart and Gibson independently discovered that five coordinate 2,6-bis(arylmino)pyridyl Fe(II) and Co(II) dihalides

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(Figure 2.5) form active catalysts for the oligomerisation or polymerisation of ethylene and higher α-olefins when activated with MAO. Remarkably, the activities are higher than those observed for metallocene catalysts. These catalysts offer several advantages over the metallocenes, spanning from ease of preparation and handling to facile tuning of their polymerisation activity by modification of the ligand architecture. It has been established that the size, nature and regiochemistry of the catalysts are crucial in controlling the polymerisation and oligomerisation of α-olefins. For example Fe(II) catalysts with only one methyl substituent on the aryl ring have significant selectivity for

![Figure 2.5: General structure of 2, 6-bis(imino)pyridine Fe(II) and Co(II) complexes](image)


ethylene oligomerisation to linear α-olefins that follows a Schulz-Flory distribution. Reducing the size of the substituents on the aryl rings enhances the catalytic activity of both Fe(II) and Co(II) catalysts but reduces the molecular weight of the polymer. On the other hand, increasing the steric bulk of the aryl substituents leads to a slight reduction in activity but doubles the molecular weight of the polymers formed. The nature of the metal centre is also known to have profound effect on the catalytic behaviour of these catalysts. For example the Fe(II) catalysts show higher activity than the Co(II) analogues and the Co(II) catalysts also produce polymers with lower molecular weights.\textsuperscript{26}

In addition to ethylene, these Fe(II) and Co(II) catalysts also promote efficient oligomerisation of other α-olefins (C\textsubscript{6}-C\textsubscript{20}) producing up to 80% linear oligomers\textsuperscript{27} and 90% of the oligomerisation products are dimers. These catalysts are active over a wide range of temperature (30-80 °C) although activity drops at lower temperature.\textsuperscript{28} To date a wide range of multidentate nitrogen-donor bis(imino)pyridine late transition metal complexes that are active for ethylene and higher olefin oligomerisation and polymerisation have been reported in literature.\textsuperscript{29} Most notable is the work of Bianchini\textsuperscript{30} and coworkers that reports a new type of bimetallic complexes of 2,6-bis(imino)pyridine and (imino)pyridine ligands (2-XV and 2-XVI).\textsuperscript{30} Complexes 2-XV and 2-XVI on

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activation with MAO give active catalysts that oligomerise ethylene to α-olefins (C₄-C₁₄). The dinuclear Co catalysts are exceptionally active with TOF of up to 61 000 mol C₂H₄/mol Co.h compared to a typical mononuclear catalyst in Figure 2.5 that has a TOF of 1 000 mol C₂H₄/mol Co.h. Similar catalytic effect is seen with the Fe catalysts though not as drastic. Interestingly complexes of type 2-XVI on activation with MAO give active catalysts for the polymerisation of ethylene to linear high density polyethylene (LHDPE).³⁰b The type 2-XV Co catalyst is the most active Co ethylene polymerisation catalyst known to date (TON = 64 000 kg PE/mol Co.h.).²⁹ Another significant feature of these ligands is their potential in developing mixed bimetallic compounds. This thus opens avenues for their application as tandem catalysts. It would be interesting to see how such an approach develops in future.

Another new tridentate Fe(II) catalysts based on alkenyl substituted bis(imino)pyridine ligands (2-XVII) have been reported by Alt and coworkers³¹ and catalyze the oligomerisation and polymerisation of ethylene depending on ligand architecture. The unique characteristic of type 2-XVII catalysts is the observed formation of the odd numbered α-olefins (ca. 29%) in the ethylene oligomerisation products. This has been

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attributed to metathesis of internal olefins formed in the oligomerisation reaction. The same phenomenon has been observed by Small.\textsuperscript{31b}

As a follow up to the discovery of tridentate Fe(II) and Co(II) olefin oligomerisation and polymerisation catalysts, the zeal for designing five coordinate Ni(II) halides has also gained momentum in recent years. The N^N^N ligand backbones have been modified by several research groups\textsuperscript{32} to produce catalysts that have moderate to high α-olefin

oligomerisation and polymerisation activities. For example 2-quinoxaliny1-6-iminopyridines Ni(II) complexes (2-XVIII) have been shown to moderately catalyze ethylene oligomerisation to mostly butenes.\textsuperscript{32a} Recently Sun \textit{et al.}\textsuperscript{33} reported ethylene oligomerisation catalysts based on N-((Pyridin-2yl)methylene)quinolin-8-amine derivatives (2-XIX). Depending on the steric bulk of the substituents on the ligand framework the complexes are either monomeric or dimeric in solid state. Upon activation with Et\textsubscript{2}AlCl, activities as high as 49 000 kg oligomer/mol Ni.h are obtained.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{2-XVII.png}
\caption{2-XVII}
\end{figure}

One of the key challenges in the design of olefin oligomerisation and polymerisation catalysts is the stability of the active catalyst species. Various approaches have been adopted by different research groups to achieve this objective. One such approach is the development of hemi-labile ligand systems. The next section covers recent advances in the use of hemi-labile ligands in order to enhance catalyst stability.

### 2.3.4 Hemi-labile nitrogen-donor late transition metal catalysts

The term “hemi-labile ligand,” first introduced by Jeffrey and Rauchfuss in 1979, refers to polydentate ligands which contain at least one substitutionally labile donor group. There are several examples in the literature about the influence of transition metal complexes which contain hemi-labile ligands in the activation of small molecules. In

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olefin oligomerisation or polymerisation catalysis the role of a hemi-labile ligand is mainly to stabilize the active cationic species and hence improving stability of the catalysts. For a hemi-labile ligand to be effective the balance between the donor ability of the hemi-labile group and the incoming monomer is crucial. It is essential that the incoming monomer be more strongly coordinating than the hemi-labile moiety to gain access to a metal centre. A typical sequence of events in the generation and stabilisation of the active species is shown in Scheme 2.3.

![Scheme 2.3](image)

The palladium complexes 2-XX and 2-XXI are typical examples of supposed hemi-labile ligand containing compounds that have been tested for ethylene oligomerisation reactions.\(^{36}\) However, both compounds have extremely low activity (86 mg product after 24 h) or completely inactive suggesting that neither the O-Me or O-H in 2-XX and 2-XXI respectively are hemi-labile.

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Bianchini and coworkers\textsuperscript{37} have successfully established that hemi-labile arm that contain heterocycles are effective in stabilizing the Co(II) catalysts of type 2-XXII. The thienyl analogue was found to be more effective then the furan catalysts. More recently new ethylene oligomerisation $\alpha$-diimine Fe(II) catalysts bearing pendant hemi-labile donor atoms $\alpha$-diimine have been reported by Small\textsuperscript{38} and his group. The sulfur-donor complexes (2-XXIII) give highly active ethylene oligomerisation catalysts (TON of 36 500 kg oligomer/mol.Fe.h) while the oxygen donor (2-XXIV) and nitrogen donor complexes are inactive. In the case of 2-XXIV, the formation of a non-labile complex could arise from the hard base and hard acid interaction (O vs Fe). On the hand the soft base is likely to be labile. This suggests that hemi-lability can be achieved in forming


stable active late transition metal catalysts but it must be bore in mind the concept of hard-hard and soft acid-bases.

\[ \text{2-XXII} \]

\[ \text{2-XXIII} \quad \text{2-XXIV} \]

### 2.3.5 Pyrazolyl based nickel and palladium catalysts

One nitrogen-donor ligand that has not been explored extensively for olefin oligomerisation and polymerisation catalysis is pyrazole and pyrazolyl containing compounds. Since 2002 the Darkwa group has used pyrazole and pyrazolyl nickel and palladium complexes as ethylene oligomerisation and polymerisation catalysts. The appeal for pyrazolyl compounds is in their ease of synthesis and modification of ligand architecture that offers better control of the electronic and steric factors of the catalysts. The first report on pyrazolyl palladium catalyst (2-XXV) for ethylene oligomerisation
and polymerisation reaction was by Jordan et al.\textsuperscript{39} but the catalysts exhibit very low activity.\textsuperscript{39} The first active pyrazole nickel and palladium catalysts (2-XXVI) for ethylene polymerisation were reported in 2004\textsuperscript{40b} and 2002\textsuperscript{40a} respectively. When activated with MAO complexes of type 2-XXVI give moderately active ethylene polymerisation catalysts with TON of 3441 and 1768 kg PE/mol catalyst.h.\textsuperscript{40} Both catalysts produce LHDPE.

![Chemical structures](image)

In attempts to increase the electrophilicity of the metal centres to enhance the catalytic activity of the complexes, electron-withdrawing carbonyl linkers were introduced to produce pyrazolyl palladium catalysts.\textsuperscript{41a} Activities as high as 2 590 kg PE/mol Pd.h were


obtained compared to palladium catalysts 2-XXVI. However, the benzenecarbonyl catalysts are relatively unstable. When 2,6-bis(pyrazol-1-ylcarbonyl)pyridine was used as a ligand the stability of the resultant palladium catalysts improved but at the expense of activity.41b This is presumed to be the result of a second pyrazolyl unit coordinating after activation to give an inactive species (Scheme 2.4 route B). To solve the problems of stability and deactivation another ligand design was necessary.

Scheme 2.4

The current work is a response to the above two problems and is aimed at producing more stable pyrazolyl nickel and palladium catalysts. One approach was to replace the carbonyl linkers with electron-donating methylene groups (Figure 2.6a). The possibility of ligands in Figure 2.4a to coordinate in tridentate fashion as described in Scheme 2.4 was addressed by the use of bidentate (Figure 2.6b) and hemi-labile (Figure 2.6c-d) pyrazolyl compounds. This way we aimed to achieve a balance between catalyst stability
and activity. Based on the above problems, the rationale and objectives of this thesis are described in the next sections.

![Pyrazolyl ligands studied in this thesis](image)

**Figure 2.6: Pyrazolyl ligands studied in this thesis**

### 2.4 Rationale of study

Transition metal catalysed olefin transformation reactions has played a significant role in the petrochemical, fine chemical and pharmaceutical industries. For example the conversion of lighter $\alpha$-olefins ($C_2$-$C_8$) to higher $\alpha$-olefins ($C_{10}$-$C_{20}$) which have found wide applications in the manufacture of plastics, detergents, plasticizers and adhesives is currently receiving much attention. As a result, the development of homogenous catalysts that would oligomerise, polymerise or co-oligomerise these $\alpha$-olefins is of great importance. Homogeneous single-site transition metal catalysts offer several advantages over the well established heterogeneous catalysts. More notable is the ease of control of
product properties in addition to understanding the mechanisms involved in such reactions. This thus allows subtle and intelligent design of active, selective and stable catalysts for specific purposes.

This project therefore aimed to design active and stable nitrogen-donor nickel and palladium catalysts that are highly active for $\alpha$-olefin oligomerisation and polymerisation reactions. In the course of this study we tried to use nitrogen-donor (pyridinyl)benzoazoles as another ligand to form olefin oligomerisation and polymerisation palladium catalysts. These complexes failed woefully in ethylene catalysis, but were found to be very efficient Heck-coupling catalysts. Chapter 6 of this thesis describes the chemistry of these (pyridinyl)benzoazole compounds.

2.5 Objectives

From the rationale above, the objectives of this thesis were as follows:

1. The synthesis and characterization of new pyrazolyl palladium(II) and nickel(II) complexes and their use as olefin oligomerisation and polymerisation catalysts. This was aimed at identifying catalysts that are either as active as or more active than the Brookhart and Gibson type catalysts.

2. The synthesis and characterisation of new substituted (pyridinyl)benzoazole palladium complexes as olefin oligomerisation and polymerisation catalysts was the original aim of this thesis. However, the inability of these compounds to
catalyse olefin oligomerisation and polymerisation reaction led to their use as Heck-coupling catalysts.

3. As the project proceeded, it became imperative to understand the pathways of deactivation or inactivity of some of the compounds investigated. A secondary aim of using Density Functional Theory (DFT) calculations to understand the deactivation pathways or inactivity emerged. This was expected to shed more light on how catalyst performance could be improved.

Chapters 3-6 describe the results of the work done in attempts to realise the above objectives. Chapter 7 summarises the major findings and conclusions derived from the whole thesis and the future prospects of this study.
CHAPTER 3
Multidentate (pyrazol-1-ylmethyl)pyridine palladium complexes: Synthesis, molecular structures, reactions with ethylene and phenylacetylene polymerisation

This chapter is adapted from the paper published in Polyhedron 26 (2007) 851-861 and is entirely based on the experimental work of the first author, Stephen O. Ojwach. Copyright 2006 Elsevier Ltd. The contributions of the first author include synthesis of the ligands and complexes, ethylene and phenylacetylene catalysis, molecular modeling and drafting of the manuscript.

3.1 Introduction
Multidentate nitrogen-donor ligands, such as 2,6-bis(organylimino)pyridine and 2,6-bis(pyrazol-1-ylmethyl)pyridine late transition metal complexes, are good catalysts for the oligomerisation and polymerisation of olefins. Other nitrogen-donor ligands, such as bidentate α-diimine, are also known to form cationic nickel and palladium complexes that polymerise or oligomerise olefins depending on the steric bulk of the ligand backbone. These cationic α-diimine nickel and palladium complexes are often prepared by direct halide abstraction using silver or alkali metal salts of a very weakly -

coordinating or non-coordinating ligands that will not compete with a monomer for the vacant coordination site of an active catalyst\(^3\). It is therefore essential to have a weakly coordinating ligand that would not compete with the incoming monomer for the vacant site of the metal centre of a catalyst and yet would protect the site in the absence of the monomer.

Recently 2,6-bis(pyrazol-1-ylcarbonyl)pyridine palladium complexes have been used as ethylene polymerisation catalysts.\(^4\) The ligands in these precursors are potentially tridentate but only coordinate in a bidentate mode through one pyrazolyl and the pyridine nitrogen atoms, leaving the second pyrazolyl unit uncoordinated. When the complexes are reacted with methylaluminoxane (MAO) as co-catalyst, they form active catalysts for the polymerisation of ethylene to give linear high density polyethylene (LHDPE).\(^4\) However, the activity of the 2,6-bis(pyrazol-1-ylcarbonyl)pyridine palladium catalysts are considerably lower in comparison to 1,3-bis(pyrazol-1-ylcarbonyl)benzene palladium dichloride catalysts.\(^5\) The lower activity is probably due to the potential of 2,6-bis(pyrazol-1-ylcarbonyl)pyridine to bind in a tridentate coordination mode upon removal of a chloride that results in the ethylene monomer competing with the second pyrazolyl unit for the vacant site on the metal in the catalyst.


The stability of the carbonyl linker catalysts was also found to be lower than the bis(pyrazole)palladium(II) catalysts\textsuperscript{5b} and in an attempt to produce more stable catalysts the carbonyl linker has been replaced with a methylene group. Some of the chemistry of 2,6-bis(pyrazol-1-ylmethyl)pyridine have earlier been explored by Steel \textit{et al.}\textsuperscript{6} and others.\textsuperscript{7} However, most of the complexes prepared from PdCl\textsubscript{2} have only proposed structures which have been proven wrong by our current study.

In a report by Steel \textit{et al.}\textsuperscript{6a} a palladium dichloride complex with this 2,6-bis(pyrazol-1-ylmethyl)pyridine was formulated as a trinuclear complex (3-I). Compound 2,6-bis(pyrazol-1-ylmethyl)pyridine was proposed to complex with two palladium dichloride fragments with each binding in a bidentate fashion through one pyrazolyl nitrogen and the pyridine nitrogen. The proposed structure was mainly based on elemental analysis and no \textsuperscript{1}H NMR data was reported for this compound because of its poor solubility. A lack of NMR data for 3-I and the solid state structure of 2,6-bis(3,5-ditertiarybutylpyrazol-1-ylcarbonyl)pyridine palladium dichloride reported by Mohlala \textit{et al.}\textsuperscript{5a}.


el.\textsuperscript{4} casted some doubt on the validity of the proposed structure of 3-1. To improve solubility, 3,5-dimethyl and 3,5-ditertiarybutyl-pyrazolyl analogues of this ligand were prepared and indeed produced soluble palladium complexes which were fully characterized by NMR spectroscopy. The \textsuperscript{1}H NMR spectral data and CHN analysis suggested that one of the pyrazolyl units might not be coordinated. Single crystal X-ray analysis confirmed this suggestion. The rest of this chapter describes how these complexes were prepared, characterised and studied as polymerisation catalysts in ethylene and phenylacetylene reactions.

![3-1](image)

3.2 Experimental section

3.2.1 Materials and instrumentation

Synthetic and \textsuperscript{1}H NMR experimental manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques and glove box. All solvents were of analytical grade and were dried and distilled prior to use. Toluene and dichloromethane were dried and distilled from sodium/benzophenone and P\textsubscript{2}O\textsubscript{5} respectively. The following chemicals: 2,6 bis(chloromethyl)pyridine, tetrabutylammonium bromide, silver triflate and phenylacetylene (98\%) were obtained from Sigma-Aldrich and used as
received. NaBAr₄ (Ar = 3,5-(CF₃)₂C₆H₃) was obtained from Boulder Scientific and used as received. The starting materials 2,6-bis(3,5-dimethylpyrazol-1-ylimethyl)pyridine (L¹)⁶ 3,5-ditertbutylpyrazole,⁸ [PdClMe(COD)],⁹ and [PdCl₂(NCMe)₂],¹⁰ were synthesised following the literature procedures. The NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 200 MHz and ¹³C at 50.1 MHz) at room temperature. The chemical shifts are reported in δ (ppm) and referenced to the residual proton of CHCl₃ in the NMR solvent. Coupling constants are measured in Hertz (Hz). Elemental analyses were performed by the micro analytical laboratory at the University of Cape Town, South Africa, as a service. Polymer molecular weights were determined by gel permeation chromatography on a Waters 600E instrument equipped with a Waters differential refractometer detector (THF, at 30 °C, rate = 1.0 mL/min) and PL–MIXED-Cᵀm columns, using polystyrene standards at the University of Stellenbosch, South Africa also as a service.

3.2.2 Synthesis of ligands and palladium complexes

3.2.2.1 2,6-bis(3,5-di-tertbutylpyrazol-1-ylimethyl)pyridine (L₂)

A mixture of 2,6-bis(bromomethyl)pyridine (1.00 g, 3.79 mmol) and 3,5-di-tert-butylpyrazole (1.36 g, 7.58 mmol) in benzene (40 mL), 40% aqueous NaOH (12 mL) and 40% aqueous tetrabutylammonium bromide (10 drops) was refluxed for 18 h. The organic layer was then separated and evaporated in vacuo. The crude product obtained

was washed with water (40 mL) to afford an analytically pure L2 as a white solid. Yield = 1.38 g (75%). $^1$H NMR (CDCl₃): $\delta$ 1.23 (s, 18H, $^1$Bu, pz); 1.31 (s, 18H, $^1$Bu, pz); 5.55 (s, 4H, CH₂); 5.93 (s, 2H, pz); 6.32 (d, 2H, py, $^3$J_HH = 8.0 Hz); 7.46 (t, 1H, py, $^3$J_HH = 8.0 Hz). Anal. Calc. for C₂₉H₄₅N₅: C, 75.16; H, 9.72; N, 15.12. Found: C, 75.01; H, 9.55; N, 15.43.

### 3.2.2.2 [{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}PdCl₂] (1)

To a solution of L₁ (0.11 g, 0.39 mmol) in CH₂Cl₂ (20 mL) was added [PdCl₂(NCMe)₂] (0.10 g, 0.39 mmol). The resultant pink solution was stirred for 12 h and the product precipitated by addition of hexane (20 mL) to give a pink solid. Yield = 0.10 g (56 %). $^1$H NMR (CDCl₃): $\delta$ 2.45 (s, 6H, CH₃, pz); 2.51 (s, 6H, CH₃, pz); 5.85 (d, 2H, CH₂, $^2$J_HH = 15.2 Hz); 5.93 (s, 1H, pz); 6.17 (d, 2H, CH₂, $^2$J_HH = 15.0 Hz); 6.28 (s, 1H, pz); 8.11 (d, 2H, py, $^3$J_HH = 8.4 Hz); 8.26 (t, 1H, py, $^3$J_HH = 8.4 Hz). Anal. Calc. for C₁₇H₂₁N₅PdCl₂: C, 43.22; H, 4.44; N, 14.83. Found: C, 43.31; H, 4.10; N, 14.91.

### 3.2.2.3 [{2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine}PdClMe] (2)

To a solution of L₁ (0.30 g, 1.07 mmol) in Et₂O (20 mL) was added a solution of [PdClMe(COD)] (0.27 g, 1.07 mmol) in Et₂O (20 mL). A light yellow precipitate formed immediately. The mixture was stirred for 3 h, filtered and the material isolated recrystallised from CH₂Cl₂-hexane to give a light yellow solid. Yield = 0.31 g (68 %). $^1$H NMR (CDCl₃): $\delta$ 0.97 (s, 3H, CH₃, Pd-Me); 2.34 (s, 6H, CH₃, pz); 2.49 (s, 6H, CH₃, pz); 5.68 (d, 2H, CH₂, $^2$J_HH = 15.4 Hz); 5.74 (d, 2H, CH₂, $^2$J_HH = 15.4 Hz); 5.91 (s, 2H, pz); 8.08 (t, 1H, py, $^3$J_HH = 8.4 Hz); 8.15 (d, 2H, py, $^3$J_HH = 8.2 Hz). $^{13}$C NMR (CDCl₃): $\delta$ -7.4;
3.2.2.4 \{2,6-bis(3,5-di-tertbutylpyrazol-1-ylmethyl)pyridine\}PdCl$_2$ (3)

To a solution of [PdCl$_2$(NCMe)] (0.20 g, 0.78 mmol) in CH$_2$Cl$_2$ (20 mL) was added L$_2$ (0.36 g, 0.78 mmol). The clear orange solution was stirred for 24 h after which an equal volume of hexane was added and kept at -4 °C to afford compound 3 as a yellow solid. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a CDCl$_3$ solution of 3 that was used to run $^1$H NMR spectrum. Yield = 0.35 g (71%). $^1$H NMR (CDCl$_3$): $\delta$ 1.27 (s, 9H, $^1$Bu, pz); 1.34 (s, 9H, $^1$Bu, pz); 1.41 (s, 9H, $^1$Bu, pz); 1.75 (s, 9H, $^1$Bu, pz); 5.72 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 18.6 Hz); 5.78 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 15.4 Hz); 5.92 (s, 1H, pz); 5.97 (s, 1H, pz); 6.23 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 15.6 Hz); 7.01 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 19.0 Hz); 7.44 (2H, d, py, $^3$J$_{HH}$ = 8.0 Hz); 7.69 (1H, t, py, $^5$J$_{HH}$ = 8.0 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.1; 30.2; 30.6; 31.1; 31.4; 31.8; 32.0; 33.0; 56.4; 56.7; 100.8; 104.3; 122.9; 124.0; 140.4; 153.2; 154.0; 155.2; 162.0; 164.3; 164.6. Anal. Calc. for C$_{29}$H$_{45}$N$_5$PdCl$_2$.0.5CH$_2$Cl$_2$: C, 52.33; H, 6.59; N, 10.17. Found: C, 52.72; H, 7.08; N, 10.26.

3.2.2.5 \{2,6-bis(3,5-di-tertbutylpyrazol-1-ylmethyl)pyridine\}PdClMe (4)

Compound 4 was prepared according to the procedure for 2 using L$_2$ (0.21 g, 0.45 mmol) and [PdClMe(COD)] (0.12 g, 0.45 mmol). Yield = 0.17 g (60%). $^1$H NMR (CDCl$_3$): $\delta$ 1.03 (s, 3H, CH$_3$, Pd-Me); 1.23 (s, 9H, $^1$Bu, pz); 1.35 (s, 9H, $^1$Bu, pz); 1.41 (s, 9H, $^1$Bu, pz); 1.61 (s, 9H, $^1$Bu, pz); 5.35 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 18.6 Hz); 5.53 (d, 1H, CH$_2$, $^2$J$_{HH}$ = 19.0 Hz); 7.44 (2H, d, py, $^3$J$_{HH}$ = 8.0 Hz); 7.69 (1H, t, py, $^5$J$_{HH}$ = 8.0 Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.1; 30.2; 30.6; 31.1; 31.4; 31.8; 32.0; 33.0; 56.4; 56.7; 100.8; 104.3; 122.9; 124.0; 140.4; 153.2; 154.0; 155.2; 162.0; 164.3; 164.6. Anal. Calc. for C$_{29}$H$_{45}$N$_5$PdCl$_2$.0.5CH$_2$Cl$_2$: C, 52.33; H, 6.59; N, 10.17. Found: C, 52.72; H, 7.08; N, 10.26.
15.0 Hz; 5.93 (s, 1H, pz); 5.95 (s, 1H, pz); 6.11 (d, 1H, CH$_2$; $^2J_{HH} = 15.4$ Hz); 6.87 (d, 1H, CH$_2$; $^2J_{HH} = 19.2$ Hz); 7.21 (d, 2H, py, $^3J_{HH} = 8.0$ Hz); 7.69 (t, 1H, py, $^3J_{HH} = 8.0$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.1; 30.4; 30.6; 31.1; 31.5; 32.6; 55.7; 100.3; 103.8; 121.8; 122.2; 138.5; 152.8; 153.7; 162.1. Anal. Calc. for C$_{30}$H$_{48}$N$_5$PdCl: C, 58.06; H, 7.80; N, 11.28. Found: C, 58.10; H, 8.32; N, 10.13.

The synthesis of 5, 6 and 7 are described as examples of how the cationic complexes were prepared.

3.2.2.6 [{2,6-bis(3,5-dimethylpyrazolylmethyl)pyridine}PdCl]BAr$_4$ (5)

A mixture of 1 (0.10 g, 0.21 mmol) and NaBAr$_4$ (0.20 g, 0.20 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred for 30 min. The resultant mixture containing some Pd black was filtered over celite to give a yellow solution. Hexane (20 mL) was added to the filtrate and kept at -4 °C to afford single crystals suitable for X-ray analysis. Yield = 0.12 g (41%). $^1$H NMR (CDCl$_3$): $\delta$ 2.30 (s, 6H, CH$_3$, pz); 2.35 (s, 6H, CH$_3$, pz); 5.14 (d, 2H, CH$_2$; $^2J_{HH} = 15.0$ Hz); 5.70 (d, 2H, CH$_2$; $^2J_{HH} = 15.0$ Hz); 5.95 (s, 2H, pz); 7.22 (d, 2H, py, $^3J_{HH} = 8.0$ Hz). 7.55 (t, 1H, py, $^3J_{HH} = 8.2$ Hz); 7.49 (s, 4H, BAr$_4$); 7.68 (s, 8H, BAr$_4$). Anal. Calc. for C$_{50}$H$_{35}$BCl$_3$F$_{24}$N$_5$Pd: C, 43.35; H, 2.54; N, 5.10. Found: C, 44.01; H, 2.26; N, 4.72.

3.2.2.7 [{2,6-bis(3,5-dimethylpyrazolylmethyl)pyridine}PdMe]BAr$_4$ (6)

Complex 6 was prepared following the protocol described for 5 using complex 2 (0.05 g, 0.11 mmol) and NaBAr$_4$ (0.10 g, 0.11 mmol) to afford colourless single crystals suitable for X-ray analysis. Yield = 0.15 g (30 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.09 (s, 3H, CH$_3$, Pd-
Me); 2.30 (s, 6H, CH₃, pz); 2.35 (s, 6H, CH₃, pz); 5.14 (d, 2H, CH₂, ²JHH = 15.0 Hz); 5.70
(d, 2H, CH₂, ²JHH = 15.0 Hz); 5.95 (s, 2H, pz); 7.22 (d, 2H, py, ³JHH = 8.0 Hz). 7.55 (t, 1H, py, ³JHH = 8.2 Hz); 7.49 (s, 4H, BAr₄); 7.68 (s, 8H, BAr₄). Anal. Calc. for
C₅₀H₃₆BF₂₄N₅Pd: C, 46.92; H, 2.73; N, 5.47. Found: C, 47.35; H, 2.48; N, 5.48.

3.2.2.8 [(2,6-bis(3,5-di-tertbutylpyrazolylmethyl)pyridine)PdCl]BAr₄ (7)
Complex 7 was synthesized according to the procedure described for 6 using 3 (0.09 g, 0.13 mmol) and NaBAr₄ (0.12 g, 0.13 mmol) which gave 7 as a crystalline orange solid.
Yield = 0.11 g (58%). ¹H NMR (CDCl₃): δ 1.43 (s, 18H, tBu, pz); 1.52 (s, 18H, tBu, pz); 5.68 (d, 2H, CH₂, ²JHH = 15.2 Hz); 6.08 (s, 2H, pz); 6.21 (d, 2H, CH₂, ²JHH = 15.2 Hz); 7.27 (d, 2H, py, ³JHH = 8.0 Hz); 7.50 (t, 1H, py, ³JHH = 8.0 Hz); 7.49 (s, 4H, BAr₄); 7.68 (s, 8H, BAr₄). Anal. Calc. for C₅₉H₅₇BF₂₄N₅PdCl: C, 49.05; H, 3.98; N, 4.85. Found: C, 49.51; H, 4.00; N, 4.97.

3.2.3 Phenylacetylene oligomerisation and polymerisation reactions
In a typical experiment, a solution of AgOTf (0.05 g, 0.2 mmol) in a 20 mL mixture of CH₂Cl₂ and MeCN (1:1) was added to a solution of 1 (0.05 g, 0.1 mmol) in CH₂Cl₂ (20 mL). A white precipitate of AgCl formed immediately, but the mixture was stirred for five minutes and filtered to give a yellow solution of the active catalyst. To this yellow solution was added 50 equivalents of phenylacetylene (0.64 mL, 5 mmol). The yellow solution gradually turned dark red and was stirred for a further 1 h. After the reaction period, the solution was evaporated to dryness to afford a dark brown crude product, which was dissolved in a minimum amount of CH₂Cl₂ and the polymer precipitated by addition of methanol (40 mL). The polyphenylacetylene precipitate was isolated by
filtration, dried and weighed to obtain the percent polymer (Yield = 0.33 g, 51%). The methanol filtrate was allowed to evaporate to dryness to obtain oligomer fractions. Both the oligomers and polymers were characterized by $^1$H NMR spectroscopy and gel permeation chromatography.

3.2.4 Molecular modeling

Molecular modeling experiments were performed using Gaussian03.11 Geometry and energies of the reactants, intermediates and products were computed using a hybrid density functional theory at the B3LYP/LANL2DZ level of theory. All calculations were performed using restricted Hartree-Fock approximations and all structures were optimized without symmetry constraints. The basis set LANL2DZ was used as a standard basis set and was not augmented.

3.2.5 X-ray crystallography

Data Collection

In a typical experiment a colourless crystal of 6 with approximate dimensions 0.49 x 0.43 x 0.18 mm$^3$ was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$_\alpha$ ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about $\omega$ with the exposure time of 10 seconds per frame. A total of 121 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 13911 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 41777 data were harvested by collecting three sets of frames with 0.25º scans in $\omega$ with an exposure time 33 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.$^{12}$
**Structure Solution and Refinement**

The systematic absences in the diffraction data were uniquely consistent for the space group \( P2_1/n \) that yielded chemically reasonable and computationally stable results of refinement.\(^{12}\) A successful solution by the direct methods provided most non-hydrogen atoms from the \( E \)-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless otherwise indicated.

All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The fluorine atoms F4, F5, F6 were disordered over three positions in a 55:25:20 ratio and were refined isotropically. This CF\(_3\) group was refined with an idealized geometry. There is also one solvate molecule of dichloromethane per Pd complex in the lattice. The final least-squares refinement of 765 parameters against 10940 data resulted in residuals \( R \) (based on \( F^2 \) for \( I \geq 2\sigma \)) and \( wR \) (based on \( F^2 \) for all data) of 0.0640 and 0.1738, respectively. The final difference Fourier map contained several peaks near the disordered CF\(_3\) group and were considered noise. The molecular diagrams are drawn with 50% probability ellipsoids.

3.3 Results and discussion

3.3.1 Synthesis of bis(pyrazol-1-ylmethyl)pyridine palladium complexes

Compound 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (L2) was prepared in good yields (75%) via phase transfer catalyzed alkylation of 3,5-ditertbutylpyrazole and 2,6-bis(bromomethyl)pyridine following the literature procedure\(^6\) described for the synthesis of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L1). Compounds L1 and L2 were reacted with either [PdCl\(_2\)(NCMe)\(_2\)] or [PdClMe(COD)] to produce the corresponding complexes 1-4 in moderate to good yields (Scheme 3.1).

![Scheme 3.1](image)

The \(^1\)H NMR spectra of L1 and L2 gave signature peaks of the four CH\(_2\) linker protons as singlets at 5.28 and 5.55 ppm respectively and typical peaks of methyl and tertbutyl at 2.25 and 2.51 ppm and 1.21 and 1.31 ppm respectively. These peaks were diagnostic in the next step to confirm that complexation of the ligands with the palladium salts had occurred. On complexation of L1 and L2, the CH\(_2\) linker protons appeared as AB quartets. In complexes 1 and 2 these signals are between 5.68-6.17 ppm (L1 singlet, 5.28 ppm) confirming the presence of diastereotopic protons in axial and equatorial positions. This inequality arises from different chair and boat conformations that depict the
existence of restricted rotations in the complexes hence the protons could be subjected to
different contributions from ring currents from the pyrazole or pyridine groups on the
NMR time scale. A similar spectrum has been reported for the related Cu complex,
[Cu{(Me2pz-CH2)2py}(PPh3)]ClO4,7a in which the CH2 linker protons were observed as
AB quartets at 4.75 and 5.25 ppm. In complexes 3 and 4, the CH2 linker protons appeared
as four distinct AB quartets with geminal coupling constants ranging from 15.4 to 19.2
Hz (Figure 3.1). This highlights the increased restricted rotation in 3 and 4 due to the
more sterically demanding di-tertbutyl groups, producing both the chair and boat
conformations. The large peak separation of the signals ($\Delta\delta = 1.38$ ppm), however, is
rather unusual. A smaller peak separation between the CH2 linker protons ($\Delta\delta = 0.70$
ppm) of the related Ru complex of L1, [Ru{($\eta^6$-C6H6)(Me2pz-CH2)2py}]PF6,13 has been
reported. Recently Cavell and co-workers reported an even smaller peak separation ($\Delta\delta =$
0.07 ppm) for geminal coupling of the bridging methylene protons of
[Pd($t$BuC$^N$C)Me]BF4; a feature they attributed to slow inversion of the complex.14 In
contrast to the $^1$H spectrum of 3 that shows the CH2 as four quartets, Cavell and co-
workers found that in the chloro analogue of [Pd($t$BuC$^N$C)Cl]BF4 the CH2 protons
appear as a singlet (5.69 ppm). They ascribed this to the lower trans effect of the chloride
ligand, which reduces the Pd-N(py) bond length and gives the ligand backbone greater
ability to undergo unhindered rotation.13

The $^1$H NMR spectra of 3 and 4 could be used to diagnose the bidentate bonding mode of compound L2 in these complexes. For example in the $^1$H NMR spectrum of 3 one set of peaks at 1.41 and 1.75 ppm for tertbutyl protons and 5.92 ppm for the pyrazolyl ring proton were assigned to the bound pyrazolyl unit while peaks at 1.27 and 1.34 ppm and 5.97 ppm were assigned to the ‘dangling’ pyrazolyl unit (Figure 3.1). $^1$H spectrum of 4 also showed one set of peaks at 1.41 and 1.61 ppm for the tertbutyl protons and 5.53 ppm for the pyrazolyl ring proton were assigned to the bound pyrazolyl unit while another set of peaks at 1.23 and 1.35 ppm for the tertbutyl groups and 5.35 ppm for the pyrazolyl ring proton were assigned to the non-coordinating pyrazolyl unit. These assignments are consistent with the solid state structure of 3 (vide infra). Similar $^1$H NMR spectrum has been reported for compound [Pd{(3,5-Bu<sub>2</sub>pz-CO)<sub>2</sub>py}Cl<sub>2</sub>]<sup>4</sup> that contains four signals at 1.14 and 1.65 ppm assigned to the tertbutyl groups of the “dangling” pyrazolyl unit and 1.17 and 1.76 ppm assigned to the tertbutyl groups of the bound pyrazolyl unit.
3.3.2 Reactions of complexes 1-4 with NaBAr₄

In attempts to generate catalysts for the oligomerisation or polymerisation of ethylene, complexes 2 and 4 were reacted with either stoichiometric equivalent of NaBAr₄ or 1000-fold excess of modified methylaluminoxane (MMAO) in a high pressure reactor and the reactor charged with ethylene. No formation of ethylene oligomers or polyethylene was observed. In subsequent experiments performed on a preparative scale according to Scheme 3.2, ¹H NMR spectroscopic analyses suggested the formation of cationic species in which the L₁ and L₂ bind in a tridentate fashion upon chloride abstraction. Figure 3.2 shows the ¹H NMR spectrum of complex 7. For instance tridentate coordination of L₂ in 7 was deduced from the appearance of the four tert-butyl groups as two singlets. This is indicative that both the pyrazolyl units participate in the coordination to Pd hence are equivalent. The cationic species, 5, 6 and 7, were isolated as BAr₄⁻ salts and solid state structures of 5 and 6 (Figures 3.7 and 3.8 respectively) confirmed the tridentate ligand coordination deduced from the NMR data.

![Scheme 3.2](image-url)
Recently Mohlala et al.\textsuperscript{4} reported that [Pd\{(3,5-Me\textsubscript{2}pz-CO\textsubscript{2}py\}Cl\textsubscript{2}] and [Pd\{(3,5-Bu\textsubscript{2}pz-CO\textsubscript{2}py\}Cl\textsubscript{2}] can be activated with MAO to catalyse the polymerisation of ethylene to LHDPE. The inability of the cationic species 6 and 8 to catalyse ethylene polymerisation can be attributed to the strong coordination of the ‘dangling’ pyrazolyl unit in 2 and 4 which blocks the vacant coordination site created upon abstraction of chloride from 2 or 4 since coordination of ethylene is a pre-requisite for polymerisation. In the carbonyl linker complexes, [Pd\{(3,5-Me\textsubscript{2}pz-CO\textsubscript{2}py\}Cl\textsubscript{2}] and [Pd\{(3,5-Bu\textsubscript{2}pz-CO\textsubscript{2}py\}Cl\textsubscript{2}], used to catalyze the polymerisation of ethylene\textsuperscript{4}, it is likely that upon activation with MAO, similar tridentate cationic species are formed but under high ethylene pressure, one of the coordinated pyrazolyl units dissociates from the Pd centre to allow the ethylene to coordinate and undergo subsequent insertion to form polyethylene (Scheme 3.3). When 6 and 8 were subjected to ethylene pressures up to 50 bar, there was no formation of polyethylene. This observation highlights the strength of the Pd-N(pz) bonds in 6 and 8.
relative to the binding affinity of the ethylene monomer and would explain why neither 6 nor 8 catalyzed polyethylene formation. The fact that carbonyl linker compounds catalyze the polymerisation of ethylene is an indicative that the pyrazolyl rings in these units are weaker binding than their methylene linker analogues.

![Scheme 3.3]

**Scheme 3.3**

### 3.3.3 DFT studies of the activation and ethylene coordination barriers of the palladium complexes

In order to understand why complexes 1-4 did not polymerise ethylene, density functional theory studies at the B3LYP/LANL2DZ level of theory to determine the energies of formation of the tridentate species and ethylene coordination barriers for the cationic compounds of the simplified analogues were performed. For comparison, ethylene coordination barriers for the Brookhart type palladium α-diimine catalyst previously studied by Mokoruma et al.\textsuperscript{15} at the B3LYP/BS1 level of theory were also computed. The energies for the formation of the tridentate bound cationic species 1b from the bidentate system 1a were computed indirectly from enthalpies of formation of 1a, 1b and Cl\textsuperscript{−} under the same approximations (Eq 3.1).

Calculations of the enthalpies of formation of the tridentate species were performed to establish the feasibility of the transformation shown in Eq. 3.1. In a typical chemical reaction, a negative enthalpy would mean that the reaction is feasible (spontaneous) while a positive enthalpy implies that the process is not feasible. From the results obtained in Eq. 3.1 a positive enthalpy of formation of $\text{1b}$ from $\text{1a}$ was found as $\Delta H = 107.4 \text{ kcal/mol}$ (1 kcal = 4.184 J). This indicates the transformation of $\text{1a}$ to $\text{1b}$ is not spontaneous and that the neutral complex $\text{1a}$ is more stable than $\text{1b}$. Figure 3.3a shows the optimised structures of $\text{1a}$ and $\text{1b}$.

Figure 3.3a: Optimized geometries of compounds $\text{1a}$ and $\text{1b}$ as computed by DFT-B3LYP/LANL2DZ.
As proposed by Brookhart and co-workers\textsuperscript{3a} the active intermediate (Figure 3.3b, \textbf{B1}) for the olefin coordination process is the three coordinate 14 electron system with a vacant olefin coordination site. The coordination of ethylene to the cationic compound \textbf{1b} must first involve breaking of one of the Pd-pz bonds to form the ethylene complex \textbf{1c}. From the DFT calculations, this process was not thermodynamically feasible with an energy barrier of $\Delta H = +1.7$ kcal/mol and $\Delta G = +12.6$ kcal/mol. This positive value is consistent with our experimental findings which did not result in any polymer formation due to the inability of ethylene monomer to break one of the Pd-pz bonds to initiate the polymerisation process. The coordination energy barrier for the Brookhart catalyst (\textbf{B1}) to form the ethylene complex (\textbf{B2}) was found to be $\Delta H = -29.4$ kcal/mol with $\Delta G = -18.4$ kcal/mol and is significantly lower (favorable) compared to the bis(pyrazolyl)pyridine palladium complex ($\Delta H = 107.4$ kcal/mol). This is in good agreement with the findings of Morokuma \textit{et al.}\textsuperscript{15} ($\Delta G = -20.1$ kcal/mol) at the B3LYP/BS1 level of theory with Gaussian94 program. This might explain why the Brookhart catalysts are highly active in ethylene polymerisation reactions compared to the inactive bis(pyrazolylmethyl)pyridine palladium complexes. Typical $\Delta G$ values of ethylene coordination to the vacant metal centres are known to be between -30 to -60 kcal/mol.\textsuperscript{16} Figure 3.3b shows the optimised structures of the ethylene complexes.

Electrophilicity of the bis(pyrazolylmethyl)pyridine palladium complexes was also investigated and compared to those of the previously reported carbonyl linker complexes\textsuperscript{10} and the Brookhart type catalysts by Mulliken population analysis. The trend clearly depicts the effect of the linker on the palladium metal centre charge; the carbonyl linker complexes, \([\text{Pd}\{\text{pzCO}\}_2\text{py}\}\text{MeCl}]\) has significantly higher net charge of 0.407 compared to the methylene linker complex \(1\text{a}\) of 0.347. As expected the Brookhart type catalyst (\textbf{B1}) was found to be the most electrophilic with a net charge of 0.500. The lower electrophilicity of the methylene linker pyrazolyl palladium complexes could also be responsible for their inabilities to polymerise ethylene due to reduced chances of ethylene coordination to the metal centre. Consistent with literature reports\textsuperscript{17} that coordination of ethylene to a metal centre results in decreased electrophilicity of the metal centre, ethylene coordination to the metal centres to form \(1\text{c}\) and \(\textbf{B2}\) resulted in the

Figure 3.3b: Optimized geometries of the ethylene complexes as computed by DFT-B3LYP/LANL2DZ
reduction of the positive net palladium net charge. For example the ethylene complexes \(1c\) and \(B2\) have charges of 0.166 and 0.297 compared to the charges of 0.347 and 0.500 of \(1b\) and \(B1\) respectively.

3.3.4 Stability of cationic and neutral species of 1-4

Following the attempts to establish the ability of \(2\) and \(4\) to produce active catalysts for ethylene polymerisation as described in section 3.3.2, the stability of cationic species that contain CH\(_2\) and CO linkers generated from complexes \(1-4\), \([\text{Pd}\{(3,5-\text{Me}_2\text{pz-CO})_2\text{py}\}\text{Cl}_2]\) and \([\text{Pd}\{(3,5-\text{tBu}_2\text{pz-CO})_2\text{py}\}\text{Cl}_2]\) was investigated. In a typical experiment \(1\) (6 mg, 0.012 mmol) and NaBAR\(_4\) (12 mg, 0.012 mmol) were placed in a J-Young NMR tube and about 0.4 mL CDCl\(_3\) added. The reaction was then followed by \(^1\text{H}\) NMR spectroscopy. In all cases the cationic species of \(5-8\) were formed within 10 min but the formation of \([\text{Pd}\{(3,5-\text{Me}_2\text{pz-CO})_2\text{py}\}\text{Cl}]^+\) (9) and \([\text{Pd}\{(3,5-\text{tBu}_2\text{pz-CO})_2\text{py}\}\text{Cl}]^+\) (10) took up to 4 h to go to completion. The stabilities of \(5-10\) also varied. By using the proton peaks of the BAR\(_4^-\) counter ion in these salts as internal standard, it was established that species \(5-8\) were stable for 30 days without any signs of decomposition while \(9\) and \(10\) had \(t_{1/2}\) of 14 and 2 days respectively (Table 3.1). Figure 3.4 is a \(^1\text{H}\) NMR spectrum that shows the formation and decomposition of the cationic species 9. From the \(^1\text{H}\) NMR spectrum, the complete formation of 9 is evident from the appearance of only signal at 6.57 ppm assigned to the 4-H pyrazolyl proton and the disappearance of the two signals at 6.21 and 6.41 ppm corresponding to the 4-H pyrazolyl protons of \([\text{Pd}\{(3,5-\text{tBu}_2\text{pz-CO})_2\text{py}\}\text{Cl}_2]\). Decomposition is depicted by the appearance of two signals between 6.30 to 6.48 ppm assigned to the ligand protons and some unidentified decomposition products.
at 6.10 and 6.20 ppm. The low stabilities of 9 and 10 compared to 5-8 could arise from the reduced donor ability of the pyrazolyl nitrogen resulting from the presence of electron-withdrawing carbonyl linkers.

Table 3.1: Selected $^1$H NMR signals and half lives ($t_{1/2}$) of the cationic complexes 5-10 in CDCl$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR (CDCl$_3$)</th>
<th>$t_{1/2}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_2$</td>
<td>4H-pz</td>
</tr>
<tr>
<td>5</td>
<td>5.25, 5.95</td>
<td>5.99</td>
</tr>
<tr>
<td>6</td>
<td>5.14, 5.70</td>
<td>5.95</td>
</tr>
<tr>
<td>7</td>
<td>5.74, 6.31</td>
<td>6.07</td>
</tr>
<tr>
<td>8</td>
<td>5.68, 6.21</td>
<td>6.08</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>6.38</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>6.57</td>
</tr>
</tbody>
</table>
Another interesting observation made during attempts to grow crystals of complexes 1-4 is that the species that crystallised depended on the procedure used. Attempts to grow crystals of 1 and 3 directly from the mother liquor (reaction mixture) gave crystals of cationic species of tridentately bound L1 and L2 which have \([\text{Pd}_2\text{Cl}_6]^{2-}\) as counter ion (Figures 3.9 and 3.10) within 7 days. On the other hand, when 3 was precipitated out initially from the reaction mixture and subsequently re-dissolved in \(\text{CH}_2\text{Cl}_2\), X-ray quality crystals of 3 were obtained (Figure 3.6). However, when crystals of 3 were dissolved in \(\text{CDCl}_3\) and monitored by \(^1\text{H}\) NMR spectroscopy for 21 days no sign of forming the cationic species 12 was observed. The formation of 11 and 12 from the mother liquor is therefore presumed to occur via a decomposition pathway that might be
initiated by the presence of traces of [PdCl₂(NCMe)₂] (Scheme 3.4). The traces of [PdCl₂(NCMe)₂] might undergo disassociation to form PdCl₂ salt. Abstraction of the Cl⁻ ligand from the neutral complex by PdCl₂ produces a 14-electron cationic species and a PdCl₃⁻ anion. Stabilization of the 14-electron species through coordination of the previously non-coordinated pyrazolyl unit results in the formation of the tridentately bound cationic species. Dimerisation of the PdCl₃⁻ produces the counter anion Pd₂Cl₆ (Scheme 3.4). Since Pd₂Cl₆ has a net negative charge of -2, two moles of cationic palladium complexes are formed to balance the compounds 11 and 12.

Scheme 3.4

In a typical decomposition of palladium complexes, one expects the falling off of the ligand unit to give Pd(0). However the donor ability of the ligand could result in more stable palladium complexes and hence resist ligand disassociation. Herrmann et al.¹⁸

have reported that silver complexes of tetrahydropyrimid-2-ylenes do not undergo ligand disassociation readily. Attempts to transfer the carbene ligand from silver to palladium failed but instead the Cl⁻ ligand was transferred to the palladium metal. They attributed this behaviour to the stronger donor ability of the tetrahydropyrimid-2-ylenes carbene ligand that hinders ligand dissociation. The formation of the stable cationic complexes of 11 and 12 instead of decomposition to Pd(0) is thus believed to be driven by the stronger donor abilities of L₁ and L₂.

Both 11 and 12 crystallized with solvent molecules and rapidly lost solvent when crystals were removed from the mother liquor, the solids formed were insoluble. It was therefore difficult to further characterize these materials.

3.3.5 Oligomerisation and polymerisation of phenylacetylene

The binding affinity of the monomer is important to the formation of polymers in these reactions since in experiments using phenylacetylene instead of ethylene, formation of phenylacetylene oligomers and polymers was observed (Table 3.2). In the phenylacetylene reactions the active catalysts were generated by reacting complexes 1-4 with AgOTf as halide abstractor in a mixture of CH₂Cl₂ and MeCN (3:1). The ability of catalysts generated from 1-4 to oligomerise and polymerise phenylacetylene therefore highlights the significance of the reactivity and the binding affinity of the incoming monomer in displacing or competing with one of the Pd-N(pz) bonds prior to coordination to the metal centre. Scheme 3.5, route A shows how the active catalysts were generated in situ from the chloro methyl complexes 2 and 4. The activities of catalysts 1-4 were found
to range from 36-51% conversions. Catalysts 1 and 2 bearing methyl substituents on the pyrazolyl ligand showed higher activity than the tertbutyl analogues 3 and 4 (Table 3.2, entries 1-4). It is likely that the bulkier tertbutyl group hinders monomer coordination resulting in low product yields. However, the low percentage conversions observed for catalysts 1-4 (36-55%) compared to 90% conversion\textsuperscript{19} obtained for the carbonyl linker and bis(pyrazole)palladium(II) complexes under similar conditions suggests the possibility of a competing deactivation pathway. This could arise from the formation of the inactive cationic tridentate species (Scheme 3.5, route B) which blocks monomer coordination. This phenomenon might also support the slow initiation observed for catalysts 1-4 as opposed to rapid initiation observed for simple pyrazole and carbonyl linker pyrazolyl palladium complexes.\textsuperscript{19}

Table 3.2: Phenylacetylene oligomerisation and polymerisation data

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>%Conversion</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>%Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>51</td>
<td>2552</td>
<td>1575</td>
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</tr>
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<td>2</td>
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<td>47</td>
<td>3444</td>
<td>1893</td>
<td>1.82</td>
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</tr>
<tr>
<td>3</td>
<td>3</td>
<td>36</td>
<td>2303</td>
<td>1466</td>
<td>1.57</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>38</td>
<td>2062</td>
<td>1350</td>
<td>1.52</td>
<td>74</td>
</tr>
<tr>
<td>5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1</td>
<td>35</td>
<td>2716</td>
<td>1697</td>
<td>1.72</td>
<td>-</td>
</tr>
<tr>
<td>6&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1</td>
<td>55</td>
<td>2230 (620)</td>
<td>1523 (619)</td>
<td>1.48 (1.00)</td>
<td>-</td>
</tr>
<tr>
<td>7&lt;sup&gt;g&lt;/sup&gt;</td>
<td>2</td>
<td>47</td>
<td>3613 (684)</td>
<td>2187 (678)</td>
<td>1.65 (1.01)</td>
<td>-</td>
</tr>
<tr>
<td>8&lt;sup&gt;h&lt;/sup&gt;</td>
<td>2</td>
<td>12</td>
<td>860</td>
<td>797</td>
<td>1.01</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Conditions: Time = 60 min unless stated otherwise; amount of monomer = 0.64 mL; solvent: CH$_2$Cl$_2$:MeCN (40 mL); 3:1, temp = 25 °C; [Pd] = 1.0 x 10$^{-3}$ mol; Phenylacetylene:[Pd] = 50:1.

<sup>b</sup>Determined by the total mass of the crude product as a percentage of monomer used.

<sup>c</sup>Determined by room temperature GPC using polystyrene standards.

<sup>d</sup>Determined by $^1$H NMR analysis.

<sup>e</sup>Time = 30 min.

<sup>f</sup>Time = 120 min.

<sup>g</sup>Crude product (mixture of oligomer and polymer).

<sup>h</sup>Oligomer fraction.

Time dependent polymerisation experiments with catalyst 1 (Table 3.2, entries 1, 5 and 6) showed little variation in the percent conversion of monomer after 60 min. This is a typical feature involving catalyst decomposition with time<sup>20</sup> and in our case would suggest active catalysts forming tridentate species via route B in Scheme 3.5.

---

The stereochemistry of the polymers was determined by $^1$H NMR spectroscopy. A typical $^1$H NMR spectrum of polymers obtained showed a sharp singlet at 5.85 ppm for the vinylic protons, and broad singlets at 6.65 and 6.91 ppm corresponding to the phenyl ortho and meta protons respectively. From the $^1$H NMR spectra (Figure 3.5), it is evident that all the polymers were a mixture of cis-transoidal and trans-cisoidal$^{21}$ with the percentage cis content ranging from 44-80 (Table 3.2, entries 1-4). The cis and trans content of the polyphenylacetylene formed were established by the NMR method reported by Perec et al.$^{21a}$ (Eq. 3.2). However, there was no clear dependence of the polymer stereochemistry with respect to catalyst structure.

\[
cis \% = \frac{A_{5.82}}{(A_{\text{total}}/6)} \times 100 \quad \text{or} \quad cis \% = \frac{A_{5.82} \cdot 10^4}{A_{\text{total}} \cdot 16.66}
\]  

(3.2)

where $A_{5.82}$ = the integrated peak area of the vinyl proton in the cis isomer and $A_{\text{total}}$ = the total integrated peak area of the polymer spectrum.

Figure 3.5: Typical $^1$H NMR spectrum of polyphenylacetylene obtained
Room temperature GPC analysis showed the presence of both oligomers ($M_w = 620-860$) and low molecular weight polymers ($M_w = 2062-3444$) (Table 3.2, entries 1-4, 7 and 9). For example analysis of the crude products from catalysts 2 (Table 3.2, entry 7) gave a bimodal distribution GPC trace corresponding to oligomers of average $M_w$ of 684 and polymers of average $M_w$ of 3613. Upon purification of this product, the oligomers (methanol soluble fraction) and polymers (methanol insoluble) gave average $M_w$ of 860 and 3444 respectively.

The study of ligand steric effects with the objective of understanding the quantitative relationship between ligand bulk and reactivity has been instrumental in the rational ligand design in transition metal catalysts. It has been shown that even one substituent on the ligand backbone is sufficient to introduce new features into the catalytic behaviour and reactivity in metal complexes. The vastly used steric and stereochemical parameters for ligand characterization include Tolman cone angle ($\theta$) developed by Tolman and refers to the sum of the half-vertex angles for $n$ unsymmetrical groups in a ligand multiplied by two (Eq. 3.3). However this approach only considers the behaviour of individual ligands in certain systems without consideration of all inter-ligand steric

effects in a given molecule. This has rendered the Tolman angle approach less accurate and has limited its application. To advance the understanding of ligand steric effects on catalytic behaviour of metal complexes, the group of Coville\textsuperscript{23} has developed quantification of ligand-ligand interaction using solid angles in organometallic complexes. The solid angle ($\Omega$) is defined as the surface area of that part of a solid projected onto the surface of a unit sphere. It is calculated from the formula given in Eq. 3.4.

\[ \theta = 2 \sum_{i=1}^{n} \frac{\theta_i}{2} \]  
\[ \Omega = \frac{A}{r^2} \]  

Where $\theta$ = the Tolman cone angle  
$n$ = the number of unsymmetrical groups in a ligand  
$\Omega$ = Solid angle  
$A$ = Area of the shadow projected by the ligand on metal sphere  
$R$ = radius of the metal sphere

In order to probe the influence of ligand-ligand steric repulsions on the catalytic behaviour of complexes 1-4 in phenylacetylene polymerisation reactions, the structurally

characterised complexes 3, 5, 6, 11, and 12 from the point of view of the ligand solid angles expressed in percentage of the metal coordination sphere shielded by each ligand were examined using program Solid G developed by Guzei and Wendt.\textsuperscript{24} Such an approach provided a quantitative measure of the steric bulk of the ligands. The tridentate ligands in 5, 6, and 11 shield on average 59.6(10)\% of the palladium coordination sphere. The $\kappa^3$-(tBuN$^N^N^N$) ligand in 12 shields an enormous 70.1\% of the central metal, and the difference of over 10\% from its methyl analogue is very significant in terms of dynamic behaviour. As a reference, even ca. 1\% changes in the value of a ligand solid angle can affect the ligand’s coordination mode.\textsuperscript{24b} However, it is interesting to note the size of the $\kappa^2$-(tBuN$^N^N^N$) ligand in 3; the shielding percentage of this ligand is only 51.0\%, and thus the flexibility of (tBuN$^N^N^N$) can play a major role in the kinetics of the system.

### 3.3.6 Molecular structure determination by single crystal X-ray crystallography

Single crystals suitable for X-ray analysis of complexes 3 and 5 were grown by slow evaporation of dichloromethane solvent at room temperature while crystals of 6 were grown by slow diffusion of hexane into dichloromethane at -4 °C. In other attempts to obtain crystals of 1 and 3, cationic tridentate palladium complexes 2[(L1)PdCl]$^+$ (11) and 2[(L2)PdCl]$^+$ (12) with [Pd$_2$Cl$_6$]$^{2-}$ counter ions were obtained as described earlier. Crystallographic data for 3, 5, 6, 11 and 12 are presented in Table 3.3, while selected bond lengths and angles are given in Table 3.4. Solid state structures of 3, 5, 6, 11 and 12

are shown in Figures 3.6-3.10 respectively. The five palladium complexes contain the central metal in a slightly distorted square planar geometry. In the structure of 3 (Figure 3.6) the nitrogen atom, N5, of the free pyrazolyl unit is directed away from the palladium metal. It is therefore evident that the rotation about the CH₂ linker in the \(K^2\ldots2,6\ldots\{(3,5-tBu₂pzCH₂)₂py\} ligand yields a \(K^3\ldots2,6\ldots\{(3,5-tBu₂pzCH₂)₂py\} ligand in the cationic species 5 (Figure 3.7). The \([Pd₂Cl₆]^{2-}\) in the structures of 11 and 12 occupies a crystallographic inversion centre with the two cationic palladium complexes residing on each side of the anion. The spatial arrangement of the cationic palladium moieties in 11 and 12 is such that the Pd-Cl bonds of the cationic complexes are facing away from the central \([Pd₂Cl₆]^{2-}\) unit.

![Figure 3.6: Molecular structure of complex 3 shown with 50% probability ellipsoids](image)
Figure 3.7: Molecular structure of cation of 5 drawn with 50% probability. The boron counter ion is omitted for clarity.

Figure 3.8: Molecular structure of cation of 6 shown with 50% probability ellipsoids. The boron counter ion is omitted for clarity.
Table 3.3: Crystal data and structure refinement parameters for compounds 3, 5, 6, 11 and 12.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>3</th>
<th>5</th>
<th>6</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₃₁H₄₇Cl₈N₅Pd</td>
<td>C₅₀H₃₅B Cl₂F₂₄ N₅ Pd</td>
<td>C₅₀H₃₆B F₂₄ N₅ Pd</td>
<td>C₃₈H₄₆Cl₂₀ N₁₀ Pd₄</td>
<td>C₆₄H₁₀₂Cl₂₀ N₁₀ Pd₄</td>
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<td>100(2) K</td>
<td>100(2) K</td>
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<td>Space group</td>
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<td>P₁</td>
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<td>10.8623(16)</td>
<td>9.6999(17)</td>
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<td>17.848(3)</td>
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<td>26.862(4)</td>
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<td>90°</td>
<td>87.410(3)°</td>
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<td>Completeness to theta</td>
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<td>1.036</td>
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<td>3.243 and -1.802 e.Å⁻³</td>
<td>1.353 and -1.309 e.Å⁻³</td>
<td>1.275 and -1.660 e.Å⁻³</td>
<td>0.835 and -0.636 e.Å⁻³</td>
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### Table 3.4: Selected bond lengths [Å] and bond angles [°] for 3, 5, 6, 11 and 12

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<th>Bond lengths [Å]</th>
<th>3</th>
<th>5</th>
<th>6</th>
<th>11</th>
<th>12</th>
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<td>X = Cl(2) Pd(1)-N(1)</td>
<td>2.026(3)</td>
<td>2.007(4)</td>
<td>2.028(2)</td>
<td>2.011(5)</td>
<td>2.029(2)</td>
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<td>2.042(3)</td>
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<td>2.010(5)</td>
<td>1.9925(19)</td>
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<tr>
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<td>2.029(3)</td>
<td>2.2838(18)</td>
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<tr>
<td>N(1) –N(2)</td>
<td>1.371(4)</td>
<td>1.366(6)</td>
<td>1.369(3)</td>
<td>1.381(7)</td>
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<td>1.367(6)</td>
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<table>
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<tr>
<th>Bond angles [°]</th>
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<td>175.1(1)</td>
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<td>93.73(15)</td>
<td>92.13(11)</td>
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<td>175.1(2)</td>
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<td>86.9(2)</td>
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The average bond lengths of the Pd-N$_{(p)z}$ of 2.026(3) Å, 2.015(4) Å, 2.028(2) Å, 2.011(5) Å and 2.029(2) Å of complexes 3, 5, 6, 11 and 12 respectively are all slightly shorter than the average Pd-N(pz) bond length of 2.06(9) Å obtained by averaging 607 bonds in 229 relevant complexes reported to the Cambridge Structural Database (CSD)$^{25}$ but the difference is not statistically significant because of the high uncertainties for the average Pd-N$_{(p)z}$ bond length of 2.06(9) Å.
The longer Pd–N(pz) distance (2.028(2) Å) of 6 compared to Pd–N(pz) (2.007(5) Å) of 5 is statistically significant and might arise from the high *trans* influence of the methyl group compared to the chloro group. It is, however, conceivable that with the chloro or methyl group in *cis* position relative to the N(pz), the differences in Pd-N(pz) distances for 5 and 6 could be steric rather than electronic. Nevertheless, a similar trend is observed in the Pd-N(py) bond lengths 2.128(2) Å for 6 and 2.031(4) Å for 5. A shorter Pd-N(py) bond length of 2.036(3) Å has been recently reported for the chloro complex, [Pd(C^N^C)Cl]BF₄ compared to 2.116(3) Å of the methyl analogue, [Pd(C^N^C)Me]BF₄.²⁶

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Figure 3.10: Solid state structure of solvated complex 12 shown with 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

The average bond length of Pd-N\(_{\text{py}}\) of 2.028(2) Å and Pd-C of 2.044(1) Å of 6 are significantly shorter than those reported for the carbene methylene bridged cationic Pd complex [Pd(C\(^2\)N\(^2\)C)Me]BF\(_4\) of 2.0154(9) Å and 2.044(1) Å respectively [20]. The Pd–Cl bond distances of 2.2887(11) Å (3), 2.2803(13) Å (5), 2.2838(18) Å (11) and 2.2872(6) Å (12) in the mononuclear complexes agree well with the average bond distances of 2.33(5) Å determined by averaging 2055 Pd–Cl bonds in 1268 relevant complexes reported to the CSD.\(^{25}\) Interestingly, the average Pd–N\(_{\text{pz}}\) bond distances of 2.026(3) Å (3) and 2.029(2) Å (12) and Pd–Cl bond distances of 2.887(11) Å (3) and 2.2872(6) Å (12) are statistically similar even though the Pd metal in 12 is more electrophilic and is expected to have shorter bond distances. Surprisingly, the longer Pd-N\(_{\text{pz}}\) distance of 2.029(2) Å is observed for 11 than for 12 (2.011(2) Å) that contains a bulkier tridentate ligand.
3.4 Conclusions

The potentially tridentate bis(pyrazol-1-ylmethyl)pyridine ligands (L1 and L2) form monometallic palladium complexes with one uncoordinated pyrazolyl unit when complexed with either [PdCl₂(NCMe)₂] or [PdClMe(COD)]. In attempts to generate active catalysts for ethylene oligomerisation and polymerisation reactions, chloride abstraction from 2 and 4 gave inactive cationic tridentate species. The same palladium precursors however, formed catalysts that catalyzed the oligomerisation and polymerisation of the more reactive phenylacetylene. The products formed were a mixture of phenylacetylene oligomers and low molecular weight polyphenylacetylene. Competitive coordination of phenylacetylene and the second pyrazolyl unit to the palladium centre appears to be responsible for the low activity of the catalysts. Molecular modeling revealed that coordination of ethylene to the metal centre of the tridentate cationic species of bis(pyrazolylmethyl)pyridine palladium complexes is thermodynamically not favoured. The high ethylene coordination barriers in addition to the low charge of the palladium metal centre might explain why the bis(pyrazolylmethyl)pyridine palladium complexes did not produce active catalysts for ethylene polymerisation.

The difficulties encountered in using ligands L1 and L2 palladium complexes for ethylene oligomerisation or polymerisation reactions led to the change of ligand design from ligands containing two pyrazolyl units and one pyridine to one pyrazolyl unit and one pyridine. This work is described in chapter 4.
CHAPTER 4

Cationic (pyazol-1-ylmethyl)pyridine palladium complexes: Synthesis, molecular structures, and reactions with ethylene, and sulfur dioxide

4.1 Introduction

Cationic palladium(II) complexes containing symmetrical 1,4-diazabutadiene ligands with bulky aryl substituents (4-I) at the nitrogen atoms have been shown to efficiently catalyze \( \alpha \)-olefin oligomerisation and polymerisation reactions.\(^1\) On the other hand, palladium complexes of nitrogen-donor ligands such as 2,2'-dipyridyl or 1,10-phenanthroline with less sterically demanding substituents (4-II) results in the dimerisation of ethylene.\(^2\)

\[\text{R} = \text{H, Me, iPr; } R' = \text{H, Me} \]
\[\text{L} = \text{Et}_2\text{O, NCMe; } \text{Ar} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\]


Recently cationic 2-(acetyl-2,6-diisopropylphenylimine)pyridine palladium catalysts (4-III)\(^3\) were shown to oligomerise ethylene with activities of 105 kg oligomer/mol Pd.h. Laine and his group\(^4\) have also utilised a similar ligand in preparing palladium catalyst precursors for ethylene polymerisation. Interestingly though, the dichloride palladium complex (4-IV) could not be activated with MAO to give active ethylene polymerisation catalysts.\(^4b\)

![Structural formula of 4-III and 4-IV](image)

\[ R = \text{Me}, 'pr; R' = \text{H, Me}; R'' = \text{H, Me} \]

Recently pyridine-imidazole palladium complexes (4-V) have been studied and illustrate the influence of ligand structure on palladium catalyzed olefin/CO co-polymerisation reactions.\(^5\) The basicity of the ligands can be tailored by changing the nature of remote alkyl substituents on the imidazoline moiety. Catalysts containing less basic ligands gave higher activities (27.2 g polymer/mol Pd.h) than those containing more basic ligands.

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(3.4 g polymer/mol Pd.h). Dependence of catalytic activity on basicity of the ligands was thus evident with the less basic ligands giving the most active catalyst precursors. DFT studies of the catalysts reveal that electronic effect of the alkyl group has an influence on the relative stability of the cationic species. This decreases with increase in electron withdrawing character of the N-alkyl group of the imidazole ring.

In another experiment Milani and her group\(^6\) found palladium complexes of large fused aromatic N-N ligands (4-VI) form efficient catalysts for CO/styrene co-polymerisation. The complexes are more active (TON = 519 g polymer/g Pd.h) than the known [Pd(phen)]BF\(_4\) catalysts (TON = 270 g polymer/g Pd.h).\(^{2b}\) Catalyst 4-VI produces predominantly syndiotactic CO/styrene polyketone co-polymers.

\[\begin{align*}
4-V & : \begin{array}{c}
\text{R} = \text{H, Me; R'} = \text{H, CN} \\
\text{Ar} = 3,5-(\text{CF}_3)\text{C}_6\text{H}_3
\end{array} \\
4-VI & : \begin{array}{c}
\text{R} = \text{H, Me; R'} = \text{H, CN} \\
\text{Ar} = 3,5-(\text{CF}_3)\text{C}_6\text{H}_3
\end{array}
\]

Another approach to the design of stable α-olefin oligomerisation and polymerisation catalysts has been through the use of “hemi-labile ligands” first introduced by Jeffrey and Rauchfuss in 1979. In olefin oligomerisation or polymerisation catalysis, the role of hemi-labile donor group is mainly to stabilize the active cationic species, hence improving stability of the catalysts. The crucial interplay in catalyst design using hemi-labile ligands is the balance between the donor ability of the hemi-labile group and the incoming monomer. It is essential that the incoming monomer be more strongly coordinating than the hemi-labile group in order to gain access to the metal centre.

Palladium complexes that contain hemi-labile P^N^O^8 ligands (4-VII) have been shown to give active or inactive ethylene oligomerisation catalysts depending on the donor strength of the O-R functionality. While catalysts with methoxy group (4-VII) show low activity (86 mg product after 24 h), no catalytic activity was observed for those with O-H group, (eq. 4.1). It is believed the non-labile phenolate group coordinates to the metal centre without disassociation as required for an active catalyst and hence blocks ethylene coordination to give the ethylene complex 4-VII and subsequent insertion to initiate the oligomerisation process. Catalyst 4-VII however, showed high stability in solution presumably arising from the stabilising role of the methoxy group.

Chapter 3 described how palladium complexes of potential tridentate bis(pyrazol-1-ylmethyl)pyridine ligands give inactive cationic species due to their non-lability. The initial aim of the work in this chapter was to address the problem of tridentate coordination of bis(pyrazol-1-ylmethyl)pyridine ligands reported in Chapter 3 using bidentate (pyrazol-1-ylmethyl)pyridine ligands that would allow olefin coordination to the metal centre upon activation. In order to enhance the stability of the cationic species that were expected to be the active catalysts, weakly-coordinating solvents and hemi-labile donor groups were introduced in the ligand framework. In this chapter the synthesis and characterisation of cationic 2-(pyrazol-1-ylmethyl)pyridine palladium complexes are described. Incorporation of weakly coordinating phenoxy and electron-withdrawing CF$_3$ substituted pyrazolyl units in an attempt to make hemi-labile ligands is also described. Reactions of the palladium complexes with NaBAR$_4$, in attempts to generate active ethylene oligomerisation catalysts are described. The ability of the chloromethyl palladium complexes to undergo sulfur dioxide insertion into metal-carbon bonds was also investigated. These were attempts to probe if the cationic species could coordinate other small molecules apart from ethylene.
4.2 Experimental section

4.2.1 Materials and methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were of analytical grade and were dried and distilled prior to use. Toluene, diethyl ether (Et₂O) dichloromethane (CH₂Cl₂), and acetonitrile (MeCN) were dried and distilled from sodium/benzophenone or P₂O₅. Tetrabutylammonium bromide, 2-picolyllchloride hydrochloride, 3,5-bis(trifluoromethyl)pyrazole, potassium hydride, and phenol were obtained from Sigma-Aldrich and used as received. Sodium tetrakis(3,5-bis(trifluoromethyl)benzene, NaBAR₄, (Ar = 3,5-(CF₃)₂C₆H₃) was obtained from Boulder Scientific and used as received. Starting materials [PdCl₂(COD)]₉, [PdClMe(CO D)]¹⁰ and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine¹¹ (L₃) were synthesized following literature procedures. NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 300 MHz and ¹³C at 75.0 MHz) at room temperature. Chemical shifts are reported in δ (ppm) and referenced to the residual CHCl₃ in the NMR solvent. Coupling constants are measured in Hertz (Hz). Elemental analyses were performed by the micro-analytical laboratory at the University of Cape Town, South Africa. Mass spectra (MS-ESI) were recorded on a Waters API Quattro Micro spectrometer at the University of Stellenbosch, South Africa. Theoretical studies by density functional theory (DFT) were performed at the B3LYP/LANL2DZ level of theory with Gaussian03.¹²

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4.2.2 Synthesis of ligands and palladium complexes

4.2.2.1 2-(3,5-di-tert-butylpyrazol-1-ylmethyl)pyridine (L4)

A mixture of 2-picolyllchloride hydrochloride (1.37 g, 8.33 mmol) and 3,5-di-tert-butylpyrazole (1.50 g, 8.33 mmol) in benzene (40 mL), 40% aqueous NaOH (12 mL) and 40% aqueous tetrabutylammonium bromide (10 drops) was refluxed for 18 h. The organic layer was then separated, dried over anhydrous MgSO₄ and evaporated in vacuo. The crude product obtained was washed with water (40 mL) and the crude material purified by column chromatography, using a mixture of CH₂Cl₂:hexane (4:1) as eluent, to afford analytically pure compound L₄ as a solid. Yield = 1.38 g (80%). "H NMR (CDCl₃): δ 1.23 (s, 18H, 'Bu, pz); 1.31 (s, 18H, 'Bu, pz); 5.55 (s, 4H, py-CH₂-pz); 5.93 (s, 2H, pz); 6.32 (d, 2H, py, ³J_HH = 8.0 Hz); 7.46 (t, 1H, py, ³J_HH = 8.0 Hz). "C NMR (CDCl₃): δ 30.2; 31.5; 34.3; 36.3; 55.4; 106.6; 120.1; 124.2; 135.3; 143.7; 149.3; 152.4; 157.8. Anal. Calc for C₁₇H₂₅N₃: C, 75.23; H, 9.28; N, 15.48. Found: C, 75.18; H, 9.66; N, 15.42. MS (ESI) m/z (%) 272 (M⁺,100); 181 (M⁺-pyCH₂, 20).

4.2.2.2 2-(3,5-bis-trifluoromethyl-pyrazol-1-ylmethyl)-6-(3,5-dimethyl-pyrazol-1-ylmethyl)-pyridine (L5)

To a suspension of KH (0.10 g, 3.00 mmol) in THF (20 mL) was added a solution of 3,5-bis(trifluoromethyl)pyrazole (0.15 g, 0.70 mmol) in THF (20 mL) and the mixture stirred for 1 h. A solution of 2-(chloromethyl-6-pyrazol-1-ylmethyl)pyridine (0.17 g, 0.70 mmol) in THF (10 mL) was then added and refluxed for 24 h. The mixture was then filtered and the solvent removed under vacuum to give a crude product as a yellow solid. Purification by column chromatography on silica gel using a mixture of CH2Cl2:MeOH (9:1) as eluent, afforded L5 as a pure white solid. Yield = 0.10 g (33%). 1H NMR (CDCl3): δ 2.14 (s, 3H, CH3, pz); 2.23 (s, 3H, CH3, pz); 5.28 (s, 2H, CH2); 5.58 (s, 2H, CH2); 5.86 (s, 1H, pz); 6.78 (d, 1H, py, 3JHH = 8.2 Hz); 6.84 (s, 1H, pz); 6.99 (d, 1H, py); 7.58 (t, 1H, py, 3JHH = 8.0 Hz). 19F NMR (CDCl3): δ -62.5 (s, CF3, pz); -60.0 (s, CF3, pz). 13C NMR (CDCl3): δ 10.9; 13.3; 53.9; 56.8; 106.5; 119.6; 120.6; 138.1; 140.1; 148.1; 153.7; 157.3.

4.2.2.3 2-(3,5-dimethyl-pyrazol-1-ylmethyl)-6-phenoxy-methyl-pyridine (L6)

To a suspension of KH (0.15 g, 3.75 mmol) in THF (20 mL) was added phenol (0.24 g, 2.50 mmol) and the mixture refluxed at 60 °C for 1.5 h. 2-(chloromethyl-6-pyrazol-1-ylmethyl)pyridine (0.50 g, 2.00 mmol) in THF (10.00 mL) was then added and the solution refluxed for a further 12 h to give a deep orange solution. The solvent was removed in vacuo, the crude product re-dissolved in CH2Cl2 and excess potassium phenoxide filtered off. The filtrate was washed with water (20 mL) and organic layer separated, dried over anhydrous MgSO4 and solvent removed to afford L6 as an orange
solid. Yield = 0.35 g (60%). $^1$H NMR (CDCl$_3$): δ 2.16 (s, 3H, CH$_3$, pz); 2.24 (s, 3H, CH$_3$, pz); 5.30 (s, 2H, CH$_2$); 5.75 (s, 2H, CH$_2$); 5.86 (s, 1H, pz); 6.43 (m, 1H, ph); 6.63 (d, 1H, ph, $^3$J$_{HH}$ = 7.5 Hz); 7.00 (m, 2H, ph); 7.45 (t, 1H, py, $^3$J$_{HH}$ = 8.0 Hz). $^{13}$C NMR (CDCl$_3$): δ 10.8; 13.8; 53.2; 76.6; 105.4; 119.2; 121.6; 137.0; 139.5; 147.8; 156.8.

4.2.2.4 [{2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine}PdCl$_2$] (13)

To a solution of [PdCl$_2$(COD)] (0.20 g, 0.70 mmol) in CH$_2$Cl$_2$ (30 mL) was added L$_3$ (0.13 g, 0.70 mmol) to give a yellow precipitate. The mixture was stirred for 4 h and filtered to afford complex 13 as an analytically pure compound. Yield = 0.22 g (80%). $^1$H NMR (DMSO-d$_6$): δ 2.39 (s, 3H, CH$_3$, pz); 2.41 (s, 6H, CH$_3$, pz); 5.80 (d, 2H, py-CH$_2$-pz, $^2$J$_{HH}$ = 15.4 Hz); 6.17 (d, 2H, py-CH$_2$-pz, $^2$J$_{HH}$ = 15.4 Hz); 6.10 (s, 2H, pz); 7.62 (t, 1H, py, $^3$J$_{HH}$ = 7.6 Hz). 7.95 (d, 1H, py, $^3$J$_{HH}$ = 7.4 Hz); 8.11 (t, 1H, py, $^3$J$_{HH}$ = 7.6 Hz); 8.78 (d, 1H, py, $^3$J$_{HH}$ = 7.4 Hz). $^{13}$C NMR (CDCl$_3$): δ 11.53; 13.9; 52.8; 107.9; 123.1; 124.5; 139.1; 140.5; 151.8; 152.3. Anal. Calc for C$_{12}$H$_{13}$N$_3$PdCl$_2$: C, 36.24; H, 3.59; N, 11.53. Found: C, 36.48; H, 3.42; N, 11.42.

4.2.2.5 [{2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine}PdClMe] (14)

To a solution of [PdClMe(COD)] (0.20 g, 0.75 mmol) in Et$_2$O (30 mL) was added ligand L$_3$ (0.14 g, 0.75 mmol) to form a light yellow precipitate. The mixture was stirred for 5 h and filtered to give an analytically pure light yellow compound. Yield = 0.23 g (85%). $^1$H NMR (CDCl$_3$): δ 0.96 (s, 3H, CH$_3$, Pd-Me); 2.30, 2.34 (s, 3H, CH$_3$, pz); 2.36, 2.45 (s, 3H, CH$_3$, pz); 5.78, 5.91 (s, 2H, pz); 7.31 (t, 1H, py, $^3$J$_{HH}$ = 7.4 Hz). 7.43 (d, 1H, py, $^3$J$_{HH}$ = 7.4 Hz); 7.75, 7.86 (t, 1H, py, $^3$J$_{HH}$ = 7.8 Hz); 8.65, 8.95 (d, 1H, py, $^3$J$_{HH}$ = 5.6 Hz). $^{13}$C NMR
4.2.2.6 \{2-(3,5-di-tertbutylpyrazol-1-ylmethyl)pyridine\}PdCl₂ (15)

To a solution of [PdCl₂(COD)] (0.30 g, 1.00 mmol) in CH₂Cl₂ (40 mL) was added ligand \textbf{L₄} (0.28 g, 1.00 mmol) and the resultant clear orange solution stirred for 24 h. The solution was then concentrated under vacuum, hexane (10 mL) added and kept at -4 °C to give orange single crystals suitable for X-ray analysis. Yield = 0.22 g (50%). ¹H NMR (CDCl₃): δ 1.43 (s, 9H, \textsuperscript{t}Bu, pz); 1.71 (s, 9H, \textsuperscript{t}Bu, pz); 5.76 (d, 2H, py-CH₂-pz, \textsuperscript{2}J_{HH} = 15.4 Hz); 5.93 (s, 2H, pz); 6.90 (d, 2H, py-CH₂-pz, \textsuperscript{2}J_{HH} = 15.4 Hz); 7.45 (t, 1H, py, \textsuperscript{3}J_{HH} = 5.8 Hz). ¹³C NMR (CDCl₃): δ 30.5; 31.7; 34.2; 35.6; 56.1; 107.2; 120.4; 124.7; 135.1; 144.2; 149.8; 153.4; 158.3. Anal. Calc for C₁₇H₁₆N₃PdCl₂: C, 40.51; H, 5.16; N, 7.87. Found: C, 40.90; H, 5.04; N, 7.80.

4.2.2.7 \{2-(3,5-di-tertbutylpyrazol-1-ylmethyl)pyridine\}PdClMe (16)

To a solution of [PdClMe(COD)] (0.20 g, 0.75 mmol) in Et₂O (20 mL) was added \textbf{L₄} (0.21 g, 0.75 mmol). A light yellow precipitate formed immediately. The mixture was stirred for 4 h and filtered to give a light yellow solid which was recrystallised from a mixture of CH₂Cl₂:hexane (20:10) to give single crystals suitable for X-ray analysis. Yield = 0.18 g (58%). ¹H NMR (CDCl₃): δ 0.98 (s, 3H, CH₃, Pd-Me); 1.44 (s, 9H, \textsuperscript{t}Bu, pz); 1.55 (s, 9H, \textsuperscript{t}Bu, pz); 5.65 (d, 2H, py-CH₂-pz, \textsuperscript{2}J_{HH} = 13.4 Hz); 5.83 (s, 2H, pz); 6.78 (d, 2H, py-CH₂-pz, \textsuperscript{2}J_{HH} = 15.4 Hz); 7.40 (t, 1H, py, \textsuperscript{3}J_{HH} = 7.6 Hz). 7.52 (d, 1H, py, \textsuperscript{3}J_{HH}
= 7.8 Hz); 7.88 (t, 1H, py, \(^3J_{HH} = 7.6\) Hz); 8.60 (d, 1H, py, \(^3J_{HH} = 5.2\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 1.2; 30.3; 31.7; 33.4; 35.1; 55.3; 107.0; 120.8; 123.9; 135.3; 143.8; 148.7; 153.3; 158.1. Anal. Calc for C\(_{18}\)H\(_{19}\)N\(_3\)PdCl: C, 48.78; H, 6.01; N, 9.35. Found: C, 49.12; H, 6.53; N, 9.29.

### 4.2.2.8 \([2-(3,5-Bis-trifluoromethyl-pyrazol-1-ylmethyl)-6-(3,5-dimethyl-pyrazol-1-ylmethyl)pyridine]\)PdClMe (17)

This complex was synthesised following the procedure described for 16 using L\(_5\) (0.20 g, 0.30 mmol) and [PdClMe(COD)] (0.10 g, 0.30 mmol). Yield = 0.12 g (70%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.09 (s, 3H, CH\(_3\), Pd-Me); 2.17 (s, 3H, CH\(_3\), pz); 2.33 (s, 3H, CH\(_3\), pz); 5.20 (d, 2H, CH\(_2\), \(^2J_{HH} = 15.6\) Hz); 5.92 (s, 1H, pz); 6.44 (d, 2H, CH\(_2\), \(^2J_{HH} = 17.4\) Hz); 6.71 (d, 1H, py, \(^3J_{HH} = 8.2\) Hz); 6.84 (s, 1H, pz); 6.94 (s, 1H, pz); 7.30 (d, 1H, py, \(^3J_{HH} = 8.3\) Hz); 7.72 (t, 1H, py, \(^3J_{HH} = 8.3\) Hz). \(^{19}\)F NMR (CDCl\(_3\)): \(\delta\) -62.5 (s, CF\(_3\), pz); -60.0 (s, CF\(_3\), pz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 10.9; 13.3; 53.9; 56.8; 106.5; 119.6; 120.6; 138.1; 140.1; 148.1; 153.7; 157.3. Anal. Calc for C\(_{19}\)H\(_{21}\)N\(_5\)F\(_6\)PdCl: C, 39.67; H, 3.68; N, 12.17. Found: C, 39.84; H, 4.01; N, 12.61.

### 4.2.2.9 \([2-(3,5-dimethylpyrazol-1-ylmethyl)-6-phenoxy methyl)pyridine]\)PdClMe (18)

Compound 18 was prepared according to the procedure described for 16 using L\(_6\) (0.12 g, 0.40 mmol) and [PdClMe(COD)] (0.11 g, 0.40 mmol). Product was isolated as a light orange solid. Yield = 0.14 g (75%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.09 (s, 3H, CH\(_3\), Pd-Me); 2.37 (s, 3H, CH\(_3\), pz); 2.47 (s, 3H, CH\(_3\), pz); 5.68 (s, 2H, CH\(_2\)); 5.94 (s, 1H, pz); 7.72 (t, 1H, py, \(^3J_{HH} = 8.3\) Hz). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 12.2; 15.1; 52.5; 77.3; 100.1; 108.4; 125.2; 143.3;
152.0. Anal. Calc for C$_{20}$H$_{25}$N$_3$OPdCl: C, 51.63; H, 5.42; N, 9.03. Found: C, 51.24; H, 5.81; N, 8.84.

4.2.2.10 \{2-(3, 5-dimethylpyrazol-1-ylmethyl)pyridine}PdMeNCMe\_BAr$_4$ (19)

To a mixture of complex 14 (0.10 g, 0.29 mmol) and NaBAr$_4$ (0.25 g, 0.30 mmol) was added MeCN (20 mL) and the cloudy solution stirred for 24 h to give a pale yellow solution. The solvent was then removed under vacuum to afford a light yellow crystalline solid. Yield = 0.12 g (30%). $^1$H NMR (CDCl$_3$): $\delta$ 0.95 (s, 3H, CH$_3$, Pd-Me); 0.99 (s, 3H, CH$_3$, Pd-Me); 2.17 (s, 3H, CH$_3$, Pd-NCMe); 2.22 (s, 3H, CH$_3$, pz); 2.27 (s, 3H, CH$_3$, pz); 5.81, (s, 2H, pz); 5.90 (s, 2H, pz); 7.22 (m, 1H, py). 7.40 (m, 1H, py, $^3J_{HH} = 7.4$ Hz); 7.41 (s, 4H, H$_p$, BAr$_4$); 7.69 (s, 8H, H$_o$, BAr$_4$); 7.81 (t, 1H, py, $^3J_{HH} = 5.2$ Hz); 8.31, 8.43 (d, 1H, py, $^3J_{HH} = 5.2$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ -7.9; 11.5; 13.1; 14.5; 14.4; 52.5, 107.4; 117.5; 126.9; 129.8; 140.1; 150.0; 152.8; 158.0; 161.4. Positive mode MS (ESI) m/z (%) 349 (M$^+$, 100); 308 (M$^+$-NCMe, 25); 186 (M$^+$-PdMeNCMe, 40). Negative mode MS (ESI) m/z (%) 863 (M$^-$, 100). Anal. Calc for C$_{46}$H$_{31}$BF$_{24}$N$_4$Pd: C, 41.74; H, 2.54; N, 3.01. Found: C, 41.84; H, 2.15; N, 2.40.

4.2.2.11 \{2-(3,5-bis-trifluoromethyl-pyrazol-1-ylmethyl)-6-(3,5-dimethyl-pyrazol-1-ylmethyl)-pyridine}PdMe\_BAr$_4$ (20)

In a J-Young NMR tube containing a solution of 17 (4.00 mg, 0.007 mmol) in CDCl$_3$ (0.2 mL) was added a solution of NaBAr$_4$ (6.00 mg, 0.007 mmol) in CDCl$_3$ (0.2 mL) and the $^1$H NMR spectrum acquired after vigorous shaking. The solution was left to stand at room temperature for several days to afford colorless single crystals suitable for X-ray
analysis. \(^1\)H NMR (CDCl\(_3\)): δ 1.27 (s, 3H, CH\(_3\), Pd-Me); 2.17 (s, 3H, CH\(_3\), pz); 2.33 (s, 3H, CH\(_3\), pz); 5.16 (d, 2H, CH\(_2\), \(^2\)J\(_{HH}\) = 15.6 Hz); 5.63 (s, 1H, pz); 5.98 (s, 1H, pz); 6.20 (d, 2H, CH\(_2\), \(^2\)J\(_{HH}\) = 17.4 Hz); 6.71 (d, 1H, py, \(^3\)J\(_{HH}\) = 8.2 Hz); 7.23 (d, 2H, py, \(^3\)J\(_{HH}\) = 8.6 Hz); 7.34 (t, 1H, py, \(^3\)J\(_{HH}\) = 8.3 Hz); 7.48 (s, 4H, BAr\(_4\)-); 7.66 (s, 8H, BAr\(_4\)-). \(^{19}\)F NMR (CDCl\(_3\)): δ -62.6 (s, BAr\(_4\)-); -60.2 (s, CF\(_3\), pz); -56.0 (s, CF\(_3\), pz). \(^{13}\)C NMR (CDCl\(_3\)): δ -5.7; 11.5; 15.0; 52.1; 55.8; 109.2; 117.5; 122.6; 124.7; 134.7; 142.0; 148.8; 152.2; 162.6.

4.2.2.12 \([2-(3,5\text{-dimethylpyrazol-1-ylmethyl)pyridine}\text{PdCl}(\text{O})\text{S(O)}\text{Me}]\) (21)

Sulfur dioxide was bubbled through a solution of complex 14 (0.10 g, 0.29 mmol) in CH\(_2\)Cl\(_2\) (20 mL) for 10 minutes. The colourless solution turned yellow. The solution was then stirred for 2 h under SO\(_2\) atmosphere. After the reaction time, hexane saturated with SO\(_2\) (10 mL) was layered onto the solution and stored at -4 °C to afford a yellow crystalline product. Yield = 0.09 g (76%). \(^1\)H NMR (CDCl\(_3\)): δ 2.34 (s, 3H, CH\(_3\), pz); 2.38 (s, 3H, CH\(_3\), pz); 2.43 (s, 3H, CH\(_3\), pz); 2.59 (s, 3H, CH\(_3\), pz); 3.17, (s, 3H, CH\(_3\), Pd-SO\(_2\)Me); 3.24 (s, 3H, CH\(_3\), Pd-SO\(_2\)Me); 5.21 (d, 1H, CH\(_2\), \(^2\)J\(_{HH}\) = 15.2 Hz) 5.29 (d, 1H, CH\(_2\), \(^2\)J\(_{HH}\) = 15.0 Hz); 5.584, (s, 2H, pz); 5.93 (s, 2H, pz); 6.18 (d, 1H, CH\(_2\), \(^2\)J\(_{HH}\) = 15.0 Hz) 6.22 (d, 1H, CH\(_2\), \(^2\)J\(_{HH}\) = 15.4 Hz) 7.49 (m, 2H, py). 7.92(t, 1H, py, \(^3\)J\(_{HH}\) = 7.8 Hz); 8.95, 9.28 (d, 1H, py, \(^3\)J\(_{HH}\) = 5.6 Hz). \(^{13}\)C NMR (CDCl\(_3\)): δ 11.2; 11.6; 14.5; 15.2; 30.8; 49.0, 51.5; 53.1; 53.6; 108.0; 108.4; 124.5.0; 140.4; 151.6; 151.9. MS (ESI) m/z (%) 408 (M\(^+\), 15); 372 (M\(^+\)-Cl, 30); 308 (M\(^+\) SO\(_2\), 100); 186 (M\(^+\)-PdMe, 95).

Anal. Calc for C\(_{12}\)H\(_{16}\)N\(_3\)PdSO\(_2\)Cl\(_1\)/2CH\(_2\)Cl\(_2\): C, 33.40; H, 3.79; N, 9.35; S, 7.12 Found: C, 33.31; H, 3.83; N, 9.00; S, 6.48.
4.2.3 Crystallographic Experimental Section

Data Collection

Single crystals X-ray analysis of 13, 15, 16 and 20 were performed as described for complex 15. An orange crystal with approximate dimensions 0.49 x 0.46 x 0.39 mm$^3$ was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centred in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K$_\alpha$ ($\lambda = 0.71073 \text{ Å}$) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of $\omega$ scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about $\omega$ with the exposure time of 5 seconds per frame. A total of 69 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4402 strong reflections from the actual data collection. The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 8900 data were harvested by collecting three sets of frames with 0.30° scans in $\omega$ with an exposure time 5 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.$^{13}$

**Structure Solution and Refinement**

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The $E$-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.\textsuperscript{13} A successful solution by the direct methods provided most non-hydrogen atoms from the $E$-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients. There is also one solvate molecule of dichloromethane per Pd complex in the lattice. The final least-squares refinement of 371 parameters against 5933 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for all data) of 0.0393 and 0.1145, respectively. The final difference Fourier map was featureless. The molecular diagrams are drawn with 50\% probability ellipsoids.

4.3 Results and discussion

4.3.1 Synthesis and characterisation of neutral (pyrazol-1-ylmethyl)pyridine palladium complexes

Compounds 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L\textbf{3}) and 2-(3,5-di-\textit{tert}-butylpyrazol-1-ylmethyl)pyridine (L\textbf{4}) were prepared following literature methods described by Steel \textit{et al}.\textsuperscript{11} Compounds L\textbf{5} and L\textbf{6} were isolated in good yields by reacting (2-chloromethyl-6-3,5-dimethylpyrazol-1-ylmethyl)pyridine with an equivalent amount
of potassium salt of 3,5-bis(trifluoromethyl)pyrazolate and potassium phenolate respectively (Scheme 4.1).

Reactions of compounds L3-L6 with either [PdCl₂(COD)] or [PdClMe(COD)] (Scheme 4.2) gave the desired complexes 13-18 in high yields. All the compounds synthesized were characterised by a combination of ¹H, ¹³C and ¹⁹F NMR spectroscopy, mass spectrometry, elemental analyses and single crystal X-ray crystallography for complexes 13, 15, 16. From the ¹H NMR spectra of L5 and L6, two signals of the CH₂ linker protons at about 5.28 and 5.58 ppm (L5); 5.30 and 5.75 ppm (L6) were observed. This indicates the unsymmetrical nature of L5 and L6 as opposed to one signal for the CH₂ protons at 5.31 and 5.55 ppm for the symmetrical compounds L1 and L2 respectively described in Chapter 3.
\[ \text{Scheme 4.2} \]

\[ [\text{PdClX(COD)}] \]

\[ \text{CH}_2\text{Cl}_2/\text{Et}_2\text{O} \]

\[ \text{R = Me, } X = \text{Cl (13); R = Me, } X = \text{Me (14)} \]
\[ \text{R = } \text{tBu, } X = \text{Cl (15); R = } \text{tBu, } X = \text{Me (16)} \]

\[ [\text{PdClMe(COD)}] \]

\[ \text{L} \]

\[ \text{CH}_2\text{Cl}_2/\text{Et}_2\text{O} \]

\[ \text{R = Me, } L = 3,5-(\text{CF}_3)\text{pz (17)} \]
\[ \text{R = Me, } L = \text{OPh (18)} \]

\[ 19^\text{F} \text{ NMR spectrum of L5 showed two signals at about 62.5 and 60.0 ppm typical of aryl-} \]
\[ \text{CF}_3 \text{ fluorine signals.}^{14} \] The \[ 13^\text{C} \text{ NMR spectra of compounds L4-L6 were consistent with} \]
\[ ^1\text{H} \text{ NMR data. For instance two signals at about 53.1 and 76.2 ppm assigned to the two} \]
\[ \text{CH}_2 \text{ linker carbons were observed for L5.} \]

\(^1\)H NMR spectroscopy was used to diagnose the identity of the isolated palladium complexes of ligands L3-L6. While the \(^1\)H NMR spectra of the dichloride complexes 13 and 15 showed signature peaks, corresponding to the CH\(_2\) linker protons, as doublets between 5.60–6.80 ppm; the spectra of 14 (Figure 4.1) and 16 showed broad signals at 5.30 and 6.40 ppm. Interestingly, two sets of signals were recorded for two methyl substituents on the pyrazolyl units (2.30 and 2.45; 2.33 and 2.35), 4-H\(_{pz}\) (5.78 and 5.91) and the pyridine protons for 14. This indicates the existence of two isomers, which may arise from the flexibility of the CH\(_2\) linker that produces chair and boat conformations. Figures 4.1 and 4.2 show the \(^1\)H NMR spectra of 14 and 15 respectively that illustrates the discussion above.

Figure 4.1: \(^1\)H NMR spectrum of compound 14 showing the CH\(_2\) protons as broad peaks and two sets of signals for the pyrazolyl protons.
Figure 4.2: $^1$H NMR spectrum of complex 15 showing the $CH_2$ protons as two distinct doublets.

Figure 4.3 shows the boat conformations of complex 16. The unsymmetrical nature of compounds 14 and 16; due to the presence of the Pd-Me functionality as compared to the dichloride analogues 13 and 15; could also explain the origin of the two set of signals in 14 and 16.

Figure 4.3: Boat conformations of complex 16 showing the axial and apical orientations of the $CH_2$ linker protons.
The nature of the binding mode of L5 and L6 could also be deduced from the $^1$H spectra of the corresponding complexes 17 and 18. For example the CH$_2$ linker protons of complex 17 were observed as doublets at about 5.20 and 6.40 ppm compared to the two singlets (5.28 and 5.58 ppm) in the respective ligand L5. Coordination of L5 through the nitrogen atoms of the pyridine and 3,5-Me$_2$pz could be established from the unchanged signals of the 3,5-(CF$_3$)$_2$pz moiety especially in $^1$F NMR; -62.5 and 60.0 ppm in both L5 and 17 (Figure 4.5). $^1$F NMR spectrum of cationic species 20, obtained upon chloride abstraction, showed three signals at -62.4, 60.2, 58.0 ppm due to CF$_3$ groups of the BAr$_4^-$ anion. The upfield signal at -62.4 pm was assigned to the CF$_3$ groups of the BAr$_4^-$ counter ion. Coordination of 3,5-(CF$_3$)$_2$pz group in the cationic species was evident from the downfield signals of the CF$_3$ signals in $^1$F NMR spectrum of 20 (60.2 and 58.0 ppm) compared to peaks at -62.5 and -60.0 ppm in the neutral compound 17 (Figure 4.4).

Figure 4.4: $^1$F NMR spectra of ligand L5 (a), complexes 17 (b) and 20 (c).
4.3.2 Synthesis and characterisation of cationic (pyrazol-1-ylmethyl)pyridine palladium complexes

In attempts to isolate cationic species that could be readily used as ethylene polymerisation catalysts, complexes 14 and 17 were treated with 1 equivalent of NaBAr₄. In the case of 14, the reaction was performed in the presence MeCN, as the stabilising solvent and gave the cationic compound 19 in good yields (Scheme 4.3). Attempts to isolate an Et₂O adduct were unsuccessful due to rapid decomposition of the expected product. This finding is in good agreement with literature reports that high lability of the Et₂O makes its adducts more reactive and therefore generally unstable.¹⁵

![Scheme 4.3](image)

Ar = 3,5-(CF₃)₂C₆H₃; Solvent, S = OEt₂, NCMe, NCPh

The identity of the cationic species of complex 14 could be deduced from the upfield peak at 2.17 ppm assigned to the NCMe protons. Coordinated NCMe protons are typically observed between 1.78-2.41 ppm.¹⁴ An interesting feature of the ¹H NMR spectrum of cationic compound 19, compared to the neutral complex 14, was the appearance of the Pd-Me protons as two singlets (0.95 and 0.99 ppm) in 19 but 0.97 ppm

in 14. This can originate from the increased hindered rotation about the \( \text{CH}_2 \) linker protons due to the bulkier MeCN groups as compared to the smaller Cl ligand. This gives rise to prolonged life time of two isomers; namely chair and boat conformations\(^{11}\) on an NMR time scale. Another explanation for the two signals for the Pd-Me protons could be due to the presence of cis and trans isomers, \( A \) and \( B \), respectively (Equation 4.2). This trans-cis labilisation might arise from one: the methyl ligand being trans to the pyridine nitrogen and cis to the pyrazolyl nitrogen. In the second case, the methyl ligand could be cis to the pyridine nitrogen and trans to the pyrazolyl nitrogen. This trans-cis isomerisation has also been reported for the \([(\text{py}-2-\text{CMe=NAr})\text{PdMeNCMe}]\text{BAr}_4\) complex.\(^{3}\) However, compound \([(\text{py}-2-\text{CMe=NAr})\text{PdMeNCMe}]\text{BAr}_4\) shows two sets of resonances even for the MeCN protons at about 2.31 and 2.41 ppm while compound 19 showed only one signal at 2.17 ppm.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{N} \\
\text{Pd} & \quad \text{Pd} \\
\text{Me} & \quad \text{Me} \\
\text{NCMe} & \quad \text{NCMe} \\
& + \text{BAr}_4^- \\
\\
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{N} \\
\text{Pd} & \quad \text{Pd} \\
\text{Me} & \quad \text{Me} \\
\text{NCMe} & \quad \text{NCMe} \\
& + \text{BAr}_4^- \\
\end{align*}
\]

(4.2)

To further investigate this trans-cis isomerisation, DFT studies of the simplified analogues of the two geometrical isomers (\( A \) and \( B \)) at the B3LYP/LANL2DZ level of theory were performed. The energies of \( A \) and \( B \) indicate a very small rotational energy barrier between the two isomers (Figure 4.5). The isomer in which the methyl ligand is
trans to the pyridine nitrogen atom was more stable by 0.9 kcal/mol. The observed one signal of MeCN protons in the $^1$H NMR spectrum of 19 in addition to the small rotational energy barriers between the cis and trans isomers might discount the hypothesis of cis-trans labilisation in compound 19. Thus the appearance of the Pd-Me and CH$_2$ linker protons as two sets of peaks could be attributed to the presence of chair and boat conformations. These results are consistent with the earlier results of Rulke et al.$^{16}$ on similar methyl pyridine imine palladium complexes which shows similar energies for the cis and trans isomers.

![Optimized structures](image)

**Figure 4.5:** Optimized structures (at the B3LYP/LANL2DZ level of theory) of simplified analogues of the two isomers of 19. The more stable conformation (B) is observed when the methyl group is trans to the pyridine nitrogen atom.

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Compound 19 was further characterised by both positive mode and negative mode electron spray ionization mass spectrometry. The positive mass spectrum (Figure 4.6) shows m/z = 349 that corresponds to the molecular ion of 19. The negative ion mass spectrum corresponds to the BAr₄⁻ counter ion. Fragmentation pattern of 19 was found to be as a result of initial loss of MeCN molecule to form a 14-electron fragment (m/z = 308), which then looses a PdMe fragment to give a peak at m/z =186 assignable to L₃ (Scheme 4.4)

Figure 4.6: ESI mass spectrum of the cationic palladium complex of 19 (inset shows the mass spectrum of the calculated and found isotopic distribution of 19).
An interesting phenomenon that was observed in attempts to grow single crystals suitable for X-ray analysis of 14 was the decomposition of 14 to a dichloro complex 13 (Eq. 4.3). Such decomposition of the complex [(3,5-\textsuperscript{t}Bu\textsubscript{2}pz)PdClMe] to the dichloro analogue [(3,5-\textsuperscript{t}Bu\textsubscript{2}pz)PdCl\textsubscript{2}] has also been reported by Li et al.\textsuperscript{17}

To fully probe the decomposition of the chloromethyl complex 14 to the dichloro analogue 13, \textsuperscript{1}H NMR spectrum of 14 was monitored in chlorinated solvents (CD\textsubscript{2}Cl\textsubscript{2} and CDCl\textsubscript{3}) and non-chlorinated solvent (DMSO-d\textsubscript{6}) at room temperatures over a period of time. While the spectra in CD\textsubscript{2}Cl\textsubscript{2} and CDCl\textsubscript{3} showed gradual decomposition, as

indicated by reduced intensity of the Pd-Me signal, with half lives of 12 and 5 days respectively, the spectrum in DMSO-d$_6$ remained invariant even after 30 days. This shows that the decomposition is solvent dependent, with rapid degradation observed in more polar chlorinated solvents. Temperature effect on this decomposition was evident from the isolation of the crystals of the methyl analogue, 4, which were obtained at lower temperatures of -4 °C indicating that this transformation is also enhanced at higher temperatures.

Brookhart and coworkers have observed the formation of CHD$_2$Cl (2.90 ppm) as a decomposition of [($\eta^5$-C$_5$Me$_5$)Co(P(MeO)$_3$CH$_2$CH$_2$($\mu$-H)]BF$_4$ complex. They attributed the formation of CHD$_2$Cl to chloride abstraction from the CD$_2$Cl$_2$ solvent.\textsuperscript{18}

\subsection*{4.3.3 Molecular structure determination of complexes 13, 15, 16 and 20}

Single crystals suitable for X-ray analyses of compounds 15 and 16 were grown by slow diffusion of hexane into a CH$_2$Cl$_2$ solution at -4 °C. Attempts to grow single crystals suitable for X-ray analysis of 14 from CDCl$_3$ solvent at room temperature resulted in the isolation of crystals of the dichloride analogue, 13 (\textit{vide upra}). Crystals of 20 were grown by slow evaporation of the CDCl$_3$ solvent at room temperature. Tables 4.1 and 4.2 show the crystallographic refinement data and selected bond lengths and angles for compounds 13, 15, 16 and 20 respectively. The molecular structures of 13, 15, 16 and 20 are given in Figure 4.7-4.10 respectively.

The four palladium complexes, 13, 15, 16 and 20 contain the central metal atom in slightly distorted square-planar arrangements. The average Pd–N\(_{(pz)}\) bond distances (2.034(3) Å) of complex 13 expectedly is slightly shorter than that of 15 (2.06(3) Å), with the tert-butyl groups. This could be attributed to steric factors. While the Pd–N(pz) bond distance (2.06(3) Å of 13 agrees well with the average Pd–N\(_{(pz)}\) bond lengths (2.06(3) Å) determined for 607 bonds in 229 related complexes reported to the CSD,\(^{19}\) the Pd–N\(_{(pz)}\) distance (2.034(3) Å) of 1 is slightly shorter. The average Pd-N\(_{(pz)}\) bond distance of
compound 16 of 2.1861(12) is significantly longer than the average Pd-N\(_{(pz)}\) bond distances of 13 and 15 of 2.034(3) and 2.060(3) respectively possibly due to the trans-influence of the methyl group compared to the electron withdrawing Cl' ligand. The Pd-N\(_{5(pz)}\) bond length of 2.030(3) Å of cationic complex 20 is statistically longer compared to the bond length of 2.043(2) Å of a related complex 6 described in Chapter 3 possibly due to the presence of electron-withdrawing CF\(_3\) groups.

Figure 4.8: Molecular structure of 15 drawn with 50% probability ellipsoids.
The average Pd–Cl bond distances (2.2869(10) Å) and (2.2924(10) Å) in complexes 13 and 16 respectively are statistically indistinguishable and agree well with the average bond length (2.33(5) Å) obtained in 2055 Pd-Cl bonds of 1268 related compounds reported to the Cambridge Structural Database (CSD).\textsuperscript{19}

Figure 4.9: Molecular structure diagram of 16 shown with 50\% probability ellipsoids.

Table 4.1: Crystal data and structure refinement for compounds 13, 15, 16 and 20

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>15</th>
<th>16</th>
<th>20</th>
</tr>
</thead>
<tbody>
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<td>Empirical formula</td>
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<td>1388.00</td>
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<td>100(2)</td>
<td>100(2)</td>
<td>105(2)</td>
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<td>Wavelength (Å)</td>
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<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<td>Pbca</td>
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<td>a (Å)</td>
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<td>18.0151(8) Å</td>
<td>10.9194(4) Å</td>
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<tr>
<td>b (Å)</td>
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<td>10.473(4) Å</td>
<td>11.4423(5) Å</td>
<td>18.0256(7) Å</td>
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<td>c (Å)</td>
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<td>11.454(5) Å</td>
<td>18.6523(8) Å</td>
<td>27.1635(11) Å</td>
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<td>90</td>
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<tr>
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<td>γ (°)</td>
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<td>90</td>
<td>90</td>
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<td>1948.2(4) Å</td>
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<td>5308.2(4) Å</td>
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<td>8</td>
<td>4</td>
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<td>1.480</td>
<td>1.737</td>
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<td>1760</td>
<td>2744</td>
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<td>2.18 to 26.38</td>
<td>1.89 to 29.14</td>
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<td>100.0</td>
<td>99.5</td>
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<tr>
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<td>1.072</td>
<td>1.014</td>
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<td>R₁ = 0.0678, wR₂ = 0.1683</td>
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<td>Largest diff. peak and hole (e.Å⁻³)</td>
<td>1.350 and -0.626</td>
<td>1.073 and -0.843</td>
<td>0.446 and -0.370</td>
<td>2.499 and -1.861</td>
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Table 4.2: Selected bond lengths [Å] and bond angles [°] for 13, 15, 16 and 20

<table>
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<th>20</th>
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<td>2.037(3)</td>
<td>2.0476(3)</td>
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<tr>
<td>Pd-N(1)</td>
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<td>2.060(3)</td>
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<td>Pd-Cl(1)</td>
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<td>2.2943(11)</td>
<td>2.3207(4)</td>
<td></td>
</tr>
<tr>
<td>Pd-C(1)</td>
<td></td>
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<td>2.0279(16)</td>
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<td>Pd-N(5)</td>
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<td>Cl(1)-Pd-Cl(2)</td>
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<td>173.86(6)</td>
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Figure 4.10a: Molecular drawing of the Pd complex of 20 shown with 50% probability ellipsoids. All hydrogens and minor components of the disordered atoms are omitted.

Figure 4.10b: Molecular drawings of the palladium cation and boron anion of 20 showing the components of the disordered F atoms.
4.3.4 Attempted ethylene oligomerisation and polymerisation studies with cationic (pyrazo-1-ylmethyl)pyridine palladium complexes

Attempts were made to use the cationic complexes (19 and 20) as catalysts for the oligomerisation or polymerisation of ethylene. In one such approach to generate active catalysts \textit{in situ} (Scheme 4.5) a mixture of CH$_2$Cl$_2$ and MeCN or Et$_2$O was used. The choice of MeCN or Et$_2$O was based on the fact that they are weakly coordinating and hence would not compete with the incoming ethylene monomer for the vacant site of the metal and yet protect the metal in the absence of the monomer.$^7, 8, 20$ There was no oligomer or polymer formation in experiments that were performed in a mixture of CH$_2$Cl$_2$/Et$_2$O and CH$_2$Cl$_2$/NCMe. GC analysis of an aliquot of each sample showed only peaks corresponding to the respective solvents in the chromatograms. When CH$_2$Cl$_2$ and OEt$_2$ were used, palladium black formation was observed. This indicates decomposition that might be attributed to the weak coordinating ability of OEt$_2$.

![Scheme 4.5](image-url)

Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$  
S = OEt$_2$, NCMe,

\textbf{Scheme 4.5}
In experiments using CH₂Cl₂ and MeCN the lack of reactivity can be attributed to the relatively stronger binding affinity of MeCN compared to ethylene. The MeCN thus might block ethylene coordination hence hinder the ethylene reaction. Similar observations have been made by Brookhart and his group.¹a They observed that in experiments using MeCN for the palladium α-diimine complexes, no ethylene reactivity was observed. Indeed ¹H NMR analysis of the residue obtained indicated the formation of 19.

In order to circumvent the competition between ethylene and MeCN coordination, catalyst 19 was isolated as previously reported by Kress et al.³ for the palladium catalyst 4-III. The cationic species prepared (19) was used in the ethylene reaction as described in Scheme 4.6. Approximately 35 mg of catalyst 19 in CH₂Cl₂ solvent (100 mL) at ethylene pressures of 45 bar for 2 h at 30 °C was used (Scheme 4.6). After the reaction time, excess ethylene was vented off and the reaction quenched by addition of a small amount of MeOH. No precipitate was observed. The solvent was then removed under reduced pressure to give a white residue (Yield = 0.07 g). ¹H NMR and ¹³C NMR spectra of the product (Figure 4.11) showed signature peaks of low density (branched) polyethylene at 0.87 ppm and 1.25 ppm.¹a From the NMR spectrum, the degree of branching was found to contain 26 carbons atoms/1000 carbon atoms using equation 4.4. The ¹H NMR spectrum showed signals at 7.48 and 7.68 ppm that are peaks of BAr₄ protons.
Figure 4.11: $^{13}$C NMR spectra of polyethylene produced from catalyst 19 at 45 bar, 2 h and 30 °C.

\[
\alpha = \frac{2}{3} \times \frac{A_{1.25}}{A_{0.87}} \times 1000
\]  

\[\text{where } \alpha = \text{the number of branching per 1000 carbon atoms} \]

\[A_{1.25} = \text{integrated area of peak at 1.25 ppm} \]

\[A_{0.87} = \text{integrated area of peak at 0.87 ppm} \]

Attempts to optimise the catalytic conditions in order to improve the product yields were done by changing the reactions conditions. For instance the catalyst loadings were varied from 10-40 μmol and elevated temperatures of (i.e 60 °C) were employed. Unfortunately
all these manipulations did not improve the catalysts performance and negligible products were produced. Even experiments at low temperatures (0 °C and -78 °C) did not enhance the catalyst’s activity.

Complexes 17 and 18 that contain the relatively weaker donor ligands, 3,5-(CF₃)₂pz and OPh groups respectively that were expected to be hemi-labile have also been tested for their ability to catalyse ethylene oligomerisation or polymerisation reactions. In a previous experiment ligand 3,5-(CF₃)₂pz was found to be weakly coordinating to the palladium metal compared to 3,5-Me₂pz. It was therefore expected that the combination of 3,5-(CF₃)₂pz and 3,5-Me₂pz in one ligand unit (L5) would help enhance both the stability and activity of the catalyst. The weakly coordinating 3,5-(CF₃)₂pz group was expected to stabilise the cationic active species and at the same time be displaced by an incoming ethylene monomer to initiate oligomerisation or polymerisation of ethylene. However, in experiments carried using complex 17 and NaBAR₄ at ethylene pressure of 45 bar no ethylene oligomers or polyethylene formation was observed (Scheme 4.6).

![Scheme 4.6](image)

$^1$H NMR analysis of the residue after solvent evaporation showed signature peaks of the CH$_2$ linker protons as doublets at 5.16 ppm and 6.20 ppm. This indicated the formation of tridentate bound cationic complex 20 as previously described in section 3.2. It was therefore conceivable that L5 showed similar tridentate coordination upon chloride abstraction as described for L1 and L2 described in chapter 3.

Another experiment was performed using complex 18 containing the phenoxy donor group and NaBAr$_4$ under ethylene pressure of 45 bar (Scheme 4.7). After the reaction period, CH$_2$Cl$_2$ solvent was removed to give a white residue (Yield = 0.05 g). Analysis of the residue by $^1$H NMR spectroscopy showed signature peaks of branched polyethylene at 0.87 and 1.25 ppm. The reactivity of 18 with ethylene to produce polyethylene shows that the phenoxy group is weaker binding relative to ethylene; thus dissociates to allow ethylene coordination compared to the 3,5-(CF$_3$)$_2$pz unit in 17. However, the low activity of 18 suggests that the phenoxy group does not form a very good hemi-labile unit and as such competes with ethylene monomer for the coordination to the metal centre. Attempts to optimise the reaction conditions to increase the polymer yields did not result in increased catalytic activity. For instance reactions performed at 60 °C in chlorobenzene resulted in the formation of palladium black indicating decomposition of the catalysts.
4.3.5 Stability studies of cationic complexes

In order to understand the poor catalytic activity of the cationic species 19 in ethylene reactions, the stability of cationic species generated from 14 using different stabilising solvents was investigated by $^1$H NMR spectroscopy and DFT calculations. The half lives were determined by reacting 14 with one equivalent of NaBAr$_4$ and a slight excess of Et$_2$O, MeCN or PhCN in CDCl$_3$ in a J-Young NMR tube. In this way the cationic species were generated in situ and the half lives determined by monitoring the disappearance the Pd-Me signal using BAr$_4$ peaks as a reference peak. DFT calculations were performed at B3LYP/LANL2DZ level of theory to determine the enthalpies of formation of the respective cationic complexes. This was done by computing the enthalpies of formation of three coordinate species of 14 obtained after chloride removal, Et$_2$O, MeCN or PhCN.
and solvent stabilised cationic species under the same level of theory (Equation 4.5). The enthalpy of formation of $[\text{PdMe(L3)}\text{NCMe}]^+$ species has been used to illustrate how the enthalpies of formations were obtained by DFT. Table 4.3 shows the relative half lives and enthalpies of formation of the $[\text{PdMe(L3)}\text{OEt}_2]^+$, $[\text{PdMe(L3)}\text{NCMe}]^+$ and $[\text{PdMe(L3)}\text{NCPh}]^+$ cationic complexes respectively while Figure 4.12 shows the optimized geometries of the $[\text{PdMe(L3)}\text{NCPh}]^+$ and $[\text{PdMe(L3)}\text{OEt}_2]^+$ cationic complexes. The negative enthalpies of formation obtained (-39.8, -37.9 and -28.5 kcal/mol) for the cationic species showed that their formations were thermodynamically favoured.

\[
\begin{align*}
\Delta H &= H_3 - (H_1 + H_2) \\
\Delta H &= -0.060448 \text{ a.u} \times 627.5 \text{ kcal/mol/a.u} \\
\Delta H &= -37.9 \text{ kcal/mol}
\end{align*}
\]
Table 4.3: Half lives and enthalpies of formation of cationic species of 14

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$t_{1/2}$ (CDCl$_3$)</th>
<th>$\Delta H$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_2$O</td>
<td>N/A</td>
<td>-28.5</td>
</tr>
<tr>
<td>NCMe</td>
<td>24 h</td>
<td>-37.9</td>
</tr>
<tr>
<td>NCPH</td>
<td>120 h</td>
<td>-39.8</td>
</tr>
</tbody>
</table>

As expected the MeCN and PhCN stabilised species showed much longer half lives (24 h and 120 h respectively) than the Et$_2$O cationic species (Table 4.3). Results of DFT calculations also showed a similar trend; the Et$_2$O adduct had the lowest stability of -28.5 kcal/mol compared to -37.9 and -39.8 kcal/mol for the MeCN and PhCN respectively. The poor donor ability of Et$_2$O is believed to be responsible for the lower stability of its adduct compared to the stronger donor ligands MeCN and PhCN.

Figure 4.12: Optimized geometries of [PdMe(L3)NCPh]$^+$ (a) and [PdMe(L3)OEt$_2$]$^+$ (b) computed at the B3LYP/LANL2DZ level of theory.
In summary the MeCN and PhCN cationic adducts were found to be stable in solution (24 and 120 h respectively). The phenoxy group in ligand L6 also showed some stabilising role in the resultant cationic active species. It is therefore conceivable that the poor activity of the catalysts obtained from these (pyrazol-1-ylmethyl)pyridine palladium complexes might not be due to low stability alone. As such other factors such as poor electrophilicity of the Pd metal centre might play a role in low catalytic activities of these (pyrazol-1-ylmethylmethyl)pyridine palladium complexes. As a result the crucial step of ethylene coordination to the vacant palladium metal centre might be severely limited thus no appreciable catalytic activity was achieved.

4.3.6 Reactions of chloromethyl palladium complexes with sulfur dioxide

In attempts to investigate if the chloromethyl palladium complexes 14 and 16 could allow the coordination of other small molecules like sulfur dioxide (SO₂), complex 14 was reacted with SO₂ to give complex 21 in good yields (Scheme 4.8). SO₂ gas was bubbled through a solution of 14 in CH₂Cl₂ to maintain steady flow of the gas into the complex solution. Colour changes from colourless solution of 14 to yellow were a clear indication of the reaction of the SO₂ with 14. Addition of hexane saturated with SO₂ gas into the reaction solution precipitated complex 21 as a pure crystalline yellow product in 76% yield.

$^1$H NMR spectroscopy was useful in identification of compound 21 (Figure 4.13). The downfield chemical shift position of the Pd-Me protons from 0.97 ppm in 14 to 3.17 and 3.24 ppm in 21 indicated insertion of SO$_2$ into the Pd-C bond to give Pd-SO$_2$Me complex. Literature reports show that insertion of small polar molecules such as CO as in (dppf)Pd(C(O)Me)Cl shifts methyl protons by more than 1.00 ppm from the signals of the original complexes prior to insertion.\textsuperscript{23} It is worth to note that instead of one singlet of the Pd-Me protons at 0.97 ppm in the $^1$H NMR spectrum of 14, the $^1$H NMR spectrum of compound 21 exhibited two signals for the Pd-SO$_2$Me protons at 3.17 and 3.24 ppm. More interesting is the appearance of the CH$_2$ linker protons as four distinct AB quartets between 5.19 to 6.22 ppm ($^2$J$_{HH}$ = 15.0 Hz) in 21 compared to broad peaks at 5.20 and 6.40 ppm in 14. This clearly shows that the insertion of the SO$_2$ molecule alters the molecular dynamics of compound 21 on the NMR time scale and hints at an increased restricted rotation about the CH$_2$ linker as shown by the two sets of resonances that

indicate the presence of two isomers (chair and boat conformations). $^{13}$C NMR spectral data was also consistent with the $^1$H NMR data; a shift of the Pd-Me signal from about -8.0 ppm in 14 to 30.8 ppm in the insertion product 21 was observed.

![Figure 4.13: $^1$H NMR spectrum of 21 showing the two distinct singlets and doublets of the Pd-Me and CH$_2$ linker protons (inset) respectively.](image)

Compound 21 was also characterised by electron-spray ionization mass spectrometry (ESI-MS). Mass spectrum of 21 (Figure 4.14) shows molecular ion peak at m/z = 408 (20%) that corresponds to 21. Fragmentation pattern involves the loss of a Cl$^-$ ion first to give a 14-electron fragment at m/z = 372 (Scheme 4.9). Subsequent loss of SO$_2$ resulted in the cationic fragment [(L3)PdMe]$^+$ as the base peak. The loss of a PdMe fragment produced a peak at m/z = 188 that corresponds to L3.
Figure 4.14: ESI mass spectrum of complex 21

Scheme 4.9
4.4 Conclusions

(Pyrazolylmethyl)pyridine ligands form mononuclear palladium complexes when reacted with [PdClMe(COD)] or [PdCl₂(COD)] metal precursors. The cationic palladium complexes could be stabilised by either weakly coordinating solvents or donor groups to give active ethylene polymerisation catalysts producing branched polyethylene albeit with very low activities. The cationic species of MeCN and PhCN were stable in solution for several hours. Thus poor electrophilicity of the Pd metal centres other than decomposition might account for the low catalytic activities of these (pyrazolylmethylmethyl)pyridine palladium complexes. Chloromethyl palladium complexes react with SO₂ to form stable SO₂ compounds through insertion mechanism.

The low activities of the palladium complexes of both bis(pyrazol-1-ylmethyl)pyridine and (pyrazol-1-ylmethyl)pyridine ligands described in Chapters 3 and 4 prompted us to extend the synthesis of nickel complexes of these ligands and their applications in ethylene and higher α-olefin oligomerisation and polymerisation reactions. This work is described in Chapter 5.
CHAPTER 5

(Pyrazol-1-ylmethyl)pyridine nickel complexes: Synthesis, structural determination, ethylene and α-olefin oligomerisation catalysis

5.1 Introduction

The past decade has witnessed an increased interest in the design of new late transition metal catalysts for the oligomerisation and polymerisation of α-olefins.¹ One of the most studied late transition metal single-site catalyst is nickel. Majority of single site nickel catalyst precursors reported for homogeneous oligomerisation of α-olefins contain bidentate chelating ligands with P^P, P^N, P^O, N^N or N^O (5-I) donor atoms in a four coordinate complex.²⁻⁶ Very few examples of five-coordinate nickel catalysts for olefin oligomerisation and polymerisations reactions are known.¹ᵃ One such catalyst is the bis(oxazolin-2-ylmethyl)phosphonite nickel catalyst (5-II) reported by Braunstein and coworkers⁷ that oligomerises ethylene to mainly butenes.

Laine and coworkers\textsuperscript{8} have reported pentacoordinate bimetallic nickel complexes with two bidentate pyridinylimine ligand units, two terminal and two bridging bromide ligands. When these bimetallic complexes are activated with MAO they form active catalysts for the polymerisation of ethylene to branched polyethylene. Nickel catalysts having unsymmetrical bidentate pyridinylimine ligands that combine features of bipyridine alkene oligomerisation catalysts\textsuperscript{3} and that of sterically hindered $\alpha$-diimine alkene polymerisation catalysts\textsuperscript{8} have also been reported. For example, whereas $\alpha$-diimine nickel catalysts polymerise ethylene to high density linear polyethylene,\textsuperscript{9} bipyridine nickel catalysts generally produce oligomers,\textsuperscript{3} mixed pyridinylimine nickel catalysts produce low molecular weight branched polyethylene.\textsuperscript{5}

\[
\begin{align*}
\text{Ar} &= 2,6-\text{Me}_2\text{C}_6\text{H}_3, 2,6-\text{iPrC}_6\text{H}_3 \\
\text{5-I} & \quad \text{5-II}
\end{align*}
\]

\begin{enumerate}
\end{enumerate}
Recently five-coordinate pyrazolyl nickel catalysts (5-III) for the oligomerisation of ethylene have also appeared in literature. For example Ajellal et al.\textsuperscript{10} have reported nickel complexes of tridentate O or S bridged bis(pyrazolyl) ligands that are highly active for selective dimerisation of ethylene to 1-butene. One pyrazol-1-yl ligand that is predisposed to form five-coordinate nickel complexes is 2,6-bis(pyrazol-1-ylmethyl)pyridine compound. Complexation of these ligands with nickel is yet to be reported but they have been found to form iron and cobalt complexes (5-IV) that are active ethylene polymerisation catalysts; even though they exhibit very low activity.\textsuperscript{11}

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) \[ \text{5-III} \];
\node (b) at (4,0) \[ \text{5-IV} \];
\end{tikzpicture}
\end{center}

Chapters 3 and 4 described attempts to use bis(pyrazol-1-ylmethyl)pyridine and (pyrazol-1-ylmethyl)pyridine palladium complexes as catalysts in ethylene polymerisation reactions. The bis(pyrazol-1-ylmethyl)pyridine palladium catalyst precursors formed tridentately bound cationic species\textsuperscript{12} which were inactive towards ethylene polymerisation.

\begin{thebibliography}{9}
\end{thebibliography}
polymerisation. The (pyrazol-1-ylmethyl)pyridine palladium catalyst precursors described in chapter 4 were found to decompose rapidly and also exhibited very low activities even when they were stabilised by hemi-labile donor groups.

In contrast to palladium, nickel is known to form complexes with coordination number higher than four that can avoid forming inactive intermediates when activated. In addition to the higher coordination number shown by nickel, the nickel complexes are also known to be more electrophilic and hence enhance catalytic activities of the nickel catalysts. These two characteristics of nickel have thus been explored to prepare both four- and five-coordinate complexes of bis(pyrazol-1-ylmethyl)pyridine and (pyrazol-1-ylmethyl)pyridine ligands that can be activated to form active ethylene and α-olefin oligomerisation catalysts. In this chapter the synthesis and characterisation of these (pyrazol-1-ylmethyl)pyridine nickel complexes are presented. The nickel complexes on activation give active catalysts that oligomerise ethylene and α-olefins. The oligomerisation reactions are also discussed in this chapter.

5.2 Experimental section

5.2.1 Materials and Instrumentation

All synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents were of analytical grade and were dried and distilled prior to use. Hexane and dichloromethane were dried and distilled from sodium/benzophenone and P₂O₅ respectively. 2,6-bis(chloromethyl)pyridine, 2-picoyl chloride hydrochloride, tetrabutylammonium bromide, EtAlCl₂, NiCl₂ and NiBr₂
were obtained from Sigma-Aldrich and used as received. Ethylene gas (High grade) was obtained from Afrox and used as received. The starting materials 3,5-di-tert-butylpyrazole,\textsuperscript{13} 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L1), 2,6-bis(3,5-di-tert-butylpyrazol-1-ylmethyl)pyridine (L2), 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L3) and 2-(3,5-di-tert-butylpyrazol-1-ylmethyl)pyridine (L4) were synthesised following the literature\textsuperscript{14} procedures as described in Chapters 3 and 4. Mass spectra were recorded on a Waters API Quattro Micro spectrometer at the University of Stellenbosch, South Africa. Elemental analyses were performed by the micro analytical laboratory at the University of Cape Town, South Africa, as a service. Magnetic susceptibility measurements in the solid state were performed using a Cahn Faraday electromagnetic balance.

5.2.2 Synthesis of nickel complexes

5.2.2.1 \{[2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine]NiCl\}_2 (22)

To a solution of NiCl\textsubscript{2} (0.16 g, 1.25 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added a solution of 2,6-bis(3,5-dimethylpyrazolylmethyl)pyridine, L1, (0.33 g, 1.25 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL) to give a blue solution. The solution was stirred for 24 h, the solvent removed under reduced pressure and the residue obtained recrystallised from CH\textsubscript{2}Cl\textsubscript{2}/Hexane mixture (2:1) to obtain complex 22 as a blue solid. Yield = 0.44 g (84%). ESI-MS: m/z (%) 425 (M\textsuperscript{+}, 10); 267 (100). \(\mu_{\text{eff}} = 3.61\) BM. Anal. Calc. for C\textsubscript{17}H\textsubscript{21}N\textsubscript{5}NiCl\textsubscript{2}: C, 48.43; H, 4.98; N, 16.89. Found: C, 48.79; H, 5.23; N, 17.33.

Complexes 23-30 were synthesised following the procedure described for 22 using the appropriate ligand and nickel salts.

5.2.2.2 \[[2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine]NiBr_2\] (23)

Complex 23 was prepared from NiBr₂ (0.15 g, 0.68 mmol) and L₁ (0.20 g, 0.68 mmol) and obtained as a light blue solid. Yield = 0.28 g (81%). ESI-MS: m/z (%) 425 (M⁺, 10); 267 (100). Anal. Calc. for C₁₇H₂₁N₅NiBr₂·0.5CH₂Cl₂: C, 37.83; H, 3.96; N, 12.61. Found: C, 37.56; H, 4.39; N, 12.18.

5.2.2.3 \[[2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine]NiCl₂\] (24)

Complex 24 was synthesised from NiCl₂ (0.11 g, 0.86 mmol) and L₂ (0.40 g, 0.86 mmol) and isolated as a green solid. Yield = 0.25 g (50%). ESI-MS: m/z (%) 590 (M⁺, 20); 464 (100). Anal. Calc. for C₂₉H₄₅N₅NiCl₂: C, 58.71; H, 7.64; N, 11.80. Found: C, 58.48; H, 7.93; N, 12.17.

5.2.2.4 \[[2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine]NiBr₂\] (25)

Compound 25 was prepared using NiBr₂ (0.25 g, 1.20 mmol) and L₂ (0.55 g, 1.20 mmol) and obtained as a green solid. Yield = 0.49 g (60%). ESI-MS: m/z (%) 706 (M⁺ + Na⁺, 10); 464 (100). Anal. Calc. for C₂₉H₄₅N₅NiBr₂: C, 51.06; H, 6.65; N, 10.27. Found: C, 51.38; H, 6.23; N, 10.33.
5.2.2.5 [(2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine)Ni(μ-Cl)Cl]_2 (26)

Compound 26 was prepared following the procedure described for compound 22 but using NiCl₂ (0.26 g, 2.00 mmol) and 2-(3,5-dimethylpyrazolylmethyl)pyridine, L3, (0.38 g, 2.00 mmol). The product was precipitated from CH₂Cl₂ solution by adding hexane (20 mL) to give 26 as a green solid. Yield = 0.93 g (74%). μ_eff = 4.05 BM. Anal. Calc. for C₂₂H₂₆N₆Ni₂Cl₄.0.5CH₂Cl₂: C, 39.94; H, 3.99; N, 12.42. Found: C, 39.86; H, 4.00; N, 12.89.

5.2.2.6 [(2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine)Ni(μ-Br)Br]_2 (27)

Compound 27 was synthesised in a similar manner to complex 22 using NiBr₂ (0.17 g, 0.80 mmol) and L3 (0.15 g, 0.80 mmol). Recrystallisation from CH₂Cl₂-hexane solution at -4 °C gave red crystals suitable for single crystal X-ray analysis. Yield = 0.26 g (40%). Anal. Calc. for C₂₂H₂₆N₆Br₄Ni₂.0.5CH₂Cl₂: C, 31.65; H, 3.17; N, 9.85. Found: C, 31.65; H, 3.52; N, 9.50.

5.2.2.7 [(2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine)₂NiBr₄] (28)

Complex 28 was prepared following the procedure described for complex 22 but using NiBr₂ (0.25 g, 1.20 mmol) and two mole equivalents of L3 (0.45 g, 2.40 mmol) to give complex 28 as a blue solid. Yield = 0.58 g (77%). Anal. Calc. for C₂₂H₂₆N₆Br₂Ni.CH₂Cl₂: C, 40.75; H, 4.36; N, 12.45. Found: C, 40.56; H, 4.68; N, 12.93.
5.2.2.8 \textit{[2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine}NiCl$_2$\] (29)

Compound 29 was prepared following the procedure described for 22 but using NiCl$_2$ (0.20 g, 1.50 mmol) and L$_4$ (0.40 g, 1.50 mmol). Recrystallisation from CH$_2$Cl$_2$/hexane (2:1) afforded 29 as purple crystalline solid. Yield = 0.24 g (40%). Anal. Calc. for C$_{17}$H$_{25}$N$_3$NiCl$_2$: C, 50.92; H, 6.28; N, 10.48 Found: C, 50.75; H, 6.68; N, 10.12.

5.2.2.8 \textit{[2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine}NiBr$_2$\] (30)

Complex 30 was prepared following the procedure described for complex 22 but using NiBr$_2$ (0.32 g, 1.50 mmol) and L$_2$ (0.40 g, 1.50 mmol) and recrystallisation from CH$_2$Cl$_2$/hexane (2:1) gave purple crystals suitable single crystal X-ray analysis. Yield = 0.29 g (40%). Anal. Calc. for C$_{17}$H$_{25}$N$_3$NiBr$_2$: C, 41.68; H, 5.14; N, 8.58. Found: C, 41.87; H, 5.46; N, 8.35.

5.2.3 Ethylene oligomerisation reactions

Ethylene oligomerisation reactions were performed in a 600 mL stainless high pressure autoclave equipped with a mechanical stirrer, temperature controller and an internal cooling system. In a typical experiment, the autoclave was preheated to 100 °C for 1 h under vacuum and cooled to 30 °C. The appropriate amount of a nickel catalyst precursor (10.00 μmol) was introduced into a pre-heated dry Schlenk tube under nitrogen and toluene (20 mL) added using a syringe. The required amount of EtAlCl$_2$ was then injected into the Schlenk tube and canula transferred to the reactor. An additional 60 mL of toluene was canula transferred to the reactor to give a total volume of 80 mL. The reactor was then flashed three times with ethylene and the desired pressure set and the
stirrer started. After the reaction period, the reactor was cooled and excess ethylene vented. The total volume (mL) of products was determined, which was used to calculate (estimate) the mass of the products. The reaction was then quenched by addition of 10% HCl (10 mL). An aliquot of the products was taken for GC analysis.

5.2.4 Higher \( \alpha \)-olefin oligomerisation reactions

In a typical experiment, nickel catalyst precursor (10.0 \( \mu \)mol) was added to a dry Schlenk tube with a stir bar under inert atmosphere. Toluene (20 mL) was then added followed by an appropriate amount of an \( \alpha \)-olefin. The required amount of the co-catalyst, EtAlCl\(_2\), was then added via a syringe and rapid stirring began to maintain a homogeneous mixture. After the reaction period, 10% HCl (5 mL) was added to the mixture to quench the oligomerisation process and an aliquot of the product sampled for GC analysis.

5.2.5 GC-analysis of oligomerisation products

Analysis of the oligomers produced was performed on a Shimadzu GCMS-QP 2010 version 2 Gas Chromatograph fitted with flame ionisation detector and a ZB1 column with a 100% dimethylpolysiloxane solid phase and column dimensions of 30 m by 0.25 mm. The standard temperature program was as follows: 40 °C (5 min), then temperature gradient of 10 °C/min was applied to a final temperature of 300 °C and maintained at 300 °C for 5 min. In this way, effective separation of the olefins in the C\(_4\)-C\(_{30}\) range was achieved. A mixture of authentic standard samples was used to establish retention times that were used to identify the components of the products from the olefin oligomerisation reactions.
5.2.6 X-ray crystallography experimental section

Single crystal X-ray crystallography analyses were performed at the University of Wisconsin, Molecular Structure Laboratory, by DR. Ilia A. Guzei.

Data Collection
All X-ray crystallography experiments were performed in a similar manner to the description for complex 27. A red crystal with approximate dimensions 0.46 x 0.34 x 0.12 mm³ was selected under oil under ambient conditions and attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. A total of 52 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6098 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 20594 data were harvested by collecting four sets of frames with 0.25º scans in ω and φ with an exposure time 15 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption
correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.\textsuperscript{15}

**Structure Solution and Refinement**

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The $E$-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement.\textsuperscript{15} A successful solution by the direct methods provided most non-hydrogen atoms from the $E$-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The dinuclear complex occupies a crystallographic inversion center. The final least-squares refinement of 156 parameters against 3115 data resulted in residuals $R$ (based on $F^2$ for $I \geq 2\sigma$) and $wR$ (based on $F^2$ for all data) of 0.0187 and 0.0497, respectively. The final difference Fourier map was featureless. The molecular diagram is drawn with 50\% probability ellipsoids.

5.3 Results and discussion

5.3.1 Synthesis of 2,6-bis(pyrazol-1-ylmethyl)pyridine and 2-(pyrazol-1-ylmethyl)pyridine Ni(II) complexes

Reactions of L1 and L2 with either NiCl$_2$ or NiBr$_2$ in dichloromethane afforded the respective complexes 22-25 in moderate to high yields (Schemes 5.1). Compounds L3 and L4 when reacted with either NiCl$_2$ or NiBr$_2$ also gave the corresponding complexes 26-30 in moderate to high yields (Scheme 5.2). Complexes 22, 23, 27 and 28 were isolated as blue solids while 24, 25 and 26 were obtained as green solids. Compounds 29 and 30 were isolated as purple solids.

All the complexes (22-30) were found to be paramagnetic indicating that the complexes have high spin even though majority of five coordinate nickel(II) complexes (as proposed in Scheme 5.1) are low spin; however the nature of the coordinated ligand is known to influence the magnetic properties of metal complexes. The magnetic moments of 22 and 26 were found to be 3.61 BM, and 4.05 BM respectively and were affectively higher than the spin only value of 2.83 BM expected for Ni(II) complexes but fall within the observed range (2.9-4.2 BM) for high spin Ni(II) complexes. The higher magnetic


moments could arise from spin-orbital contribution to the spin only magnetic moments.\textsuperscript{16} Magnetically octahedral Ni(II) complexes should have two unpaired electrons in the $dx^2-y^2$ and $dz^2$ orbitals and the magnetic moments ranging from 2.9 to 3.4 BM. For five-coordinate Ni (II) complexes, both low and high spin configurations are possible depending on whether the crystal field stabilisation energy ($\delta_2$) is greater or smaller than the mean spin-pairing energy. For a five coordinate Ni(II) complex, the paramagnetic nature thus suggests that the $dx^2-y^2$ and $dz^2$ orbitals are closer in energy resulting in both orbitals being singly occupied (i.e pairing energy greater than $\delta_2$). For example the nickel complex $[\text{Ni(Me}_2\text{NCH}_2\text{CH}_2\text{N})\text{Cl}]^+$ has been found to be high spin with magnetic moment of 3.42 B.M.\textsuperscript{16} From the magnetic moments alone, it was not possible to determine whether complexes 22-25 were six or five-coordinate since in both cases high spin nickel(II) complexes are possible.

\textbf{Scheme 5.1}

The four-coordinate geometry in 22-25 was ruled out from the tridentate coordination mode already established crystallographically for 2,6-bis(pyrazol-1-ylmethyl)pyridine ligand when reacted with Ni(ClO$_4$)$_2$ precursor.\textsuperscript{14} A related cobalt complex obtained from
the reaction of CoCl$_2$ with 2,6-bis(pyrazol-1-ylmethyl)pyridine ligand was also found to be five-coordinate again with the ligand binding in a tridentate fashion and the cobalt metal centre adopting a square pyramidal geometry. A combination of elemental analysis and mass spectrometry was hence used to further elucidate the structures of complexes 22-25. Elemental analyses data were consistent with one ligand unit and one nickel metal centre. Mass spectrometry proved useful in identifying the molecular formulae of complexes 22-25. Figure 5.1 is a typical mass spectrum of complex 24 where a molecular ion identifies 24 and base peak identifies L2. For example the complexes showed molecular ion peaks at m/z = 425 (22), 513 (23), 590 (24), and 682 (25). In all cases fragmentation of the complexes resulted in loss of NiX$_2$ (X = Cl or Br) to give base peaks at m/z = 267 or 464 corresponding to L1 and L2 respectively. Mass spectrometry results were thus in good agreement with the proposed five-coordinate structures shown in Scheme 5.1. Attempts to isolate single crystals suitable for X-ray analysis to confirm the proposed structures of complexes 22-25 have so far been unsuccessful.

Figure 5.1: ESI-MS mass spectrum of complex 24.
The paramagnetic nature of 26-30 in Scheme 5.2 ruled out the possibility of square planar geometry. All four-coordinate square planar nickel complexes are diamagnetic. This therefore suggests that 26-30 could either be tetrahedral or square pyramidal. X-ray analysis of 27 and 30 confirmed the square pyramidal and tetrahedral geometries. It is known that bulky ligands adjacent to the nitrogen donor atoms render planarity of Ni(L-L)₂ molecule sterically impossible.¹⁸ The bulkier ligand L₄ thus favours tetrahedral geometry as confirmed by the solid state structure of 30. Compounds L₃ and L₄ gave three coordination geometries with nickel depending on the steric bulk of the ligand and molar ratio of the ligand to nickel salts. When L₃ was reacted with NiX₂ (X = Cl or Br)

in a 1:1 molar ratio, bimetallic nickel complexes 26 and 27 were obtained (Scheme 5.2). The solid-state structure of 27 obtained from the red crystals (Figure 5.2) was a five coordinate nickel compound that contained two ligand units, two terminal and bridging bromide ligands. The purple colour in solution (CH₂Cl₂) thus indicates that there exists a different geometry in solution. This is believed to arise from dissociation of the dimer to establish equilibrium between the five and four coordinate tetrahedral species (Eq. 5.1). Similar behaviour for the diphenyl(dipyrazolyl)methane nickel complexes have been reported by Baho and co-workers.¹⁹

![Diagram of complexes 26 and 27](image)

On the other hand when L₃ was reacted with NiBr₂ salt in 2:1 ratio, a six coordinate complex 28 that contains two ligand units was formed as deduced from elemental analysis. When the bulkier ligand L₄ was reacted with NiX₂ (X = Cl or Br) in 1:1 mole ratio, monometallic four-coordinate nickel complexes 29 and 30 were isolated. The solid state structure of 30 was confirmed as a distorted tetrahedral geometry (Figure 5.3) in

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which \( L_4 \) binds in a bidentate fashion. The four-coordinate geometry of \( 30 \) might be favourable due to the bulkier \( L_4 \) which prohibits dimerisation as compared to the less bulky \( L_3 \) in \( 27 \). More recently Sun and co-workers\(^{20}\) observed similar structural dependence on steric factors for the \( N-\{(pyridine-2-yl)methylene\}quinolin-8-amine \) nickel complexes. While the nickel complexes containing less bulky ligands (H and Me groups on the pyridine ring) exhibited dimeric solid state structures, the complexes that contain bulkier ligands (\( i\)-Pr and Cy groups on the pyridine ring) were found to be monomeric and adopt a tetrahedral geometry.\(^{20}\) From the structures of \( 27 \) and \( 30 \) the solid-state structures of \( 26 \) and \( 29 \) were expected to be five- and four-coordinate respectively. The structure of \( 28 \) is proposed to have an octahedral geometry that contains two units of \( L_3 \) binding in a bidentate fashion and two bromide ligands (Scheme 5.2) based on elemental analysis data. The structure of a related \( 2-(pyrzol-1-ylmethyl)pyridine \) dichloride nickel complex has been proposed by Tal and Mukherjee\(^{21}\) to have an octahedral geometry with two ligand units binding in a bidentate mode to the metal centre based on elemental analysis.

### 5.3.2 Molecular structures of complexes 27 and 30

Single crystals suitable for X-ray analysis of compounds \( 27 \) and \( 30 \) were grown by slow diffusion of hexane into \( \text{CH}_2\text{Cl}_2 \) at \(-4^\circ\text{C}\) and used for their solid state structure elucidation. Crystal data and structure refinement for complexes \( 27 \) and \( 30 \) are shown in

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Table 5.1 while selected bond lengths and angles are given in Table 5.2. Figures 5.2 and 5.3 represent the solid state structures of 27 and 30 respectively. The solid structure of complex 27 is a centrosymmetric dimer with two ligand backbones, one terminal bromine in each Ni centre and two bridging bromine atoms giving a five coordination sphere around each Ni centre. In complex 30, the central Ni atom binds to two bromine atoms and one bidentate ligand and exhibits a severely distorted tetrahedral geometry. The coordination of L3 with 27 could be regarded as a slightly distorted trigonal bipyramidal in which the equatorial plane includes the nitrogen of the pyrazolyl ring, N(1), the terminal bromine, Br(1A) and one of the μ-bridging bromine atoms, Br(2). The pyridine nitrogen, N(3), and the other constituent of the bromine bridge, Br(2A) occupy the axial coordination sites. The average Ni-N_{pz} distance of 2.0052(15) Å for 27 is significantly shorter than the reported bond distance of 2.069(2) Å for tridentate RN-O-, or S-bridged bis(pyrazolyl) Ni(II) complex. The bond lengths of Ni-N_{py} of 2.0733(14) Å, Ni-Br_{terminal} of 2.4123(3) Å and Ni-Br_{bridging} of 2.5021(3) Å are all statistically similar to the average bond lengths of Ni-N_{py} (2.0518(5) Å), Ni-Br_{terminal} (2.4198(17) Å) and Ni-Br_{bridging} (2.5738(10) Å) reported for four pyridinylimine nickel complexes reported by Laine.

The bond angles about the central metal atom in 30 vary between 93.48(5)° to 127.34(4)°. Steric repulsion of the large bromide ligands results in a wide Br-Ni-Br angle of 118.321(11)° and subsequent contraction of the N1-Ni-N3 angle to 93.48(5)°. The bond lengths of Ni-N_{pz} of 2.0052(15) Å in 27 and 2.0077(14) Å in 30 were statistically similar. Similarly the bond distances of Ni-N_{py} of 2.0733(14) Å in 27 and 2.0733(14) Å in 30...
statistically indistinguishable. The Ni-Br distances of 27 and 30 (av 2.4572(3) Å and 2.3754(3) Å respectively) are both statistically longer than the average Ni-Br distance of 2.36(3) Å obtained by averaging 72 bond distances in 45 relevant compounds reported to the Cambridge Structural Database (CSD).22

Figure 5.2. Molecular structure of complex 27 drawn with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 5.1: Crystal data and structure refinement for complexes 27 and 30

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Table 5.2. Selected bond lengths and angles for 27 and 30

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Figure 5.3a: A molecular drawing of 30. All H atoms are omitted. Complexes Ni1 and Ni1a have similar geometries while complex with Ni1b differs in the position of atom C6b.
5.3.3 Ethylene oligomerisation reactions

5.3.3.1 Investigation of nickel complexes as catalysts for ethylene reactions

In order to evaluate the nickel complexes described above for their ability to catalyse ethylene oligomerisation or polymerisation reactions, three co-catalysts (MMAO, Et₂AlCl and EtAlCl₂) were used in attempts to generate the active catalysts for these two reactions. Only EtAlCl₂ resulted in the generation of active catalysts and was thus used for further investigations. Experiments with other co-catalysts, MMAO, Et₂AlCl did not result in the formation of active catalysts. Upon activation of complexes 22-30 with EtAlCl₂ good catalytic activities for the oligomerisation of ethylene at 20 bar were observed. The ethylene oligomerisation data for catalysts 22-30 are summarised in Table 5.3. The reactions were highly exothermic. Reaction temperatures could reach as high as 115 °C in some cases even though the reactor temperature was set at 30 °C. Generally with effective internal cooling the reaction temperatures stabilised at 30 °C within 10-30
min. The major products of the oligomerisation reactions were C\textsubscript{11}, C\textsubscript{14} and C\textsubscript{16} (see Appendix A for GC characterisation) and showed deviation from the Schulz-Flory distribution.\textsuperscript{23} It is interesting to note the formation of C\textsubscript{11} as a major product.

5.3.3.2 Product composition analyses of ethylene oligomerisation reactions

Analyses of the ethylene oligomerisation reaction products were exclusively done using GC characterisation. This was done by establishing the retention times of standard authentic samples which were used to establish the composition of the ethylene oligomerisation products. Figure 5.4 shows a GC chromatogram of a mixture of standard samples in the range C\textsubscript{5}-C\textsubscript{20} while Figure 5.5 is a typical GC chromatogram of ethylene oligomerisation product. From Figure 5.5, it was evident that only three major products were formed from the reactions. Comparison of the retention times in Figures 5.4 and 5.5, the major products were identified as C\textsubscript{11}, C\textsubscript{14} and C\textsubscript{16} oligomers. In order to fully establish the presence of C\textsubscript{11}, C\textsubscript{14} and C\textsubscript{16} oligomers, the products were spiked with standard samples of 1-C\textsubscript{11}, 1-C\textsubscript{14} and 1-C\textsubscript{16} samples. For example, Figure 5.6a shows a GC chromatogram of the product from the reaction using catalyst 22. Spiking of the same sample with 1-C\textsubscript{11} (Figure 5.6b) showed increased intensity of the peak at 1-C\textsubscript{11} indicating that the peak at retention time 13.06 min corresponds to the 1-C\textsubscript{11} oligomer.

Figure 5.4: GC chromatogram of authentic standard samples of linear C₅-C₂₀ α-olefins

Figure 5.5: Typical GC trace of the oligomer products obtained using catalyst 26, Al:Ni ratio of 200:1, temp = 30 °C, pressure = 20 bar, Time = 1 h.
Figure 5.6: (a) GC chromatogram of oligomer product from reaction using catalyst 22 at 40 bar, 30 min (b). GC trace of the same sample spiked with 1-C11 showing increased intensity of the C11 fraction at retention t = 13 min.

Product composition analyses were also done by a detailed GC analysis of each major component. For example analysis of the C14 cut (Figure 5.7) showed that it contained 5 isomers. This was evident of isomerisation and “chain running” producing branched or internal olefins in addition to the linear 1-C14. One of the major products was identified as 1-C14 (ca 40%) using standard authentic 1-tetradecene. The other three isomers with a combined composition of 60% could either be linear internal or branched alpha C14
oligomer products. Expansion of the C11 and C16 also suggest similar isomerisation products. Identification of the other isomerisation products of C11, C14 and C16 fractions were not done due lack of standard samples of the isomers.

Figure 5.7: GC trace of C14 oligomer fraction made by catalyst 22 at 20 bar, 60 min, Al:Ni, 250:1 (40% linear 1-C14).

Very few late transition metal ethylene oligomerisation catalysts are known to produce odd-numbered olefins. Small24 and Alt25 have recently reported iron complexes that show this behaviour. Both authors have proposed that the formation of odd-number olefin results from “chain running” mechanism initially suggested by Brookhart26 starting with an isomerisation reaction of 1-olefin to give the corresponding 2-olefins (Scheme 5.3). After

β-hydride elimination, the 2-olefin remains in the coordination sphere of the metal centre to form olefin complex c. Subsequent coordination of ethylene produces complex d. Cross metathesis of ethylene and the 2-olefin produces coordinated odd-number olefin and 1-propene as in complex e (Scheme 5.3). Elimination of the coordinated olefins from the nickel metal produces the odd number oligomers and regeneration of the active catalysts species a. Formation of C_{11} in the ethylene oligomerisation reactions catalysed by 22-30 is believed to originate from the cross-metathesis of 2-C_{12} and C_{2}H_{4} via the above mechanistic pathway.

Scheme 5.3
Complexes 22-30 showed higher percentages of odd-number olefins (41-53%) compared to the iron catalysts reported by Small\textsuperscript{24} (29%) and Alt\textsuperscript{25} (2%). To the best of our knowledge, nickel catalysts 22-30 represent the first type of catalyst producing the highest composition of odd-numbered olefins from ethylene oligomerisation reaction.

5.3.3.3 Influence of co-catalyst concentration and catalyst structure on ethylene oligomerisation reactions

To obtain the optimum co-catalyst to catalyst precursor ratio, the co-catalyst to catalyst precursor ratio was varied from 100 to 300 using complexes 22 and 26 (Table 5.3, entries 1-3 and entries 7-9). The results indicate a significant influence of Al:Ni ratio on TON of catalysts 22 and 30. The highest TONs for 22 and 30 of 4002 and 6960 kg oligomer/mol Ni.h were observed at Al:Ni ratios of 250:1 and 200:1 respectively (Figure 5.8). These represent threshold amounts of EtAlCl\textsubscript{2} required to efficiently generate the active catalyst without causing deactivation.\textsuperscript{27} It is unclear why complex 22 required high amounts of co-catalyst compared to 26.

Having established the optimum Al:Ni ratios, complexes 22-30 were screened at Al:Ni ratios of 250:1 (22-25) and 200:1 (26-30) at 20 bar to probe the effect of ligand environment on catalytic activity (Table 5.3, entries 4-13). Catalyst 29 was found to be the most active and 27 was the least active. In general catalysts 26-30 that contain the

\begin{itemize}
\end{itemize}
Table 5.3: Ethylene oligomerisation data of complexes 22-30\textsuperscript{a}

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<th>Yield (g)\textsuperscript{e}</th>
<th>TON (kg/mol. Ni. h)</th>
<th>(%) C(_{11})</th>
<th>(%) C(_{14})</th>
<th>(%) C(_{16})</th>
<th>(%) 1-C(_{14})\textsuperscript{e}</th>
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\textsuperscript{a}Reaction conditions: Amount of catalyst; 10.00 \(\mu\)mol; Temp, 30 °C; Pressure, 20 atm; Time, 1 h; Solvent, toluene (80 mL); \textsuperscript{b}Initial temp was 30 °C, \(T_{min}\) and \(T_{max}\) = Highest and lowest temps attained during the reaction period; \textsuperscript{c}Determined by mass difference of 80 mL toluene (69.60 g) and mass of final solution; \textsuperscript{d}Determined by GC; \textsuperscript{e}Determined by GC, Linear \(\alpha\)-C\(_{14}\).

Bidentate ligands were found to be more active than those containing the tridentate ligands (22-25). For example while the tridentate bound catalysts 22 and 24 gave activities of 4 002 and 2 958 kg oligomer/mol Ni.h (Table 5.3, entry 5), the bidentate bound catalysts 26 and 29 gave appreciably higher TONs of 6 960 and 7 956 kg
oligomer/mol Ni.h (Table 5.3, entries 8 and 12). This could be due to the greater electrophilicity of the complexes containing the bidentate ligands.

![Figure 5.8: Effect of Al:Ni ratio on ethylene oligomerisation activities of catalysts 22 (red) and 26 (yellow).](image)

Another interesting observation was the greater activity of the octahedral catalyst 28 (TON = 4 520 kg oligomer/mol Ni.h) compared to 27 (TON = 2 262 kg oligomer/mol Ni.h) which has a tetrahedral geometry. It was also observed that in all cases the dichloride complexes were more active than their dibromide counterparts (Table 5.3, entries 2 vs 4; entries 8 vs 10 and entries 12 vs 13). The higher catalytic activities of the dichloride catalysts compared to the corresponding dibromide catalysts is in contrast with pyrazolyliminophosphorane nickel dichloride catalysts\textsuperscript{28} and 2-quinoxalinyl-6-iminopyridines nickel catalysts\textsuperscript{29} reported in the literature. This activity difference has been attributed to higher solubilities of dibromide precursors in toluene compared to dichloride analogues. Indeed the dibromide precursors 23, 25, 27 and 30 showed better
solubilities than the dichloride precursors \(22, 24, 26\) and \(29\). It is therefore conceivable that higher activities of \(22, 24, 26\) and \(29\) could be due to electronic factors and not solubility. To initiate ethylene oligomerisation reaction, the catalyst precursor must first be transformed into an active catalyst (activation), Eq. 5.2. An effective activation requires special co-catalyst-catalyst precursor features that are favoured both kinetically and thermodynamically.\(^{30}\) The greater activities of the dichloride precursors thus indicate a more favoured activation process by the co-catalyst (EtAlCl\(_2\)) to generate the active catalysts than the dibromide analogues (Eq. 5.2).

\[
\text{Co-catalyst} \quad \text{X} \quad \text{EtAlCl}_2
\]
\(\text{X} = \text{Cl or Br}\)  

The nature of the substituents on the pyrazolyl ring also appeared to have significant influence on the catalytic activities of complexes \(22-30\). Two opposite trends were observed. While steric bulk resulted in decreased activities for catalysts \(22-25\), the same

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resulted in an increased activity for 26-30. For example 22 and 23 with methyl substituents on the pyrazolyl ring showed higher activities than 24 and 25 that contain tert-butyl groups on the pyrazolyl ring respectively (Table 5.3, entries 2, 4-6). The TON of 22 was 4 002 kg oligomer/mol Ni.h while 24 gave a TON of 2 958 kg oligomer/mol Ni.h under similar conditions. The difference in catalytic activities of 22 and 24 could result from reduced electrophilicity of the Ni metal centre from the more electron-donating tert-butyl groups and hence reduced the rate of ethylene insertion. A similar reduction in activity due to steric factors has also been reported by Sun and Brookhart. On the other hand, greater activities were observed for catalysts 29 and 30 containing tert-butyl groups on the pyrazolyl ring compared to 26 and 27 containing the methyl groups on the pyrazolyl ring (Table 5.1, entries 8, 6, 12 and 13). This is believed to arise from increased solubilities of 29 and 30. The bulkier ligands in 29 and 30 might also play a role in protecting the active metal centre against decomposition resulting in greater catalytic activities. A similar argument has been used by Sun et al. in describing the catalytic trends of \(N\)\-\{(pyridine-2-yl)methylene\}quinolin-8-amine nickel complexes. The overall catalytic effect of the substituents on the pyrazolyl ring thus depends on the type of the catalysts used.

It was however, observed that the nature of the catalysts did not significantly influence the oligomer distribution (Table 5.3). Catalysts 22-25 that contain the tridentate ligands L1 and L2 gave slightly greater percentages of C_{11} oligomers (48-53%), Table 5.3, entries 1-6) compared to catalysts 26-30 containing the bidentate ligands L2 and L3 that gave slightly lower percentage of C_{11}, (41-44%, Table 5.1, entries 8-13). Since steric bulk
is known to favour chain propagation\textsuperscript{26} over chain termination the independence of product distribution on steric bulk of complexes 22-30 might imply that chain termination via $\beta$-hydride elimination is not the predominant mechanism. It is also evident from the percentage of 1-C\textsubscript{14} product obtained (38-40\%) that there was no significant effect of change in catalyst structure on the isomerisation process as observed by the near constant percentage of the 1-C\textsubscript{14} composition (Table 5.3).

5.3.3.4 Effect of varying reaction conditions on ethylene oligomerisation reactions

The effects of varying reaction conditions such as ethylene concentration, reaction time and catalyst concentration on catalyst activity and product distribution were extensively investigated using catalyst 22 and 26. The effect of varying temperature was not considered due to the exothermic nature of the reactions. Table 5.4 gives the results obtained with catalysts 22 and 26 under various reaction conditions.

5.3.3.4.1 Effect of reaction time on turn over numbers of 22 and 26

First investigated was the effect of reaction time in order to establish catalyst stability and catalyst/ethylene kinetics. From Table 5.4, entries 1-5 show high TON within 15 min for 22 (TON = 9 048 kg oligomer/mol Ni.h) and 4 872 kg oligomer/mol Ni.h for 26. This suggests that catalyst 22 showed higher initiation rate than 26. After 1 h, catalysts 22 and 26 showed TONs of 4,002 and 6 960 kg oligomer/mol Ni.h. Within 3 h both catalysts showed drastic drop in TON giving 1 972 kg oligomer/mol Ni.h for catalyst 22 and 2 929 kg oligomer/mol Ni h for 26 (Table 5.4, entries 11-14). It is therefore evident that both 22 and 26 showed reduction in activity with time. This could arise from catalyst
deactivation or saturation kinetics. Reduction in ethylene uptake due to saturation of the reaction mixture is known to result in lower TON.\textsuperscript{9} High ethylene uptake has been reported during the initial 5-10 min for $\alpha$-diimine nickel catalyst.\textsuperscript{9a} The reduced ethylene consumption with time was attributed to ethylene saturation of the reaction mixture.\textsuperscript{9a}

From Figures 5.9 and 5.10, it is evident that though the TONs of 22 and 26 reduces with time, the oligomer yield showed a gradual increase with time although the effect was not linear. This indicates that both 22 and 26 remained significantly active as deduced from increased product yield with time (Figures 5.9 and 5.10 respectively). The TONs of 22 and 26 after 3 h were obtained as 1 972 kg oligomer/mo Ni.h and 2 929 kg oligomer/mol Ni.h respectively. It could thus be concluded that catalysts 22 and 26 sustain appreciable activity over the 3 h period.

Figure 5.9: Effect of reaction time on product yield and TON of catalyst 22.
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<th>Yield (g)</th>
<th>TON (kg/mol.h)</th>
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<sup>a</sup>Reaction conditions: Amount of catalyst; 10.00 µmol; Al:Ni, 250; Solvent, toluene (80 mL); <sup>b</sup>Initial temp was 30 °C, T<sub>min</sub> and T<sub>max</sub> = Highest and lowest temps attained during the reaction period; <sup>c</sup>Determined by mass difference of 80 mL toluene (69.60 g) and mass of final solution; <sup>d</sup>Determined by GC; <sup>e</sup>Determined by GC, Linear α-C₁₄. <sup>f</sup>Amount of catalyst, 5.00 µmol; <sup>g</sup>Amount of catalyst, 15.00 µmol.
5.3.3.4.2 Effect of pressure on turn over numbers of 22 and 26

Increase in ethylene pressure resulted in significant increase in TONs of both 22 and 26 (Table 5.4, entries 8-10 and 15-17). For instance, doubling the pressure from 20 to 40 bar in experiments using 22 resulted in a three fold increase in activity from 5 916 to 15 312 kg oligomer/mol Ni.h (Table 5.4 entries 2 and 10). Catalyst 26 exhibited a similar trend; increase in pressure from 10 to 40 bar resulted in a six-fold increase in TON from 2 610 to 15 660 kg oligomer/mol Ni.h. Similar increases are known in ethylene oligomerisation and polymerisation catalysis. For example Doherty et al.\textsuperscript{31} recently observed that doubling ethylene pressure from 15 to 30 bar resulted in increased activity, though does not exhibit the doubling effect of the TOF for their phosphine-oxazoline palladium

catalysts; indicating that ethylene is approaching saturation behaviour. Catalysts 22 and 26 thus exhibit higher ethylene saturation levels. The approach to saturation behaviour can be described by the Michaelis-Menten\textsuperscript{32} equation (eq. 5.3).

The Michaelis-Menten equation is used in Biochemistry to determine important terms in enzyme kinetics such as maximum reaction rate ($V_{\text{max}}$) and enzyme concentration [$S$]. The equation can be rearranged into a linear expression (eq. 5.4). A plot of $1/V$ vs [$S$] gives the Lineweaver-Burk plot. The y-intercept of the graph is equivalent to the inverse of $V_{\text{max}}$; the x-intercept of the graph represents $-1/K_\text{m}$. This graph is useful in Biochemistry in that gives a quick, visual picture of the different forms of enzyme inhibition. This equation has been extended to analyse the effect of ethylene concentration on turn-over frequency of catalysts in ethylene oligomerisation reactions.\textsuperscript{31}

\begin{align}
V &= V_{\text{max}} \frac{[S]}{K_m + [S]} \quad \text{(5.3)} \\
\frac{1}{V} &= \frac{K_m}{V_{\text{max}}} \frac{1}{[S]} + \frac{1}{V_{\text{max}}} \quad \text{(5.4)}
\end{align}

where $V$ = rate of reaction; $V_{\text{max}}$ = saturation limit; [$S$] = concentration of substrate; $K_m$ = Michaelis constant.

In the ethylene reactions, ethylene concentration (pressure) is regarded as the enzyme concentration \([S]\) and the TON is equivalent to the rate of reaction \((V)\). Substitutions of ethylene pressure and TON in equation 5.4 gives equation 5.5 which is rearranged into eq 5.6. A plot of \(1/TON\) vs \(1/P(C_2H_4)\) (Lineweaver-Burk plot) should yield a straight line with a y-intercept at \(1/TON_{\text{max}}\) and a slope of \(K_m/\text{TOF}_{\text{max}}\). TON\(_{\text{max}}\) represents the turn over number under conditions where the reaction is saturated in ethylene.

\[
TON = TON_{\text{max}} \frac{[P_{C_2H_4}]}{K_m + [P_{C_2H_4}]} \quad (5.5)
\]

\[
\frac{1}{TON} = \frac{K_m}{TON_{\text{max}}} \frac{1}{[P_{C_2H_4}]} + \frac{1}{TON_{\text{max}}} \quad (5.6)
\]

The Lineweaver-Burk plot of data of catalysts 22 and 26 from Table 5.4 entries 2, 8-9; entries 15-17 (Figures 5.11 and 5.12 respectively) provide a TON\(_{\text{max}}\) of 28 393 and 19 000 kg oligomer/mol Ni.h. These TON\(_{\text{max}}\) are significantly high and indicate greater catalytic activity enhancement of 22 and 26 as pressure increases. The higher TON\(_{\text{max}}\) of 22 compared to 26 agrees with the observed trends in Table 5.2. For example doubling the pressure from 20 to 40 bar using catalyst 22 results in a 2.6 fold increase in TON from 5 916 to 15 312 kg oligomer/mol Ni.h (Table 5.4, entries 2 and 10). For catalyst 26 doubling the pressure from 20 to 40 bar results a 2.2 fold increase in TON from 6 960 to 15 660 kg oligomer/mol Ni.h (Table 5.4, entries 12 and 17).
Figure 5.11: Lineweaver-Burk plot of ethylene oligomerisation data for catalyst 22

Figure 5.12: Lineweaver-Burk plot of ethylene oligomerisation data for catalyst 26
5.3.4.3 Effect of reaction time and pressure on product distribution

Both reaction time and pressure were found to influence the product distribution. It was also observed that an increase in pressure resulted in concurrent higher exotherms and hence higher reaction temperatures. In general, an increase in reaction time and pressure gave a greater percentage of C₁₆. For instance, in experiments using 22, an increase in reaction time from 15 min to 180 min resulted in an increase of percentage C₁₆ from 11% to 33% followed by reduction of percentage in C₁₁ from 64% to 39% (Table 5.2 entries 1 and 5). A similar trend has been observed by Brookhart³¹ and Small.²⁴ Both authors attributed this trend to olefin reincorporation with time thus leading to a greater composition of the higher oligomer fractions. Catalyst 26 showed even a more drastic effect; an increase in reaction time from 15 min to 180 min resulted in an increase in percentage of C₁₆ from 2% to 35% and subsequent reduction of C₁₁ from 74% to 36% (Table 5.2, entries 11 and 14). Quite intriguing was the insignificant effect of the reaction time on the percentage composition of C₁₄ oligomers.

A similar trend was observed with increase in pressure (Table 5.2, entries 8-10 and 15-17). For example, increase in pressure from 10 to 40 bar resulted in a significant increase in the percentage of C₁₆ from 11 to 24% (Table 5.2, entries 8 and 10) for catalyst 22. Since an increase in pressure and temperature are known to favour chain termination over chain propagation¹ᵃ, ⁹ᵃ, ²⁸ the opposite trend observed for catalysts 22-30 implicates olefin reincorporation and co-oligomerisation of the lower oligomers as the predominant steps in the catalytic process. This mechanism is consistent with the observed greater percentage of higher oligomers produced over longer reaction times as well with increase
in temperature and pressure. There was, however, no significant effect of the reaction time and pressure on the degree of isomerisation as seen in a near constant percentage of the linear 1-C\textsubscript{14} isomer (ca 40\%) in the C\textsubscript{14} fraction over different reaction conditions (Table 5.4).

5.3.4 Higher \(\alpha\)-olefin oligomerisation reactions

The nickel complexes (22-28) were also investigated for their ability to catalyse the oligomerisation of higher \(\alpha\)-olefins when activated with EtAlCl\textsubscript{2} as the co-catalyst. The \(\alpha\)-olefins tested were 1-pentene, 1-hexene, 1-heptene and 1-nonene. An optimum Al:Ni ratio of 200:1 (Figure 5.13) was found to give 100\% conversion using catalyst 26 for 1-pentene reactions and has been used for subsequent oligomerisation reactions. Tables 5.5 and 5.6 summarise the oligomerisation data of the \(\alpha\)-olefins catalysed by 22-30. No catalytic activity was observed in an attempted oligomerisation of 1-nonene. This could be due to reduced reactivity of the longer chain 1-nonene monomer (Table 5.6, entry 15). Indeed relatively lower activities were observed in 1-hexene and 1-heptene reactions compared to 1-pentene reactions.

5.3.4.1 Analysis of product distribution and composition of higher \(\alpha\)-olefin oligomerisation reactions

The product distribution and composition of the oligomerisation reactions were exclusively identified by GC analyses (see Appendix A for characterisation). Only two products, C\textsubscript{12} and C\textsubscript{15}, were obtained in the 1-pentene oligomerisation reactions as identified by GC (Figures 5.14 and 5.15 and Appendix A). 1-hexene reactions also gave
two products, C_{12} and C_{18}, (Figure 5.16) while 1-heptene oligomerisation reactions gave predominantly C_{14} oligomers (Figure 5.17). The identities of the products from the oligomerisation reactions were established using the retention times of standard samples as described in the characterisation of ethylene oligomers (Figure 5.4). Interestingly the major product in the 1-pentene reaction was identified as C_{12} (75-88%). This was confirmed by spiking the 1-pentene oligomerisation sample with 1-C_{12} standard after obtaining the GC trace of the product (Figure 5.15). Increased intensity of the peak that corresponds to the C_{12} fractions indicated the presence C_{12} oligomer fraction in the product.

Figure 5.13: Effect of Al:Ni ration on 1-pentene oligomerisation using catalyst 22.
Figure 5.14: GC trace of 1-pentene oligomer fraction obtained from catalyst 22, Al:Ni of 200:1, time = 60 min.

Table 5.5 Oligomerisation of 1-pentene data

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Monomer (mL)</th>
<th>Al: Ni</th>
<th>Time (Min)</th>
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<th>% C15</th>
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<td>4</td>
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<td>100</td>
<td>78</td>
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<td>25</td>
<td>200</td>
<td>60</td>
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<td>-</td>
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</table>

*Reaction conditions: Amount of catalyst; 10.00 μmol; Temp, 30 °C; Solvent, toluene (30 mL);

*C Determined by GC. *d Neat monomer
Table 5.6: Oligomerisation of 1-hexene and 1-heptene data

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Monomer</th>
<th>Monomer (mL)</th>
<th>Time (Min)</th>
<th>% Con$^b$</th>
<th>C$^{12}$</th>
<th>C$^{14}$</th>
<th>C$^{18}$</th>
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<td>1-heptene</td>
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<td>26</td>
<td>1-nonene</td>
<td>4</td>
<td>180</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: Amount of catalyst; 10.00 μmol; Temp, 30 °C; Solvent, toluene (30 mL);

$^b$Determined by GC. $^c$Neat monomer
Figure 5.15: (a) GC trace of 1-pentene oligomerisation product using 22, Al: Ni = 200:1, 120 min (b) Same sample spiked with C_{12} showing enhanced intensity of the signal at the C_{12} fraction.

As previously described in the ethylene oligomerisation reactions, the formation of the C_{12} is believed to originate from the cross-metathesis of C_{10} product and C_{5} monomer to give C_{12} oligomer and propene as a byproduct. This might also explain the absence of a C_{10} dimer. Gibson\textsuperscript{33} previously reported the dimerisation of 1-pentene to give C_{10} as the major product using tridentate bis(imino)pyridine Fe(II) and Co(II) catalysts.\textsuperscript{33} The nickel catalysts (22-30) thus show a completely different behaviour in the 1-pentene
oligomerisation reaction and produce C\textsubscript{12} and C\textsubscript{15} instead of C\textsubscript{10}. Detailed GC analysis of the C\textsubscript{12} and C\textsubscript{15} oligomer fractions show a number of peaks indicating several isomers of the products besides linear \(\alpha\)-olefin products (Figure 5.16). This shows that there occurs isomerisation process as previously observed in the ethylene reactions. The number of isomerisation products observed in the 1-pentene reaction suggests that internal and or branched isomers must have been formed. Formation of internal olefins can be explained by isomerisation\textsuperscript{9a} while branched isomers are likely to be formed by chain-running or a 2,1 insertion mechanism.\textsuperscript{33}

Figure 5.16: GC chromatogram of 1-hexene oligomer obtained from catalyst 26, Al: Ni ratio of 200:1; time = 60 min.


The percentage of C\textsubscript{12} from 1-hexene reaction was observed to be between 75-90\% (Figure 5.16). These values are consistent with those obtained (83-90\% dimer) for the Co
bis(imino)pyridine catalysts. The other product was the C\textsubscript{18} oligomer indicating a trimerisation process. It is interesting to note that analysis of the C\textsubscript{12} fraction by spiking an authentic sample of 1-C\textsubscript{12} standard showed the absence of the linear 1-C\textsubscript{12} product (Append A6). This indicates that all the C\textsubscript{12} oligomer products were either internal or branched olefins as described for the 1-pentene reaction. This is in sharp contrast with higher percentages of 1-C\textsubscript{12} (75%-80\%) reported by Small\textsuperscript{34} using bis(imino)pyridine Fe(II) catalysts. In the 1-heptene reaction, the C\textsubscript{14} fraction showed 55\% linearity of 1-C\textsubscript{14} oligomer as determined by spiking the product with standard 1-C\textsubscript{14} sample (Figure 5.17 and Appendix A5).

![Figure 5.17: GC trace of oligomer product from 1-heptene reaction using catalyst 22; Al:Ni ration of 200:1; time = 60 min.](image)

5.3.4.2 Variation of catalysts and effect of reaction conditions on 1-pentene, 1-hexene and 1-heptene oligomerisation reactions

Having established the right Al:Ni ratios, complexes 22-28 were screened at Al:Ni ratios of 200:1 to probe the effect of ligand environment on catalytic activity (Table 5.5 and 5.6, entries). Catalysts 22-28 exhibit good catalytic activities achieving 100% conversion of the 1-pentene within 1 h. For example 26 gives complete conversion when 4 mL of 1-pentene was used after 1 h (Table 5.3, entries 4). Comparable activities were also observed for catalysts 22, 23 and 28 giving conversions of 98%, 90% and 100% respectively. The catalytic activity trends of the complexes observed agree with those observed in the ethylene oligomerisation reactions.

The effect of monomer concentration on the catalytic activities of 22 and 26 was also investigated using 1-pentene, 1-hexene and 1-heptene olefins. It was observed that an increase in monomer concentration resulted in a subsequent decrease in the percentage conversion. For example doubling the amount of 1-pentene from 4 to 8 mL resulted in slight decrease in activity from 98 to 95% for catalyst 22 (Table 5.5, entries 5, 7). No catalytic activity was observed in experiments using neat 1-pentene (Table 5.5, entry 10). This is believed to be due to reduced solubility of the catalyst precursor in 1-pentene monomer. A similar trend was observed for the 1-hexene and 1-heptene oligomerisation reactions. For instance increasing 1-hexene concentration from 4 to 10 mL resulted in reduction of conversion from 98 to 90% respectively (Table 5.6, entries 5 and 7).
Another parameter that was investigated was the influence of reaction time on both the conversion of the monomer and product distribution (Table 5.6, entries 1-7). For example in the 1-hexene reaction, reactions run for 15 min only gave 55% product while longer reaction time of 1 h gave 98% conversion (Table 5.6, entries 2 and 5). This suggests that after 15 min, activation of the catalyst precursor to give the active species is incomplete and thus few active species are present.\textsuperscript{1h, 33} With increased reaction time, maximum activation is achieved and thus higher activity. Reaction time was also observed to affect the product distribution. For instance, in the 1-pentene reaction, longer reaction times resulted in an increased amount of C\textsubscript{15} compared to shorter runs. Increasing the reaction time from 30 min to 24 h was followed by an increase in percentage of C\textsubscript{15} from 14 to 37\% for catalyst 26 (Table 5.7, entries 3 and 6). This observation supports olefin reincorporation as the predominant process in the oligomerisation reactions.\textsuperscript{32} Consistent with the observed trends in ethylene and 1-pentene oligomerisation reactions, increasing the reaction time in the 1-hexene reactions resulted in increased percentage of C\textsubscript{18} (Table 5.5, entries 1 and 6).
Table 5.7: Effect of reaction time on oligomerisation of 1-pentene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (Min)</th>
<th>% Conversion</th>
<th>%Oligomers</th>
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<td>8</td>
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<td>240</td>
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<td>70</td>
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</table>

*aReaction conditions: Amount of catalyst; 10.00 μmol; Temp, 30 °C; Solvent, toluene (30 mL);
*bDetermined by GC.  In situ sampling;  cEqual amount added in situ without catalyst precursor and co-catalyst addition.

5.3.4.3 Stability of catalysts 22 and 26 in 1-pentene oligomerisation reactions

The stability of the nickel catalysts was investigated using catalysts 22 and 26 by observing the percentage conversion of each catalyst with time as a new monomer was added (Table 5.8). The experiments were performed by initially generating the active catalyst as described for 22 and 26. To the active catalysts were added 4 mL of 1-pentene and an aliquot of the products taken for GC analysis. After 1 h, another 4 mL of 1-pentene was added without adding catalyst precursor or co-catalyst and the reaction run for another 1 h (second cycle). This was repeated four times to give five cycles. From Table 5.8, entries 1-8, it is evident that the catalysts remain significantly active even after
the fourth run. Conversion of 97% was observed in the second cycle for catalyst 22 and a conversion of 98% was observed in the fifth cycle for 26. This suggests that there was no deactivation with time of 22 and 26. This thus indicates good stabilities for 22 and 26 in the 1-pentene oligomerisation reactions. This observation also shows that the reduced TONs over long reaction times for 22 and 26 observed in the ethylene oligomerisation reactions were due to mass transport problems and not deactivation.

Table 5.8: Stability of catalysts 22 and 26 in oligomerisation of 1-pentenea

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cycle</th>
<th>% Conversionb</th>
<th>%Oligomers</th>
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aEqual amount of 1-pentene monomer (4 mL) added after 1 h without addition of nickel catalyst precursor or co-catalysts in each cycle.
5.4 Conclusions

Reactions of symmetrical 2, 6-bis(pyrazolylmethyl)pyridine with NiCl₂ or NiBr₂ salts give mononuclear tridentate nickel(II) complexes. Magnetic moments, microanalyses and mass spectrometry have been used to characterise the nickel complexes. The 2-(pyrazolylmethyl)pyridine ligands produce either five coordinate dinuclear nickel complexes or four coordinate tetrahedral complexes depending on the steric bulk of the ligand backbone. The molecular structures of 2-(pyrazolylmethyl)pyridine of complexes 27 and 30 have been confirmed by single crystal X-ray crystallography. Activation of the nickel complexes with EtAlCl₂ results in highly active ethylene oligomerisation catalysts with remarkable catalyst stability over long reaction times. The catalysts give a unique oligomer distribution that contains C₁₁ as the major product. Formation of both odd and even numbered olefins in addition to low product purity implicates isomerisation, metathesis and reincorporation mechanisms as the predominant factors controlling the oligomerisation process and not chain propagation and termination. Both steric and electronic factors influence catalyst activity and product distribution. The nickel complexes also give active catalysts for 1-pentene, 1-hexene and 1-heptene oligomerisation reactions. The major oligomer products of 1-pentene reactions are C₁₂ and C₁₅ while 1-hexene oligomerisation reactions produce C₁₂ and C₁₈ oligomers. The 1-heptene oligomerisation reactions show higher selectivity producing predominantly C₁₄ oligomers.
CHAPTER 6

Substituted (pyridinyl)benzoazole palladium complexes: Synthesis and application as Heck coupling catalysts

This chapter is adapted from the paper published in *Polyhedron* 26 (2007) 5544-5552; and is entirely based on the experimental work of the first author, Stephen O. Ojwach. Copyright 2007 Elsevier Ltd. The contributions of the first author include synthesis of the ligands and their palladium complexes, Heck coupling catalysis, and drafting of the manuscript.

6.1 **General introduction and industrial applications of Heck-coupling reactions**

Palladium-catalysed arylation of an alkene with an organic halide (eq. 6.1), first reported by Mizoroki\(^1\text{a}\) and Heck\(^1\text{b}\) in the early 1970s, has been developed into a highly versatile synthetic route to a number of organic compounds in both academic and industrial laboratories. The reaction, currently known as Heck coupling, is based on the ability of Pd(0) complexes to generate aryl or vinyl-palladium bonds by oxidative addition of aryl or vinyl halides; which can undergo various catalytic C-C bond formation reactions. The Heck reaction has been studied extensively with respect to catalyst design and development.\(^2\)

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A number of intermediates to make fine chemicals are currently prepared industrially through Heck coupling reactions. For example, 6-methoxy-2-vinylnaphthalene, an intermediate to Naproxen, a non-steroidal anti-inflammatory drug (trade name: Albermarle), is prepared from 2-bromo-6-methoxynaphthalene and ethylene in the presence of Pd(OAc)$_2$ and a phosphine ligand (Scheme 6.1).$^{3a}$

\[
\begin{align*}
R^1X + \text{Base} & \quad \xrightarrow{\text{Pd catalyst}} \quad \text{R}^2 \\
& \quad \\quad \downarrow \text{R}^2 \\
& \quad \downarrow \text{Base.HX} \\
R^1 & = \text{Ph}; R^2 = \text{H, OMe, } \text{'BuCOO} \\
\end{align*}
\]

(6.1)

Scheme 6.1

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Heck-coupling reactions do not yet appear to have significant industrial applications for technical and economic reasons. Major drawbacks in Heck coupling reactions include contamination of the products with traces of palladium metal which limits their applications especially in the pharmaceutical industry. However, significant advances have been made in developing methods for removal of traces of metals using strong coordinating compounds, such as 2,4,6-trimethylcarptotriazine or solid supports.\(^4\) In recent years a number of heterogeneous catalysts have been developed, with the primary objective of replacing molecular catalysts which are difficult and expensive to recover and recycle from the reaction mixture.\(^5\) In spite of these drawbacks, the ability to use functionalised substrates in highly efficient and selective catalysis under mild conditions makes the Heck reaction very attractive. Heck-coupling reactions benefit from lower costs of materials compared to the more expensive traditional routes like Kronhke\(^5d\) and Stille\(^5e\) reactions. This makes Heck coupling reactions suitable candidates for future academic and industrial organic synthetic applications. As such research on active Heck coupling catalyst is currently receiving considerable attention. The next section reviews recent advances in the design of active and stable Heck-coupling catalysts.

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6.1.1 Brief review of development of Heck coupling palladium catalysts

The development of catalysts for Heck coupling reactions has been the subject of several publications that describes the design of a number of palladium metal complexes which exhibit high catalytic turnovers. However, the major challenge has been the design of catalysts that could offer high activity towards the less reactive aryl chlorides and bromides which are readily available and cheaper compared to the aryl iodides.

Another challenge to researchers in this field is the development of phosphine-free palladium catalysts as phosphine ligands are highly susceptible to deactivation through P-bond cleavage.

6.1.2 Mechanisms of Heck coupling reactions

To facilitate the development of suitable Heck coupling catalysts, enormous efforts have been made to understand the mechanisms involved in palladium catalyzed Heck coupling reactions. The traditionally accepted mechanism is presented as shown in Scheme 6.2. In this mechanism, the active catalyst is the coordinately unsaturated 14-electron species, (PdL2). Oxidative addition of R1X to gives a cis-RPdXL2 (b) intermediate, which subsequently isomerises to the more stable trans- RPdXL2 geometry. Generation of a free intermediate is not shown.

coordination site crucial for alkene coordination is generally accepted to occur through the dissociation of one of the ligands, L, to form the olefin complex e. This is followed by migratory insertion of the olefin and subsequent coordination of the free ligand to form complex d. The new substituted alkene is then eliminated from the palladium metal by β-hydride elimination to give the product and complex e. Catalyst regeneration is facilitated by the addition of a base e.g Et₃N to remove the HX salt from the inactive HPdXL₂ species (e).

Scheme 6.2: Traditional mechanism of the Heck coupling reaction (R₁ = Ar or vinyl; R₂ = OMe, (EWG); L = PPh₃; X = I, Br).

To date the traditional mechanism is still debatable especially as to the exact nature and generation of the active species a. As a result there is an emerging body of work on the
mechanistic investigation of the Heck coupling reactions, spanning from experimental to theoretical studies, to improve on the known traditional mechanism. Many investigations have been carried out at low temperatures to avoid the observation of high-energy intermediates involved at conventional high temperatures of 140 °C.\(^8\) For example, using electrochemical studies, Amatore and Jutanda\(^9\) have made a significant contribution towards the identification of effective catalytic precursors and intermediates in the catalyst system of PPh\(_3\) and Pd(OAc)\(_2\). They proposed that the intermediate complex formed on mixing PPh\(_3\) and Pd(OAc)\(_2\) is an unstable species [Pd\(^{II}\)(PPh\(_3\))\(_2\)(OAc)\(_2\)]. The [Pd\(^{II}\)(PPh\(_3\))\(_2\)(OAc)\(_2\)] subsequently undergoes reduction to give [Pd\(^0\)(PPh\(_3\))\(_2\)(OAc)]\(^-\) as the active species. Spencer\(^10\) and coworkers had previously observed that the active species in the Heck coupling reaction catalysed by a mixture PPh\(_3\) and Pd(OAc)\(_2\) is [Pd\(^0\)(PPh\(_3\))\(_2\)(OAc)]\(^-\) which agrees with the results of Amatore and Jutanda.\(^9\)

Recently Kawano and coworkers\(^11\) proposed another type of mechanism (Scheme 6.3). They suggested that in reactions catalysed by preformed bidentate nitrogen donor palladium complexes the palladium complex (A) catalyses the Heck coupling reactions by first undergoing reduction to a ligand-stabilised Pd(0) complex, B, (Scheme 6.3). Oxidative addition of aryl halide, ArX, to B affords C. Migratory insertion of the olefin followed by ligand dissociation of C gives complex D. This C-D transformation process

might be essential in determining the catalytic trends of the bidentate complexes. The complex with a strong *cis*-ligation mode is likely to be less active due to the rigid backbone hindering the *cis-trans* isomerisation. The new substituted alkene in D is then eliminated from the palladium metal by β–hydride elimination to give the product and complex E. Catalyst regeneration is facilitated by the addition of a base e.g Et₃N to remove the HX salt from the inactive species E to give the active species B.

**Scheme 6.3:** Proposed Heck coupling reaction mechanism catalysed by bidentate nitrogen palladium catalysts

Despite this plethora of mechanistic studies, it is generally accepted that the catalytic activity and selectivity cannot be sufficiently described by a unified simple diagram. It is evident that the reaction intermediates and their associated active species are intimately
associated with the chosen catalyst, substrates, additives and reaction conditions.\textsuperscript{12} Developments of new catalysts over the past decades have resulted in a number of mechanistic hypotheses which are currently the subject of much speculation and deliberations.

The lack of a generally accepted and proven mechanism in Heck coupling reactions catalysed by palladium complexes has resulted in the design of several palladium complexes and their investigations as catalysts in Heck coupling reactions. This is being done to try and gain insight into the exact nature of the active catalyst and the general mechanistic steps that takes place in the Heck coupling reactions. In the subsequent section, a brief review of the design of Heck coupling palladium catalysts is described.

\textbf{6.1.3 Tris(phosphine)- based palladium catalysts}

To date phosphine-based palladium catalysts are the most widely used in Heck coupling reactions despite their ease to undergo deactivation through P-C bond cleavage.\textsuperscript{6} For example the palladium complex $[\text{PdI(Ph)}(\text{PPh}_3)_2]$\textsuperscript{13} has been shown to promote Heck coupling reactions of the deactivated aryl bromides and chlorides at high temperatures. As expected with the phosphine palladium complexes, this catalyst was found to undergo deactivation even at 60 °C. The thermal stability of the phosphine catalysts, $[\text{PdX(Ph)}(\text{PPh}_3)_2]$; $X$ = F, Cl, Br or I, has been studied in detail. The aryl

scrambling in the iodide complex was found to be much more facile than those of the bromide and chloride analogues. The iodide catalysts were thus less stable than the corresponding chloride or bromide catalysts.\textsuperscript{14}

Efforts towards the design of palladium catalysts that could efficiently couple the deactivated aryl bromides and chlorides have witnessed little success. However, there is a considerable body of catalysts that perform Heck coupling of these substrates with moderate activity. For instance, chelating phosphine palladium complexes (Figure 6.1) efficiently couple electron poor aryl bromides though long reaction times and larger concentrations are required to couple 4-bromoacetophenone and styrene.\textsuperscript{15} The only established chelating diphosphine palladium catalysts effectively applied in the Heck-coupling of aryl chlorides are the electron rich 1,3-bis(diisopropylphosphino)propane and 1,4-bis(diisopropylphosphino)butane.\textsuperscript{16} For example coupling of chlorobenzene with styrene under basic conditions and at 150 °C results in 80% conversion giving mostly trans-stilbene.

6.1.4 Palladacycles

Palladacycles have been shown to offer several advantages over the well established traditional monodentate or chelate phosphine palladium catalysts and offer one of the most suitable avenues to the design of highly effective Heck coupling catalysts.\(^\text{17}\) Of utmost significance is their high thermal stability with decomposition temperatures above 250 °C. The good activities at low temperatures of 80 °C where the P-C bond cleavage is minimized is another advantage of these catalysts. Efficient Heck coupling reactions of aryl bromides and chlorides with the palladacycle catalyst (6-I) have been achieved with conversions of about 99% and 97% for the aryl bromides and chlorides respectively. Nowotny and coworkers\(^\text{18}\) recently reported Heck coupling reactions of iodobenzene with styrene using cyclopalladated imine catalysts (6-II). However, contrary to the expected

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high thermal stability of the cyclopalladated catalysts, compounds 6-I and 6-II were found to undergo decomposition even at 140 °C.

![6-I and 6-II](image)

### 6.1.5 Tridentate PCP Pincer palladacycles

Tridentate pincer palladacycles first discovered by Milstein form relatively active Heck coupling catalysts even for the more deactivated aryl bromides.\(^{19}\) The complexes are however less active for aryl chloride reactions. The catalysts of type 6-III have been found to exhibit high thermal stability and decompose at temperatures above 180 °C. The PCP phosphinito pincer catalyst (6-IV) reported by Jensen\(^{20}\) is also air insensitive, thermally stable and more significantly promotes the coupling of aryl chloride substrates. Preparative scale coupling reactions of 4-chloroanisole with styrene using this catalyst gives high yields of 99%. To understand the catalytic properties of 6-IV, the phosphinato

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analogue, 6-V, has been synthesised and its Heck coupling reactivity studied.\textsuperscript{20b} Significantly, the catalyst showed very little activity and hence, it can be concluded that the activity of 6-IV towards aryl chlorides may be due to the phosphinito ligand. Recently, the group of Hahn\textsuperscript{21} reported Heck coupling of activated aryl bromides with styrene catalysed by pincer type bis( benzimidazolin-2-ylidene) palladium complexes. The catalysts show moderate activity (85\%) and are thermally stable and moisture insensitive.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {6-III};
  \node at (1.5,0) {6-IV};
  \node at (3,0) {6-V};
\end{tikzpicture}
\end{center}

6.1.6 \textit{N-heteroclylic carbene palladium catalysts}

The other type of palladium catalysts that have revolutionised the C-C coupling reactions are those containing heterocyclic carbene ligands. For the past two decades, the synthesis of stable N-heterocyclic carbenes (NHC) and their metal complexes has been an area of intensive research initiated by the isolation of the first stable NHC carbene by Arduengo \textit{et al.}\textsuperscript{22} To date a large number of NHCs derived from imadazole, imidazolidine,

\begin{thebibliography}{99}
\end{thebibliography}
benzimidazole have been synthesised. The superiority of these types of catalysts lies in their thermal stability, low costs and hence they are preferred alternatives to the more expensive phosphine catalysts. The palladium complexes (6-VI to 6-VIII)\textsuperscript{23} in particular have proved to be excellent catalysts in Heck coupling reactions even for the aryl bromides and chlorides.

The palladium catalysts (6-VI to 6-VIII) are air insensitive and decompose at very high temperatures of above 305 °C. Significantly these catalysts show activity even at low temperatures of 80 °C. While the dihalide complexes exhibit long induction periods in Heck coupling catalysis, the methyl-palladium complexes do not exhibit an induction period. More recently, Kunz\textsuperscript{24} and his group reported active Heck coupling reactions of aryl bromides using palladium complexes bearing methylene and ethylene bridged pyrido-annelated N-heterocyclic carbene ligands (6-IX). The catalysts show decent activity (conversions of between 80-99%) at 150 °C.


6.1.7 *Nitrogen containing palladium catalysts*

Another type of ligands that is showing promising results in the Heck coupling reactions are the bidentate nitrogen donor ligands. The ease with which their electronic and steric properties could be varied to offer desirable catalyst properties makes them suitable replacements for the phosphine palladium catalysts. Following reports by Buchmeiser and coworkers\(^{25}\) that bis(pyrimidine) palladium complexes (6-X) catalyze Heck coupling reactions of activated aryl bromides and aryl chlorides with styrene, interests in other nitrogen based catalysts is gaining momentum. In an earlier work, Kawano *et al.*\(^{11}\) reported another type of *trans*-bidentate pyridine palladium complexes (6-XI) that are highly effective in Heck reactions and identified the active species as a ligand-stabilised Pd(0) as shown in Scheme 6.3.

![Chemical structures](image)

Other nitrogen-donor compounds known to initiate Heck coupling reactions include pyrazolyl palladium complexes recently reported by Darkwa and co-workers.\(^{26}\) Thus one such group of nitrogen compounds that could stabilise active palladium species for C-C

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coupling reactions is benzoazole ligand systems. Benzoazoles have found wide applications as anti-cancer\textsuperscript{27a} and anti-malaria agents,\textsuperscript{27b} supramolecular frameworks, and as non-linear optical chromophores.\textsuperscript{27c} Despite these varied applications of benzoazoles and their late transition metal complexes, there are very few reports on the use of these complexes as olefin transformation and C-C coupling catalysts.\textsuperscript{27d} The rigid backbone and the enhanced electron density of these ligands is expected to offer good stability for the active catalysts in the Heck coupling reactions. The absence of any reactive bonds in the fused benzoazole ligands is expected to reduce catalyst deactivation associated with phosphine-based catalysts.

In attempts to impart different electronic and steric properties, as well as improve solubility of complexes, a convenient method for the synthesis of substituted benzothiazoles by incorporating alkyl groups in both the pyridine and phenyl rings have also been developed. In this chapter, the synthesis of substituted benzoazole ligands, their palladium complexes and their application as catalysts for Heck coupling of iodobenzene with butyl acrylates is described. The ability of the ligands to enhance the catalytic activity of palladium salts when the ligands are added \textit{in situ} in the Heck coupling reactions was also investigated and is discussed.

6.2 Experimental section

6.2.1 Materials and Instrumentation

All synthetic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were of analytical grade and were dried prior to use. Toluene and Et₂O were dried and distilled from sodium/benzophenone. Dichloromethane was dried and distilled from P₂O₅. Dicyclohexylcarbodiimide (DCC), 4-tert-butyl aniline, 4-pyrrolidinino pyridine (4-PP), 6-methyl picolinic acid, Lawesson’s reagent and 2-pyridin-2-yl-1H-benzoimidazole (L7) were purchased from Sigma-Aldrich and used as received. Compound 2-pyridin-2-yl-benzothiazole (L8)²⁸ [PdClMe(COD)]²⁹ and [PdCl₂(NCMe)₂]³⁰ were synthesised following literature procedures.

NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 300 MHz and ¹³C at 75 MHz) at room temperature. The chemical shifts are reported in δ (ppm) and referenced to the residual CHCl₃ in the NMR solvent. Coupling constants are measured in Hertz (Hz). Mass spectra were recorded on a Waters API Quattro Micro spectrometer at the University of Stellenbosch, South Africa. Elemental analyses were performed by the micro analytical laboratory at the University of Cape Town, South Africa. Heck coupling products were analysed on a Shimadzu GCMS-QP 2010 version 2 gas chromatograph.

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fitted with flame ionisation detector and column ZB1, 100% dimethylpolysiloxane with dimensions of 30 m by 0.25 mm.

6.2.2 Synthesis of ligands and palladium complexes

6.2.2.1 2-tert-butyl-pyridine-2-carboxylic acid (4-tert-butyl-phenyl)-amide (S1)

To a mixture of 4-tert-butylpicolinic acid (0.50 g, 2.80 mmol), 4-tert-butylaniline (0.41 g, 2.80 mmol), DCC (0.57 g, 2.80 mmol) and 4-PP (5%) was added CH$_2$Cl$_2$ (20 mL) and the mixture stirred for 24 h at room temperature. After the reaction period the mixture was filtered and solvent removed under reduced pressure to give the crude product which was purified by column chromatography on silica gel, using a solvent mixture of petroleum ether and ethylacetate (9:1). Yield = 0.75 g (85%). $^1$H NMR, (CDCl$_3$): δ 1.30 (s, 9H, $^t$Bu, phenyl); 1.37 (s, 9H, $^t$Bu, py); 7.39 (d, 1H, py, 2$^J_{HH}$ = 7.2 Hz); 7.41 (d, 2H, ph, 2$^J_{HH}$ = 8.1 Hz); 7.72 (d, 2H, ph, 3$^J_{HH}$ = 5.7 Hz); 8.33 (s, 1H, py); 8.52 (d, 1H, py, 2$^J_{HH}$ = 8.1 Hz); 10.04 (s, 1H, NH). $^{13}$C NMR (CDCl$_3$): δ 30.4; 31.3; 34.3; 35.1; 119.4; 120.0; 123.0; 125.8; 126.6; 135.2; 138.2; 147.8; 151.6; 157.3; 162.2. HRMS (ESI): Anal. Calc for C$_{20}$H$_{26}$N$_2$O: 310.4315. Found: 310.4322.

6.2.2.2 2-tert-butyl-pyridine-2-carbothioic acid (4-tert-butyl-phenyl)-amide (S2)

To a mixture of S1 (0.80 g, 2.50 mmol) and Lawesson’s reagent (0.52 g, 1.28 mmol) was added toluene (20 mL) and the solution refluxed for 48 h. The mixture was then filtered and solvent was removed under reduced pressure to afford an orange solid material which was purified by column chromatography on silica gel using solvent mixtures of petroleum ether and ethylacetate (4:1). Yield = 0.75 g (80%). $^1$H NMR, (CDCl$_3$): δ 1.32
(s, 9H, t-Bu, ph); 1.36 (s, 9H, t-Bu, py); 7.40 (d, 1H, py, $^2J_{HH} = 7.8$ Hz); 7.43 (d, 2H, ph, $^2J_{HH} = 7.5$ Hz); 7.97 (d, 2H, ph, $^2J_{HH} = 6.9$ Hz); 8.45 (s, 1H, py); 8.88 (d, 1H, py, $^2J_{HH} = 7.8$, $^3J_{HH} = 1.8$ Hz); 12.11 (s, 1H, NH). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.8; 31.3; 34.6; 35.2; 119.4; 122.4; 125.6; 128.1; 128.9; 137.9; 149.6; 150.7; 155.5; 187.3. HRMS (ESI): Anal. Calc for C$_{20}$H$_{26}$N$_2$S: 326.5014. Found: 326.5021.

6.2.2.3 2-(4-tert-butyl pyridin-2-yl)-benzoazole (L9)

To a mixture of 2-aminophenol (0.44 g, 4.00 mmol) and 2-carboxy-4-tertbutylpyridine (0.72 g, 4.00 mmol) was added polyphosphoric acid (3.00 g). The suspension was heated at 170-180 °C. After 4 h, the reaction mixture was poured into an ice-water mixture and the pH of the resulting solution adjusted to 8 using 25% NH$_4$OH. The product that precipitated was filtered, washed with H$_2$O and dried. Yield = 0.80 (79%) $^1$H NMR, (CDCl$_3$): $\delta$ 1.39 (s, 9H, t-Bu, py); 7.36 (m, 2H and 1H, ph, py); 7.67 (m, 1H, ph); 7.84 (m, 1H, ph); 8.37 (s, 1H, py); 8.71 (d, 1H, py, $^2J_{HH} = 8.1$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.5; 35.1; 111.3; 120.5; 120.7; 122.9; 124.9; 126.0; 141.8; 150.3; 151.1; 161.6; 162.0. MS (ESI) m/z (%) 253 (M$^+$,100). HRMS (ESI): Anal. Calc for C$_{16}$H$_{17}$N$_2$O: 253.1341. Found: 253.1357.

6.2.2.4 2-(4-tert-butyl pyridin-2-yl)-benzothiazole (L10)

Compound L10 was prepared following the procedure described for L9 using 2-mercaptoaniline (0.50 g, 4.00 mmol) and 2-carboxy-4-tertbutylpyridine (0.72 g, 4.00 mmol). Yield = 0.86 g (80%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.38 (s, 9H, t-Bu, py); 6.95 (d, 1H, ph, $^2J_{HH} = 7.8$); 7.40 (m, 1H, ph); 7.54 (m, 1H, ph); 7.97 (d, 1H, py, $^2J_{HH} = 9.3$ Hz); 8.10 (d, 1H, py).
1H, ph, $^2J_{HH} = 8.1$ Hz); 8.37 (s, 1H, py); 8.60 (d, 1H, py $^2J_{HH} = 6.0$ Hz). $^{13}$C NMR (CDCl$_3$): $\delta$ 30.4; 35.1; 118.1; 122.0; 123.3; 125.7; 126.4; 135.9; 149.4; 151.0; 154.0; 161.4; 161.9. MS (ESI) m/z (%) 291 ($M^{+}$+Na$^+$,20) 269 ($M^{+}$,100). HRMS (ESI): Anal. Calc for C$_{16}$H$_{17}$N$_2$S: 269.1112. Found: 269.1106.

### 6.2.2.5 6-tert-butyl-2-(4-tert-butyl-pyridin-2-yl)-benzothiazole (L11)

To a solution of S2 (1.00 g, 3.00 mmol) in a minimum amount of ethanol was added 30% NaOH, (3.20 mL, 24.00 mmol). The mixture was diluted to give 10% NaOH and stirred for about 5 min. Portions of this mixture were added at 1 min intervals to a stirred solution of K$_3[Fe(CN)$_6$]$ (3.95 g, 12.00 mmol) in H$_2$O (5.00 mL) at 85 °C. The resultant mixture was further heated at 85 °C for 1 h, solvent removed in vacuo and the residue extracted with CH$_2$Cl$_2$ (2 x 20 mL). The combined organic extracts was washed with H$_2$O (2 x 20 mL), dried over MgSO$_4$ and solvent removed to afford an orange solid. Purification by column chromatography on silica gel using solvent mixtures of petroleum ether:ethylacetate (9:1) as eluent gave L11 as a pure compound. Yield = 0.53 g (55%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.44 (s, 9H, $^t$Bu, ph); 1.49 (s, 9H, $^t$Bu, py); 6.90 (s, 1H, ph); 7.46 (t, 1H, ph, $^2J_{HH} = 6.6$ Hz, $^3J_{HH} = 2.4$ Hz); 7.58 (t, 1H, ph, $^2J_{HH} = 7.5$ Hz, $^3J_{HH} = 1.8$ Hz); 7.97 (d, 1H, py, $^2J_{HH} = 8.1$ Hz); 8.18 (d, 1H, ph, $^2J_{HH} = 7.8$ Hz); 8.37 (s, 1H, py); 8.50 (t, 1H, py, $^3J_{HH} = 7.2$ Hz, $^2J_{HH} = 2.1$ Hz). $\delta$ 30.4; 35.1; 119.1; 122.6; 123.7; 125.4; 143.5; 135.9; 149.8; 152.1; 155.1; 161.9; 162.4. HRMS (ESI): Anal Calc for C$_{20}$H$_{24}$N$_2$S: 324.4809. Found: 324.4811.
6.2.2.6  [{2-pyridin-2-yl-1H-benzoimidazole}PdClMe] (31)

To a solution of [PdClMe(COD)] (0.12 g, 0.48 mmol) in Et2O (10 mL) was added L7 (0.10 g, 0.47 mmol) in Et2O (10 mL) to give a light yellow compound precipitate. After stirring for 12 h, the mixture was filtered to isolate a light yellow solid. Yield = 0.12 g (71 %). 1H NMR, (DMSO-\textit{d}_6): δ 1.12 (s, 3H, Pd-Me); 7.43 (dd, 2H, ph, \(^2\)J\text{HH} = 7.8 Hz) 7.78 (d, 2H, ph, \(^2\)J\text{HH} = 8.1 Hz); 7.90 (m, 1H, py); 8.40 (m, 2H, py); 8.85 (m, 1H, py). 13C NMR (CDCl\textsubscript{3}): δ -5.8; 113.1; 124.8; 126.9; 134.0; 139.5; 140.8; 148.3. MS (ESI): m/z (%) 357 (M\textsuperscript{+} + NCMe, 100); 316 (M\textsuperscript{+} - NCMe, 30). Anal. Calc for C\textsubscript{12}H\textsubscript{12}N\textsubscript{3}PdCl: C, 44.34; H, 3.43; N, 11.97. Found: C, 44.73; H, 3.01; N, 11.67.

6.2.2.7  [{2-pyridin-2-yl-benzothiazole}PdClMe] (32)

This compound was prepared following the procedure described for 31 using [PdClMe(COD)] (0.13 g, 0.50 mmol) and L8 (0.10 g, 0.50 mmol). Yield = 0.15 g (80%). 1H NMR, (DMSO-\textit{d}_6): δ 1.14 (s, 3H, Pd-Me); 7.59 (d, 2H, ph, \(^2\)J\text{HH} = 8.1 Hz); 7.80 (d, 2H, ph, \(^2\)J\text{HH} = 7.8 Hz); 8.18 (m, 1H, py); 8.31 (m, 2H, py); 8.72 (m, 1H, py). 13C NMR (CDCl\textsubscript{3}): δ 120.3; 122.6; 123.3; 126.1; 28.4; 135.4; 137.9; 140.1; 148.6; 149.9. MS (ESI): m/z (%) 372 (M\textsuperscript{+} + NCMe, 100); 331 (M\textsuperscript{+} - NCMe, 30). Anal. Calc for C\textsubscript{13}H\textsubscript{11}N\textsubscript{2}SPdCl: C, 42.29; H, 3.00; N, 7.59. Found: C, 42.35; H, 3.21; N, 7.39.

6.2.2.8  [{2-(4-tert-butyl pyridin-2-yl)-benzooxazole}PdCl\textsubscript{2}] (33)

To a solution of [PdCl\textsubscript{2}(NCMe)\textsubscript{2}] (0.15 g, 0.60 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was added a solution of L9 (0.15 g, 0.60 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (10 mL). The resultant orange solution was stirred for 24 h. The solution was then concentrated \textit{in vacuo} and hexane (20 mL) added
to precipitate a light orange solid. Yield = 0.12 g (70%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.47 (s, 9H, 'Bu, py); 7.46 (t, 1H, ph, $^2$$J_{HH} = 7.8$, $^3$$J_{HH} = 4.5$ Hz); 7.60 (t, 1H, ph); 7.70 (d, 1H, py, $^2$$J_{HH} = 7.5$ Hz); 7.73 (d, 1H, ph, $^2$$J_{HH} = 7.8$ Hz); 8.11 (s, 1H, py); 8.68 (d, 1H, ph, $^2$$J_{HH} = 8.4$ Hz); 9.15 (d, 1H, py, $^2$$J_{HH} = 7.2$ Hz). $^{13}$C NMR (CDCl$_3$): 31.2; 35.4; 110.9; 111.3; 119.5; 121.1; 121.5; 121.8; 123.9; 127.4; 131.0; 149.4; 151.6. MS (ESI): m/z (%) 436 (M$^+$ + NCMe, 50); 400 (M$^+$ + Cl, 100). Anal. Calc for C$_{16}$H$_{16}$N$_2$OPdCl$_2$: C, 43.73; H, 3.87; N, 4.67. Found: C, 44.08; H, 3.59; N, 4.52.

6.2.2.9 \(
\{2-(4-\text{tert-butyl pyridin-2-yl})-benzooxazole\} \text{PdClMe}\) (34)

This compound was synthesised in a similar manner to complex 31 using L9 (0.05 g, 0.20 mmol) and [PdClMe(COD)] (0.05 g, 0.20 mmol). Yield = 0.08 g (72%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.17 (s, 3H, CH$_3$, Pd-Me); 1.43 (s, 9H, 'Bu, py); 7.56 (m, 2H, py); 7.64 (m, 1H, py); 8.16 (d, 2H, ph, $^2$$J_{HH} = 7.5$ Hz); 8.54 (d, 1H, py, $^2$$J_{HH} = 7.8$ Hz); 9.00 (d, 1H, py, $^2$$J_{HH} = 7.5$ Hz). $^{13}$C NMR (CDCl$_3$): -11.2; 30.4; 35.3; 111.0; 111.6; 119.5; 120.1; 121.3; 121.9; 125.2; 126.7; 127.7; 149.0; 149.4. (ESI): m/z (%) 414 (M$^+$ + NCMe, 100); 253 (M$^+$ - PdMeNCMe, 45). Anal. Calc for C$_{17}$H$_{19}$N$_2$OPdCl.0.5Et$_2$O: C, 51.12; H, 5.38; N, 6.28. Found: C, 50.79; H, 5.71; N, 5.96.

6.2.2.10 \(
\{2-(4-\text{tert-butyl pyridin-2-yl})-benzothiazole\} \text{PdCl}_2\) (35)

This compound was synthesised following the procedure described for 33 using L10 (0.20 g, 0.80 mmol) and of [PdCl$_2$(NCMe)$_2$] (0.20 g, 0.80 mmol) to give a pale yellow solid. Yield = 0.30 g (80%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.40 (s, 9H, 'Bu, py); 7.70 (m, 1H, ph); 7.90 (d, 1H, py, $^2$$J_{HH} = 7.2$ Hz); 8.20 (m, 1H, ph); 8.39 (d, 1H, ph, $^2$$J_{HH} = 7.5$ Hz); 8.65
(s, 1H, py); 9.03 (d, 1H, ph, $^2J_{HH} = 8.1$ Hz); 9.54 (d, 1H, py, $^2J_{HH} = 7.2$ Hz). $^{13}$C NMR (CDCl$_3$): 30.7; 35.2; 111.5; 118.9; 120.8; 121.7; 125.6; 127.1; 130.6; 149.4; 150.5. MS (ESI): m/z (%) 446 (M$^+$ + NCMe, 100); 269 (M$^+$ - PdMeNCMe, 10). Anal. Calc for C$_{16}$H$_{16}$N$_2$SPdCl$_2$.CH$_2$Cl$_2$: C, 38.71; H, 2.44; N, 5.31. Found: C, 39.10; H, 2.60; N, 5.50.

6.2.2.11 \:[2-(4-tert-butyl pyridin-2-yl)-benzothiazole]PdClMe\] (36)

This compound was synthesised in a similar manner to complex 31 using L$_10$, (0.08 g, 0.20 mmol) and [PdClMe(COD)] (0.07 g, 0.20 mmol). Yield = 0.09 g (82 %). $^1$H NMR, (CDCl$_3$): $\delta$ 1.20 (s, 3H, CH$_3$, Pd-Me); 1.45 (s, 9H, 'Bu, py); 7.55 (m, 2H, ph, 1H, py); 7.90 (d, 2H, ph, $^2J_{HH} = 8.1$ Hz); 8.50 (d, 1H, py, $^2J_{HH} = 7.8$ Hz); 9.41 (d, 1H, py, $^2J_{HH} = 8.1$ Hz). $^{13}$C NMR (CDCl$_3$): 1.3; 30.6; 35.3; 117.3; 123.1; 125.2; 127.6; 130.9; 150.1; 150.4. MS (ESI): m/z (%) 430 (M$^+$ + NCMe, 100); 269 (M$^+$ - PdMeNCMe, 48). Anal. Calc for C$_{17}$H$_{19}$N$_2$SPdCl: C, 48.01; H, 4.50; N, 6.59. Found: C, 47.99; H, 4.14; N, 6.45.

6.2.2.12 \:[6-tert-Butyl-2-(4-tert-butyl-pyridin-2-yl)-benzothiazole]PdClMe\] (37)

Complex 6 was prepared in a similar manner to 31 using L$_{11}$ (0.07 g, 0.21 mmol) and [PdClMe(COD)] (0.05 g, 0.21 mmol). Yield = 0.06 g (60%). $^1$H NMR, (CDCl$_3$): $\delta$ 1.21 (s, 3H, CH$_3$, Pd-Me); 1.40 (s, 9H, 'Bu, ph); 1.45 (s, 9H, 'Bu, py); 7.52 (d, 1H, ph, $^2J_{HH} = 7.8$ Hz); 7.67 (d, 2H, py, $^2J_{HH} = 10.5$ Hz); 7.86 (d, 2H, ph, $^2J_{HH} = 7.5$ Hz); 8.47 (d, 1H, py, $^2J_{HH} = 7.5$ Hz); 9.28 (d, 1H, py, $^2J_{HH} = 9.0$ Hz). $^{13}$C NMR (CDCl$_3$): 2.1; 30.3; 31.4; 32.9; 35.6; 117.3; 23.6; 124.3; 124.9; 126.7; 147.8; 151.6; 163.9. MS (ESI): m/z (%) 486 (M$^+$ + NCMe, 100); 462 (90); 445 (M$^+$ - NCMe, 10); 269 (M$^+$ - PdMeNCMe, 48). Anal. Calc for C$_{21}$H$_{27}$N$_2$SPdCl: C, 52.40; H, 5.65; N, 5.82. Found: C, 52.62; H, 6.03; N, 5.70.
6.2.3.1 Typical procedure for Heck coupling reactions

In a typical experiment butylacrylate (0.06 mmol), iodobenzene (0.06 mmol) and Et$_3$N (0.06 mmol) were added to a solution of the palladium catalyst (0.4%) in DMF (10 mL) at 80 °C and the reaction heated for 24 h. Samples were withdrawn at regular intervals and analysed by GC to determine the percentage conversions. The coupling product was isolated by pouring the reaction mixture into water (50 mL) and extracted with CH$_2$Cl$_2$. The organic extract was dried over anhydrous MgSO$_4$ and the solvent was removed in vacuo to give a pure product as determined by $^1$H NMR.

6.2.3.2 Reaction carousel experiments

For comparison and duplicate reactions, the Heck coupling reactions were also carried out in a Radley 12-place carousel on the same scale. Reaction mixtures were stirred and heated at (80 °C) in a heating block. Samples were drawn at regular intervals for GC analyses.

6.3 Results and discussion

6.3.1 Synthesis and characterisation of ligands and palladium complexes

Compounds L7 and L8 were prepared by literature procedures$^{28}$ while L9 and L10 were prepared using a modified ring closure of 2-aminophenol and 2-aminothiophenol$^{28}$ with 4-tert-butylpyridine carboxylic acid respectively (Scheme 6.4). Both compounds were obtained in good yields. The 4-tert-butylpyridine carboxylic acid was synthesized following the procedure described by Fife et al.$^{31}$ However, L11, could not be

---


synthesised by this method owing to the non-availability of substituted aminophenols or aminothiophenols. It was therefore synthesized by Jacobsen’s\(^{32}\) intramolecular cyclisation under alkaline conditions with potassium ferricyanide (Scheme 6.4). The carboxylic acid amide (S1) was prepared by reacting 4-tert-butylaniline with 4-tert-butylpyridine carboxylic acid and was obtained in good yields. Reactions of S1 with 0.5 mole equivalent of Lawesson’s reagent gave the corresponding carbothioic acid

\[
\begin{align*}
\text{N} & \text{O} \\
\text{N} & \text{S} \\
\text{N} & \text{H} \\
\text{L7-L10}
\end{align*}
\]

\[
\begin{align*}
\text{S1} & \text{Laweson's reagent} \\
\text{Toluene, reflux}
\end{align*}
\]

<table>
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</tr>
<tr>
<td>'Bu</td>
<td>'Bu</td>
<td>S</td>
<td>L11</td>
</tr>
</tbody>
</table>

**Scheme 6.4**
amide (S2), Scheme 6.4. Cyclisation to give L11 was achieved in quantitative yields by treatment of S2 with potassium ferricyanide under basic conditions (30% NaOH). Consistent with literature reports, attempted cyclisation of S1 to give the benzooxazole analogue did not give the desired product.28

Reactions of compounds L7-L11, with either [PdCl2(NCMe)2] or [PdClMe(COD)] gave the corresponding palladium complexes (31-37) in moderate to high yields (Scheme 6.5). While complexes 31 and 32 showed poor solubility in most organic solvents, 33-36 were slightly soluble in chlorinated solvents due to the presence of the bulkier tert-butyl group on the pyridine ring. Complex 37, containing tert-butyl groups on both the phenyl and pyridine rings, was completely soluble in chlorinated solvents.

The identities of S1 and S2 were established by 1H NMR and 13C NMR spectroscopy and high resolution mass spectroscopy (HRMS). For example the N-H signal observed at 10.04 ppm (S1) confirmed the amide bond formation from the reaction between the pyridine carboxylic acid and the aniline, and a significant downfield shift of the N-H proton from 10.02 ppm (S1) to 12.11 ppm in S2 confirmed the conversion of the C=O to C=S. The up field singlet peaks at 1.30 ppm and 1.37 ppm in S1 were diagnostic of tert-butyl groups on the phenyl and pyridine rings. Consistent with 1H NMR spectra, 13C NMR spectra show significant downfield shifts of the C=S (187.3 ppm in S2) compared C=O (162.2 ppm in S1) carbon signals. HRMS spectral data for S1 and S2 showed m/z at 310 and m/z at 326 as the base peaks corresponding to the molecular ions of S1 and S2 respectively. The HRMS data also served to show the purity of compounds S1 and S2.
Compounds L7-L11 and their complexes 31-37 were also characterised by a combination of $^1$H NMR and $^{13}$C NMR spectroscopy, mass spectrometry and microanalyses. For example the intramolecular cyclisation to give L11 was evident from the disappearance
of the N-H signal at 12.11 ppm and loss of symmetry in S2 in the phenyl ring due to the formation of the C-S bond at one of the ortho positions of the phenyl ring. 1H NMR spectra of the complexes showed significant downfield shifts of the aromatic signals in the region 7.20 to 9.40 ppm. For instance the shift of the ortho pridinyl proton from 8.60 ppm (L10) to 9.40 ppm in 35 indicates coordination to the palladium metal (Figure 6.2).

Figure 6.2: 1H NMR spectrum of L10 (top) and its corresponding complex 35 (inset; expanded spectrum of the aromatic region).

High resolution MS (ESI) mass spectra for L9-L11 show m/z peaks at 253, 269 and 324 corresponding to the molecular ions of L9, L10 and L11 respectively. The mass spectra and microanalyses data of complexes 31-37 were in good agreement with the proposed
structures of the complexes in Scheme 6.5. All the complexes showed a similar mass spectral fragmentation pattern; starting with the loss of a Cl⁻ to form an unstable 14-electron cationic palladium complexes. In a typical fragmentation, 36 was found to loose a Cl⁻ to form the 14-electron fragment (m/z = 389), which is then stabilised by MeCN used to run the mass spectrum to give [Pd(L10)Me(NCMe)]⁺ (m/z = 430) as the base peak (Scheme 6.6). Subsequent loss of [PdMe(NCMe)]⁺ results in the peak at m/z = 269 corresponding to L10. Figure 6.3 shows mass spectrum of complex 35.

![Figure 6.3: MS-ESI spectrum of complex 35](image)

In order to confirm this stabilisation of cationic complexes of 31-37, cationic complexes of 31 and 36 stabilised by MeCN were made on a preparative scale and isolated. In a typical experiment, a mixture of complex 36 and NaBar₄ was dissolved in a mixture of CH₂Cl₂ and MeCN solvent. The mixture was stirred for 24 to give a pale yellow solution.
The solvent was removed under vacuum to give a light yellow solid. This was characterised by elemental analyses and mass spectrometry.\textsuperscript{33} The mass spectral data of cationic adducts of 31 (m/z = 375) and 36 (m/z = 430) established the molecular formulae of the compounds. The synthesis and isolation of stable cationic adducts of 31 and 36 thus confirmed stabilisation of complexes 31-37 by MeCN observed in the mass spectrometry data.

\begin{center}
\textbf{Scheme 6.6}
\end{center}

\textsuperscript{33} (a) To a mixture of complex 6 (0.10 g, 0.24 mmol) and NaBAr\textsubscript{4} (Ar=3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) was added a 1:1 mixture of CH\textsubscript{2}Cl\textsubscript{2} and MeCN (20 mL) and the light yellow solution stirred for 24 h. The solvent was removed in \textit{vacuo} to afford a light yellow solid. Yield = 0.20 g (67%). Positive MS (ESI) m/z (%) 430 (M\textsuperscript{+}, 50); 269 (100). Negative MS (ESI) m/z (%) 863 (M\textsuperscript{+}, 100). Anal. Calc for C\textsubscript{54}H\textsubscript{45}BF\textsubscript{24}N\textsubscript{3}PdS.0.5CH\textsubscript{2}Cl\textsubscript{2}: C, 44.74; H, 2.79; N, 2.93. Found: C, 44.63; H, 2.45; N, 3.04. (b) Complex 1 (0.10 g, 0.28 mmol) and NaBAr\textsubscript{4} (0.25 g, 0.28 mmol). Yield = 0.13 (40%). Positive MS (ESI) m/z (%) 357 (M\textsuperscript{+}, 100); 269 (120). Negative MS (ESI) m/z (%) 863 (M\textsuperscript{+}, 100). Anal. Calc for C\textsubscript{50}H\textsubscript{38}BF\textsubscript{24}N\textsubscript{3}PdS: C, 46.64; H, 2.02; N, 4.53. Found: C, 46.88; H, 2.45; N, 4.74.
6.3.2 H eck coupling reactions

6.3.2.1 Evaluation of complexes 31-37 as Heck coupling catalysts

Complexes 31-37 were tested as catalysts in the Heck coupling reaction of iodobenzene with butyl acrylate under different conditions. All the complexes were found to catalyse the coupling of butylacrylate with iodobenzene to form exclusively trans-butylicynnamate (Eq. 6.2) as established by $^1$H NMR analysis.

$$
\text{I} + \text{CH}_{2}CHCH=CH(OH)CH_{2}CH_{2}O \xrightarrow{[\text{Pd} \text{DMF, Base}]} \text{CH}CH=CH(OH)CH_{2}CH_{2}O
$$

(6.2)

The reactions were monitored on GC from which the percentage conversions were calculated. Figure 6.4 shows the GC chromatograms of the reaction mixtures obtained after 0 h (control), 8 h, 12 h and 24 h. From Figure 6.4, the GC trace of the control shows only one peak corresponding to the iodobenzene starting material. After 8 h and 12 h, there are two peaks in the trace corresponding to the iodobenzene and product signals. And after 24 h, only one signal corresponding to the product peak is present that indicates complete conversion of the starting materials to the products (100% conversion).
Figure 6.4: GC traces of the Heck coupling reactions mixtures after 0 h (control), 8 h, 12 h and 24 h.

The Heck coupling product was also analysed by $^1$H NMR spectroscopy. The product was isolated by addition of water to the reaction mixture and was isolated as orange oil. $^1$H NMR spectrum of the product (Figure 6.5) showed four up field signals at 1.09 ppm, 1.32 ppm, 1.37 ppm and 4.21 ppm corresponding to the tert butyl protons. Two doublet signals at 6.44 ppm and 7.74 ppm were assigned to the olefinic protons. The larger separation of the two protons showed that they were trans to each other and thus confirmed the formation of the trans product. The peaks at 7.41 ppm and 7.62 ppm were assigned to the phenyl protons. The $^1$H NMR spectrum thus confirmed the purity of the product and hence indicates that only one isomer (trans) was formed.
6.3.2.2 Optimisation of Heck coupling reaction conditions

In order to optimise the reaction conditions, the coupling reactions were performed at different conditions using catalysts 31 and 36 (Table 6.1). First investigated was the effect of temperature as it is well established that most Heck reactions occur at temperatures of 120-140 °C. The benzoazole palladium catalysts 31 and 36 were found to be active at 80 °C and 120 °C without showing any signs of deactivation. Catalysts from 31 and 36 are thus more stable at 120 °C than the cyclopalladated imine catalysts which are presumed to be very stable but were reported to decompose at temperatures of 120 °C.18 It was also evident that faster induction times were achieved at 120 °C than at 80 °C (Table 1 entries 1 and 4). However, the effect of temperature on overall conversion after 24 h was less pronounced as observed from conversions of 92% at 80 °C and 98% at 120 °C.
Table 6.1: Effect of reaction conditions on Heck-coupling reactions of catalysts \(31\) and \(36\)^a

<table>
<thead>
<tr>
<th>Entry</th>
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<th>% Conversionb</th>
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^aConditions: amount of monomer, butylacrylate 0.06 mmol; Iodobenzene, 0.06 mmol; base Et\(_3\)N solvent: DMF (10 mL); ^bDetermined by GC.

The effect of catalyst loading on the performance of Heck reactions was also investigated using catalyst \(31\) (Table 6.1, entries 8-13). It was apparent that even at low catalyst loading (0.05%) there was considerable activity with a conversion of 74%. Interestingly increasing catalyst loading to 1% resulted in reduction of activity. An optimum activity was achieved at catalyst loading of 0.8%. However, the catalytic activity at this loading does not differ much from the catalyst loading of 0.1 to 0.6% (Figure 6.6). The reduced
activity at high catalyst loadings could be the result of agglomeration and thus lowering the concentration of the active catalyst.\textsuperscript{11}

![Graph showing effect of palladium loading on Heck coupling efficiency](image)

Figure 6.6: Effect of palladium loading on Heck coupling efficiency of catalysts 31.

### 6.3.2.3 Variation of catalysts in Heck coupling reaction

Having established the optimum catalytic conditions, complexes 31-37 were screened at 80 °C to probe the effect of ligand structure on the catalysts’ performance (Table 6.2). The low temperature of 80 °C slowed the initiation process enough to allow the reaction profiles to be established. Table 6.2, entries 1-6, shows that no product was formed after 0.5 and 1 h for catalysts 31 and there was only 10% conversion after 5 h. The activity of 31 reaches a maximum conversion of 97% after 24 h (Table 6.2, entry 6). It was found that complexes 32-37 containing benzooxazole and benzothiazole exhibit almost 100% conversions within 1 h (Table 6.2, entries 7-18) compared to the benzoimidazole complex.

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Table 6.2: Influence of catalyst structure on Heck-coupling reactions\textsuperscript{a}
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<td>37</td>
<td>24</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>a</sup>Conditions: amount of monomers, butylacrylate 0.06 mmol; Iodobenzene, 0.06 mmol; base, Et<sub>3</sub>N; solvent: DMF (10 mL); [Pd], 0.4%. <sup>b</sup>Determined by GC.

31 which showed no catalytic activity within 1 h. Thus the initiation rate of catalyst 31 is considerably lower compared to 32-37 (Figure 6.7). As suggested by Kawano et al.<sup>11</sup>
bidentate pyridine Pd(II) complexes catalyse Heck coupling reactions by first undergoing reduction to ligand-stabilised Pd(0). It is therefore conceivable that the electron deficient benzothiazole and benzooxazole in 32-37 might play a role in their rapid conversion to ligand-stabilised Pd(0), the active catalysts, as compared to the electron rich benzoimidazole in complex 31. Bara-Behrens and coworkers\textsuperscript{27b} have established that electron withdrawing abilities of azoles follow the trend thiazole>oxazole>imidazole; an order that explains our observed trend in the initiation rates. More recently Hayashi\textsuperscript{34} and co-workers performed electron density calculations on a series of benzoazole palladium complexes using DFT and found that benzoimidazole complexes have the highest electron density compared to benzooxazole and benzothiazole complexes.

Another observation made was that the rates of initiation of chloromethyl palladium complexes 34 and 36 were faster than the dichloride analogues 33 and 35 (Table 6.2 entries 3-6). Cavell\textsuperscript{35} had previously observed that chloromethyl palladium catalyst precursors showed faster initiation rates than the dichloride analogues in Heck coupling reactions. Thus the faster induction periods of the chloromethyl complexes 34 and 36 indicate their relative ease to undergo decomposition more than the dichloride complexes 33 and 35 and are consistent with the observations of Cavell. Indeed chloromethylpalladium complexes

are generally known to undergo rapid decomposition via reductive elimination pathway.\textsuperscript{36} Nevertheless, the catalytic activities of all the complexes after 24 h did not show any significant differences (Table 6.2).

![Conversion chart of catalysts](chart.png)

Figure 6.7: Influence of catalysts structure on the induction period in the Heck coupling reaction.

It was apparent that steric factors did not have any significant effect in the catalytic activities of the complexes as seen in the comparable activities of complexes 32, 36 and 37. It is noteworthy to point out that complexes 32-37 exhibited relatively higher activity and shorter induction periods than the recently reported pyridyl-imine palladium catalysts\textsuperscript{37} under similar conditions. For instance, while 31-37 displayed almost maximum conversion within 1 h, these imine catalysts give conversions of 35\%-75\% within 1 h and in some cases achieve maximum conversion of 95\% in 2 h.

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6.3.2.4 Stability of catalyst 31 in Heck coupling reaction

To probe the stability of the active catalysts, equal amounts of the substrates and Et₃N were added at 1 h intervals to the reaction mixture using complex 31 and performing the reaction at 120 °C (Table 6.3). After each addition, the reaction was allowed to run for 1 h and an aliquot sampled for GC analysis. Such an approach has been used by other workers such as Nowotny,¹⁸ Shreeve,³⁸ and Souza³⁹ to investigate the stability of palladium catalysts in Heck coupling reactions. From Table 6.3, the conversion in the first cycles was 92% while the conversion in the fifth cycle was 94%. This thus showed that activity of 31 remained the same even in the fifth cycle, showing that the catalyst did not deactivate with time (Table 6.3, entries 5). This observation suggests that the catalysts are “living” Heck coupling catalysts as compared to some phosphine-based catalysts⁴⁰ such as Pd(dippp)₂ (dippp = 1,3-bis(diispropylphosphino)propane) that rapidly deactivate.⁴⁰ Nowotny and the group¹⁸ had previously observed reduction in activity from 100% in the first cycle to 95% in the second cycle of the cyclopalladated imine catalysts upon second addition of another equivalent amount of substrate and base and total loss of activity in the third run.¹⁸ A more drastic drop in catalytic activity has been reported by Souza³⁹ for the Pd₂(dba)₃ catalyst where the activity dropped from 91% to 53% in the first and third cycles respectively. Catalysts 31 thus showed greater stability in the Heck coupling reactions as maximum activity were obtained even after the fifth cycle.

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Table 6.3: Stability studies of catalyst 31 in Heck coupling reactions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cycle</th>
<th>Temp (°C)</th>
<th>[Pd] (%)</th>
<th>% Con</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31</td>
<td>1</td>
<td>120</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
<td>2</td>
<td>120</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
<td>3</td>
<td>120</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
<td>4</td>
<td>120</td>
<td>1</td>
<td>93</td>
</tr>
<tr>
<td>5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
<td>5</td>
<td>120</td>
<td>1</td>
<td>94</td>
</tr>
</tbody>
</table>

<sup>b</sup>Equal amount of reactants added after 1 h without addition of Pd complex.

6.3.2.5  *In situ* generation of palladium catalyst precursors in Heck coupling reaction

Palladium complexes, [Pd(OAc)<sub>2</sub>] and [Pd(PPh)<sub>3</sub>]<sub>4</sub>, are known to efficiently catalyse Heck coupling reactions on their own although addition of certain ligands such as diphenylphosphino ferrocene (dppf) help in increasing their catalytic activities.<sup>1b</sup> In attempts to establish the comparative activities of 31-37 and [Pd(OAc)<sub>2</sub>], equimolar amounts of L<sub>7</sub> and L<sub>10</sub> were added to [Pd(OAc)<sub>2</sub>] and compared to the activity of [Pd(OAc)<sub>2</sub>] alone (Table 6.4). It was observed that addition of L<sub>7</sub> and L<sub>10</sub> enhanced the activity of [Pd(OAc)<sub>2</sub>] from 78% to 100% (Table 6.4, entries 4-6). Consistent with the initiation rates of the corresponding complexes 31 and 36, L<sub>10</sub> showed shorter induction period than L<sub>7</sub> (Figure 6.6). Amatore and Jutanda<sup>9</sup> have identified [Pd(PPh)<sub>3</sub>(OAc)<sub>2</sub>] as the intermediate species formed when [Pd(OAc)<sub>2</sub>] and PPh<sub>3</sub> are used to catalyse Heck coupling reactions. The [Pd<sup>II</sup>(PPh)<sub>3</sub>(OAc)<sub>2</sub>] subsequently undergoes reduction to give [Pd<sup>0</sup>(PPh)<sub>3</sub>(OAc)] as the active species. It is believed that both L<sub>7</sub> and L<sub>10</sub> form similar
palladium intermediates as suggested by Amatore and Jutanda\textsuperscript{9} and thus the generation of the active catalysts follows a similar mechanism.

Table 6.4: Heck coupling reactions catalyzed by in situ Pd(OAc)\textsubscript{2} and L\textsubscript{7} and L\textsubscript{10}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Time(h)</th>
<th>[Pd] (%)\textsuperscript{b}</th>
<th>Conversion\textsuperscript{c} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>1</td>
<td>0.4</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>24</td>
<td>0.4</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>L\textsubscript{7}</td>
<td>1</td>
<td>0.4</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>L\textsubscript{7}</td>
<td>24</td>
<td>0.4</td>
<td>100</td>
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<td>5</td>
<td>L\textsubscript{10}</td>
<td>1</td>
<td>0.4</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>L\textsubscript{10}</td>
<td>24</td>
<td>0.4</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: amount of monomers, butylacrylate 0.06 mmol; Iodobenzene, 0.06 mmol; base, Et\textsubscript{3}N; solvent: DMF (10 mL); Temp. = 80 °C. \textsuperscript{b}Pd:Ligand ration = 1:1; \textsuperscript{c}Determined by GC.

Figure 6.8: Influence on ligands L\textsubscript{7} and L\textsubscript{10} on Heck coupling ability of Pd(OAc)\textsubscript{2}.
6.4 Conclusions

In summary, the work in this chapter has resulted in the identification of a convenient synthetic route to substituted (pyridinyl)benzothiazole compounds. Ligands \textbf{L9} and \textbf{L10} that contains substituents on the pyridine ring were synthesised by ring closure of aminophenol or aminothiopehnol with tert-butyl picolinic acid respectively. Compound \textbf{L11} that contains \textit{tert}-butyl groups on both the pyridine and phenyl rings was prepared by catalytic cyclisation of the respective amides under alkaline conditions. The ligands, when reacted with either \([\text{PdCl}_2(\text{NCMe})_2]\) or \([\text{PdClMe(COD)}]\) fragments, give mononuclear palladium complexes. The ligands and complexes were characterised by \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectroscopy and microanalyses. The molecular formulae of the compounds were confirmed by mass spectrometry. The complexes catalyse Heck coupling reactions of iodobenzene with butylacrylates under mild conditions and at low catalyst loadings. Benzothiazole and benzooxazole containing catalysts (32-37) showed faster initiation rates than the benzoimidazole catalyst (31). Overall the catalytic activities of complexes 31-37 did differ much over long reaction times. Catalysts 31-37 were found to be air and moisture insensitive, thermally stable, and can thus be used as “living” Heck coupling catalysts.
CHAPTER 7

General concluding remarks and future prospects

7.1 General conclusions

In summary, this thesis deals with a systematic investigation of some (pyrazol-1-ylmethyl)pyridine nickel and palladium complexes as potential olefin oligomerisation and polymerisation catalysts. The two bis(pyrazol-1-ylmethyl)pyridine ligands \( L_1 \) and \( L_2 \) used produce either bidentate or tridentate palladium complexes. The ligands form monometallic palladium complexes with one uncoordinated pyrazolyl, but give tridentate cationic palladium complexes on halide abstraction. Ligands \( L_1 \) and \( L_2 \) form mononuclear five-coordinate nickel complexes with the ligands binding in a tridentate fashion. The bidentate (pyrazol-1-ylmethyl)pyridine ligands \( L_3 \) and \( L_4 \) also give mononuclear palladium complexes in which the ligands adopt a bidentate binding mode. The ligands, \( L_3 \) and \( L_4 \), on the other hand exhibit either five coordinate dinuclear nickel complexes or four coordinate tetrahedral complexes depending on the steric bulk of the ligand backbone.

On activation, the bis(pyrazol-1-ylmethyl)pyridine palladium complexes \( 1-4 \) form inactive ethylene polymerisation catalysts tridentate species. The bis(pyrazol-1-ylmethyl)pyridine palladium complexes, however, do form catalysts that catalyse the oligomerisation and polymerisation of the more reactive phenylacetylene producing a mixture of oligomers and low molecular weight polyphenylacetylene. The (pyrazolylmethyl)pyridine palladium complexes \( 13-16 \) decompose readily on activation to palladium black. Stabilisation of the cationic palladium species by weakly coordinating
solvents or donor groups produce active ethylene polymerisation catalysts producing branched polyethylene albeit with very low activities. Poor electrophilicity of the Pd metal centers of the bis(pyrazolylmethyl)pyridine and (pyrazolylmethyl)pyridine palladium complexes might also be responsible for their poor reactivity with ethylene.

The objective of circumventing the tridentate coordination of bis(pyrazolylmethyl)pyridine palladium complexes to give inactive cationic species was clearly met with the nickel complexes. Thus activation of the bis(pyrazol-1-ylmethyl)pyridine and (pyrazol-1-ylmethyl)pyridine nickel complexes with EtAlCl₂ resulted in highly active ethylene oligomerisation catalysts with remarkable catalyst stability over long reaction times. The activities reported for ethylene oligomerisation reactions (1.6 x 10⁷ g oligomer/mol.Ni.h) rival those of the well established Brookhart nickel catalysts. These nickel catalysts represent the few examples of catalysts that produce a mixture of even number and odd number olefins from ethylene oligomerisation reactions. More unique is the higher percentage of the odd number olefins produced that has never been reported in the literature to date. This formation of both odd and even numbered olefins in addition to low product purity implicates isomerisation, metathesis and reincorporation mechanisms as the predominant factors controlling the oligomerisation process other than chain propagation and termination.

The nickel complexes also give active catalysts for higher 1-pentene, 1-hexene and 1-heptene oligomerisation showing good activity and stability and unique product
distribution. The 1-pentene oligomerisation reactions produce C\textsubscript{12} as the major product and C\textsubscript{15} as the minor product. Oligomerisation of 1-hexene produces mostly C\textsubscript{12} while 1-heptene reactions give predominantly the dimer product C\textsubscript{14}. High electrophilic nature of nickel complexes relative to palladium might also contribute to the good catalytic activities of the nickel complexes compared to palladium complexes.

In Chapter 6 of the thesis, a convenient synthetic route to the substituted (pyridinyl)benzothiazole compounds was developed. The ligands form mononuclear palladium complexes which catalyse Heck coupling reactions of iodobenzene with butylacrylates under mild conditions and at low catalyst loadings. The appeal of these catalysts is their stability and hence are they suitable candidates for the development of “living” Heck coupling catalysts. The palladium catalysts were however inactive towards coupling of the more deactivated aryl bromides and chloride. This might result from the rigid bidentate nature of the complexes that hinder the formation of the more active \textit{trans}-ligated palladium complexes. The strong donor ability of the (pyridinyl)benzothiazole ligands could also reduce the ability of the palladium complexes to undergo reduction to Pd(0) which is the active species.

\textbf{7.2 Future prospects}

The findings of this research have made a significant contribution to the design of active olefin oligomerisation catalysts. One such discovery is the delicate balance between electrophilicity and stability of the catalysts. While carbonyl linker pyrazolyl palladium complexes form active ethylene polymerisation catalysts, though with low stability, the analogous methylene linker palladium complexes are highly stable but inactive. As such
a balance between these two types of palladium catalyst precursors could be found by incorporation of both methylene and carbonyl linkers in one ligand motif as depicted in 7-I.

Another observation that needs further study is the low activity of the bidentate (pyrazol-1-methyl)pyridine palladium catalysts in the polymerisation of ethylene. It was earlier presumed that the low stability of the complexes might be responsible for their poor catalytic activity. However, the high stability of the MeCN cationic adducts of these complexes cast doubt on the decomposition theory. Poor electrophilicity of the complexes might therefore be implicated. As such another ligand design that could improve the electrophilicity of the catalysts is thus necessary. The carbonyl linker pyrazolyl analogue 7-II might be useful. Catalytic evaluation of this system would help in drawing the line between extreme cases of electrophilicity and stability.
Cobalt and iron complexes are known to give unique olefin oligomerisation catalysts. As such the synthesis of (pyrazol-1-ylmethyl)pyridine cobalt and iron complexes and their investigation as potential olefins oligomerisation catalysts would be useful (Figure 7.1).

![Figure 7.1: General structures of the proposed Fe and Co (pyrazol-1-ylmethyl)pyridine complexes.](image)

Further analysis of the oligomerisation products to determine the exact nature and composition of the isomers is necessary. This work so far have achieved the identification of the linear $\alpha$-olefins due to the limitations of the analytical techniques and non-availability of commercial samples of other isomers. Considering the significant amounts of these oligomers ($C_{11}$-$C_{14}$) produced and their important applications as detergents and lubricants, scale up of the reactions might have some great industrial importance. Another crucial step here would also be to investigate the separation techniques of the three major fractions ($C_{11}$, $C_{14}$ and $C_{16}$) to obtain pure products for such commercial applications.
Despite the high activities observed to date for the homogeneous single-site transition metal olefin oligomerisation and polymerisation catalysts, their industrial applications have witnessed very little success. This is mainly due to excess reactor fouling and high exothermic nature of the reactions. Another serious setback of these homogenous catalysts is the difficulty associated with separation of the products from the metal traces. In order to overcome these problems, the (pyrazol-1-ylmethyl)pyridine nickel catalysts described in this thesis could be heterogenised. In this design, introduction of support materials could be achieved in different ways. One such route is to have a silica support on the pyridine backbone via hydroxylation. The other approaches could utilise the hydroxylation of the pyrazolyl units or the methylene linkers (Figure 7.2).

Figure 7.2: Possible structures of heterogenised (pyrazol-1-ylmethyl)pyridine nickel catalysts.
Appendix A

Supplementary material for GC characterization of oligomer products

Appendix A1: GC chromatogram of authentic standard samples of linear C5-C20 α-olefins

Appendix A2: Typical GC trace of the oligomer products obtained using catalyst 23, Al: Ni ratio of 200:1, temp = 30 °C, pressure = 20 bar, Time = 1 h.
Appendix A3: (a) GC chromatogram of ethylene oligomer products from reaction using catalyst 26 at 20 bar, 15 min. (b) GC trace same sample spiked with 1-C_{14} showing increased intensity of the peak that corresponds to C_{14}.
Appendix A4: GC chromatogram of oligomer products from reaction using catalyst 24 at 20 bar, 60 min (a). GC trace same sample spiked with 1-C_{12} showing no overlap with any peak and thus indicates the absence of C_{12} in the product.
Appendix A5: (a) Typical GC trace of 1-pentene oligomer fraction obtained from catalyst 22, Al:Ni of 200:1, time = 60 min. (b) GC trace of same sample spiked with 1-C_{15} showing enhanced peaks at C_{15} fraction.
Appendix A6: (a) Typical GC chromatogram of 1-hexene oligomer obtained from catalyst 26, Al: Ni ratio of 200:1; time = 60 min. (b) GC chromatogram of same product spiked with standard samples of linear alpha C_{12}, C_{16}, C_{18}. The slight difference in retention of the C_{12} and C_{18} samples from the oligomer products indicate that the oligomer products are either branched or internal olefins but not linear alpha oligomers.
Appendix A7: GC trace of oligomer product from 1-heptene reaction using catalyst 22; Al:Ni ratio of 200:1; time = 60 min.

Appendix A8: GC trace of oligomer product from 1-heptene reaction using catalyst 22; Al:Ni ratio of 200:1; time = 60 min spiked with linear α-C14 standard.
Appendix A9: (a) GC trace of oligomer product from 1-heptene reaction using catalyst 26; Al:Ni ratio of 200:1; time = 60 min. (b) Expanded region of C14 fraction showing distinct peaks that corresponds to the C14 isomers.
Appendix

Publications

B1

Paper 1


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