From Mono- to Poly-Nuclear Late-Transition Metal Metal Catalysts for the Polymerisation of Ethylene

Thesis Submitted for the Degree of Doctor of Philosophy

By

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In the Department of Chemistry

at the University of Leicester

May 2006
Abstract

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Jérémie Pelletier

In Chapter One, an introduction to the field of metal-mediated olefin polymerisation catalysis is undertaken. The area of non-metallocene monometallic systems and, in particular, imino-based chelated (NN-, NNN-) late transition metal systems is briefly documented with a view to introducing the emerging field of olefin polymerisation mediated by multi-component catalysts [Concurrent Tandem Catalysis (CTC) and Encapsulated Bimetallic (EB)]. The Chapter concludes with a description of the objectives set for the thesis.

Chapters Two to Five discuss the synthesis and characterisation of mono- and bimetallic complexes (cobalt, iron and nickel) containing mono- and bi-nucleating ligands that incorporate bi- and tri-dentate binding domains (viz., iminophenanthroline, iminobipyridine, iminopyridine, α-dimine). Each Chapter is dedicated to the preparation of a specific type of precatalysts [monometallic (Chapter Two), fused EB (Chapter Three), remote EB (Chapter Four) and functionalised remote EB (Chapter Five)]. In Chapter Two, the syntheses of monometallic complexes are described. Chapter Three reports the preparation of fused EB precatalysts, in which the two catalytic sites share a central aryl moiety. In Chapter Four, remote EB precatalysts have been developed, each possessing two discrete binding domains tethered by a methylene linker. Chapter Five is concerned with the functionalisation of the linker in remote EB iminopyridine-based nickel precatalysts/catalysts. All complexes incorporate electronically active groups on the ligand manifold.

Chapter Six compares the performances of the complexes from all four chapters by our complexes for the polymerisation of ethylene. Both the oligomer and the polymer portions were analysed through a range of techniques (e.g., GC, GPC, DSC, $^1$H and $^{13}$C NMR). Regardless of the metal employed, encapsulated bimetallic catalysts produced higher molecular weights PE compared to their monometallic counterparts.

In Chapter Seven, the details of the experimental procedures are disclosed.
Statement

This thesis is based on work conducted by the author, in the Department of Chemistry of the University of Leicester, during the period between October 2001 and September 2004.

All the work described in the thesis is original unless stated otherwise, stated in the text or in the references. This work is not presented for another degree.

Signed

[Signature]

Jeremie Pelletier

Date: 29/05/2006
### Abbreviation and symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>Chemical Shift</td>
</tr>
<tr>
<td>ν</td>
<td>Stretching frequency</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl Fragment</td>
</tr>
<tr>
<td>Br</td>
<td>Broad</td>
</tr>
<tr>
<td>cat.</td>
<td>Catalyst</td>
</tr>
<tr>
<td>CCD</td>
<td>Cambridge Crystallography Database</td>
</tr>
<tr>
<td>CGC</td>
<td>Constrained Geometry Catalyst</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>Pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammoniumbromide</td>
</tr>
<tr>
<td>CTC</td>
<td>Concurrent Tandem Catalysis</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformaldehyde</td>
</tr>
<tr>
<td>DPM</td>
<td>Diaminodiphenylmethane</td>
</tr>
<tr>
<td>dt</td>
<td>Doublet of triplets</td>
</tr>
<tr>
<td>DTM</td>
<td>Diaminotriphenylmethine</td>
</tr>
<tr>
<td>EB</td>
<td>Encapsulated Bimetallic</td>
</tr>
<tr>
<td>ES</td>
<td>Electrospray</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl fragment</td>
</tr>
<tr>
<td>FAB</td>
<td>Fast Atom Bombardment</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>hr</td>
<td>Hour</td>
</tr>
<tr>
<td>GCMS</td>
<td>Gas Chromatogram coupled to a Mass Spectrometer</td>
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<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>iminobipy</td>
<td>Iminobipyridine</td>
</tr>
<tr>
<td>iminophen</td>
<td>Iminophenanthroline</td>
</tr>
<tr>
<td>i-Pr</td>
<td>Isopropyl</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>J</td>
<td>Coupling Constant</td>
</tr>
<tr>
<td>l</td>
<td>Litre</td>
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<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
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<tr>
<td>LLDPE</td>
<td>Linear Low Density Polyethylene</td>
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<tr>
<td>LS</td>
<td>Light Scattering</td>
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<tr>
<td>m</td>
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<tr>
<td>MAO</td>
<td>Methylaluminoxane</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
<td>-----------</td>
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<tr>
<td>Me</td>
<td>Methyl fragment</td>
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<tr>
<td>MeOH</td>
<td>Methanol</td>
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<tr>
<td>MM</td>
<td>Molecular Mechanics</td>
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<tr>
<td>MMAO</td>
<td>Modified Methylaluminoxane</td>
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<tr>
<td>Mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>M.p.</td>
<td>Melting point</td>
</tr>
<tr>
<td>Mₙ</td>
<td>Number Average Molecular Weight</td>
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<tr>
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<td>Mass Spectrometry</td>
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<tr>
<td>Mₘw</td>
<td>Weight Average Molecular Weight</td>
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<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular Weight Distribution</td>
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<tr>
<td>m/z</td>
<td>Mass/Charge</td>
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<tr>
<td>n-Bu</td>
<td>n-Butyl fragment</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>Pdi</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
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<tr>
<td>PE</td>
<td>Polyethylene</td>
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<td>Ph</td>
<td>Phenyl fragment</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per Million</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>p-TsSO₄</td>
<td>para-Toluene sulfonic acid</td>
</tr>
<tr>
<td>Qeq</td>
<td>Charge Equilibration method</td>
</tr>
<tr>
<td>rt</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SHOP</td>
<td>Shell Higher Olefin Process</td>
</tr>
<tr>
<td>TM</td>
<td>Transition metal</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>Tₘ</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>Tₑ</td>
<td>Crystallisation temperature</td>
</tr>
<tr>
<td>WCA</td>
<td>Weakly coordinated anion</td>
</tr>
<tr>
<td>XNi</td>
<td>Molar fraction of nickel</td>
</tr>
<tr>
<td>XTi</td>
<td>Molar fraction of titanium</td>
</tr>
<tr>
<td>µₒ</td>
<td>Bohr Magneton</td>
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Complexes

\[(L1)\text{FeCl}_2\] 1a \[(L21)\text{Fe}_2\text{Cl}_4\] 10
\[(L2)\text{FeCl}_2\] 1b \[(L22)\text{Ni}_2\text{Cl}_4\] 13a
\[(L3)\text{FeCl}_2\] 1c \[(L23)\text{Ni}_2\text{Cl}_4\] 13b
\[(L4)\text{FeCl}_2\] 1d \[(L23)\text{2(NClMe)}_4\text{Ni}_4\text{Cl}_8\] 13b' 
\[(L5)\text{FeCl}_2\] 1e \[(L24)\text{Ni}_2\text{Cl}_4\] 13c
\[(L3)\text{CoCl}_2\] 2a \[(L25)\text{Ni}_2\text{Cl}_4\] 13d
\[(L5)\text{CoCl}_2\] 2b \[(L26)\text{Ni}_2\text{Cl}_4\] 13e
\[(L6)\text{FeCl}_2\] 3a \[(L26)\text{2(NClMe)}_2\text{Ni}_4\text{Cl}_8\] 13e'
\[(L7)\text{FeCl}_2\] 3b \[(L23)\text{2NiBr}_4\] 13f
\[(L7)\text{NiBr}_2\] 4 \[(L28)\text{Fe}_2\text{Cl}_4\] 14a
\[(L8)\text{NiBr}_2\] 5 \[(L29)\text{Fe}_2\text{Cl}_4\] 14b
\[(L9)\text{NiCl}_2\] 6a \[(L30)\text{Fe}_2\text{Cl}_4\] 14c
\[(L10)\text{NiCl}_2\] 6b \[(L31)\text{Fe}_2\text{Cl}_4\] 14c
\[(L11)\text{NiCl}_2\] 6c \[(L32)\text{Fe}_2\text{Cl}_4\] 15b
\[(L12)\text{NiCl}_2\] 6d \[(L33)\text{Ni}_2\text{Cl}_4\] 16
\[(L13)\text{NiCl}_2\] 6e \[(L34)\text{Ni}_2\text{Cl}_4\] 17a
\[(L14)\text{NiCl}_2\] 6f \[(L35)\text{Ni}_2\text{Cl}_4\] 17b
\[(L15)\text{NiBr}_2\] 7a \[(L36)\text{Ni}_2\text{Cl}_4\] 18a
\[(L15)(\text{DMF})_6\text{Ni}_2\text{Br}_2\text{Br}_2\] 7a' \[(L37)\text{Ni}_2\text{Cl}_4\] 18b
\[(L16)\text{NiBr}_2\] 7b \[(L38)\text{Ni}_2\text{Cl}_4\] 18c
\[(L16)(\text{DMF})_6\text{Ni}_2\text{Br}_2\text{Br}_2\] 7b' \[(L39)\text{Ni}_2\text{Cl}_4\] 18d
\[(L17)\text{NiBr}_2\] 7c \[(L40)\text{Ni}_2\text{Cl}_4\] 18e
\[(L17)(\text{DMF})_6\text{Ni}_2\text{Br}_2\text{Br}_2\] 7c' \[(L41)\text{Ni}_2\text{Cl}_4\] 18f
\[(L15)\text{Ni}_2\text{Cl}_2\] 7d \[(L42)\text{Ni}_2\text{Cl}_4\] 18g
\[(L15)(\text{DMF})_4\text{Ni}_2\text{Cl}_2\] 7d' \[(L43)\text{Ni}_2\text{Cl}_4\] 18i
\[(L19)\text{Fe}_2\text{Cl}_4\] 9a \[(L44)\text{Ni}_2\text{Cl}_4\] 18j
\[(L20)\text{Fe}_2\text{Cl}_4\] 9b \[(PS-L40)\text{Ni}_2\text{Cl}_4\] 19
Structures determined by X-ray diffraction studies

Starting Materials
\[
\begin{align*}
(4-NH_2-3,5-Me_2C_6H_2)(4-NH_2-3,5-i-Pr_2C_6H_2)CH_2 \\
(4-NH_2-3,5-i-Pr_2C_6H_2)_2 \\
(4-H_2N-3,5-i-Pr_2C_6H_2)(4-OH-C_6H_4)CH \\
(4-NH_2-3,5-i-Pr_2C_6H_2)(4-NO_2-C_6H_4)(OMe)CH
\end{align*}
\]

Ligands
\[
\begin{align*}
((2-[1,10]-C_{12}H_7N_2)HCN)(2,6-i-Pr_2-4-Br^2-C_6H_2) & \quad L4 \\
[1,4-((2-C_5H_4N)HCN)_2-2,3,5,6-Me_4C_6] & \quad L15 \\
((2-C_5H_4N)CHN(3,5-Me_2C_6H_2))_2CH_2 & \quad L22 \\
((2-C_5H_4N)CHN(3,5-Me_2C_6H_2))_2 & \quad L33 \\
((2-C_5H_4N)CHN(3,5-i-Pr_2C_6H_2))_2(C_6H_5)CH & \quad L36 \\
((2-C_5H_4N)CHN(3,5-i-Pr_2C_6H_2))_2(4-Br-C_6H_4)CH & \quad L38 \\
((2-C_5H_4N)CHN(3,5-i-Pr_2C_6H_2))(4-(CH_2CHCH_2)-C_6H_4)CH & \quad L40
\end{align*}
\]

Complexes
\[
\begin{align*}
(L3)CoCl_2 & \quad 2a \\
(L5)CoCl_2 & \quad 2b \\
(L7)NiBr_2 & \quad 4 \\
(L8)NiBr_2 & \quad 5 \\
(L15)(DMF)_6Ni_2Br_2 & \quad 7a' \\
(L16)(DMF)_6Ni_2Br_2 & \quad 7b' \\
(L17)(DMF)_6Ni_2Br_2 & \quad 7c' \\
(L15)(DMF)_4Ni_2Cl_4 & \quad 7d' \\
(L23)_2(NCMe)_4Ni_4Cl_8 & \quad 13b' \\
(L26)_2(NCMe)_2Ni_4Cl_8 & \quad 13e'
\end{align*}
\]
Chapter Two: Imino-based Monometallic Iron, Cobalt and Nickel Precatalysts - Synthesis and Characterisation

2.1 Introduction
2.2 General synthetic strategy
2.3 Synthesis of [2-iminophenanthroline]MCl₂ (M = Fe, Co) (Class A)
2.3.1 Synthesis of [1,10]-phenanthroline-2-carboxaldehyde
2.3.2 Synthesis of ligands L1-L5
2.3.3 Synthesis of complexes 1a-2b
2.4 Synthesis of [2-pyridyl-6-iminopyridine]MX₂ (M = Fe, Ni) (Class B)
2.4.1 Synthesis of 2,2'-bipyridine-6-carboxaldehyde and 6-acetyl-2,2'-bipyridine
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2.4.3 Synthesis of complexes 3a-4
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2.5.1 Synthesis of 3-(2,6-diisopropyl-phenylimino)-butan-2-one
2.5.2 Synthesis of ligand L8
2.5.3 Synthesis of complex 5
2.6 Synthesis of [2-iminopyridine]NiX₂ (X = Cl, Br) (Class D)
2.6.1 Synthesis of ligands L9-L13
2.6.2 Synthesis of complexes 6a-6f
2.7 Conclusions
2.8 References

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Acknowledgements

My first thoughts go to my family for their constant love and encouragement. I would also like to take this opportunity to show my gratitude to all the people who offered support and friendship during the last four years, and in particular to Erwan and Yohan. I am also very grateful to Veronika for always standing by me.

None of the work contained in this thesis would have been possible without the expertise of a lot of people and I am very thankful to Dr. Gregory Solan for his supervision and guidance, but also to Dr. Richard Shutt, Prof. Eric Hope, Prof. David McConville and Alan Vaughn for their help throughout ‘my journey’.

I would like to acknowledge the skills of Dr. Gerry Griffiths, Dr John Fawcett and Dr Graham Eaton who provided excellent NMR, X-ray crystallography and mass spectrometry services. Thanks also to the good people of ExxonMobil who helped me with various analysis and polymer characterisation. In addition, thanks to Kuldip Singh and Mick Lee for their help on all sorts of practical issues.

Thanks to all. Merci à tous et en particulier à Greg.
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1 General introduction
Polyolefins have established themselves globally as one of the most important manufactured products with the worldwide production of polyethylene (e.g., LDPE, LLDPE, HDPE) alone exceeding million tons (figures for 2003). Polyethylene is employed in a wide range of applications and is traditionally manufactured by two main processes, one involving free-radicals and the other making use of heterogeneous transition metal catalysts. More recently, considerable research and development has been directed towards the synthesis of well-defined homogeneous transition-metal catalysts. These exciting systems have allowed access to new and improved polyolefins.

The main objective of this thesis is to prepare novel homogeneous catalysts containing two closely located polymerisation-active late transition metal centres (i.e., encapsulated bimetallic) with a view to probing the effect of a second metal centre on the performance of the overall alkene polymerisation catalyst. In order to set the scene for this work, this chapter begins briefly by documenting the background to single-site homogeneous catalysts for alkene polymerisation. It then proceeds to focus on reported single-site systems based on imino-containing ligands; ligands that are directly related to this work. In particular, the role of steric and electronic properties on the performance of these late transition metal systems is discussed. The chapter then moves on to review the current knowledge of multi-component homogeneous catalysis for olefin polymerisation with special regard being paid to the use of either two independent homogeneous catalysts or two catalysts encapsulated on the same ligand framework. In cases where unique catalytic performances are observed, these results will be interpreted on the basis of our current knowledge of single-site systems and their potential for cooperative metal...metal interactions. Finally, the chapter identifies the aims and the objectives set for this thesis.

1.1 Homogeneous catalysis for alkene polymerisation
In section 1.1, a general overview of the basic principles of metal-mediated alkene polymerisation is presented. In particular, the mechanistic aspects and general historical events leading to the advent of highly active single-site catalysts are described. Where appropriate specific terminology will be defined; a more complete glossary can be found in the appendices.
1.1.1 Background
While free-radical and heterogeneous catalysed processes (e.g., Ziegler-Natta, Philips) have led the way for the industrial manufacture of polyolefins, the capacity of homogeneous systems to access commercially important polyolefins (e.g., LLDPE) not readily accessible by the above processes, has led to a dramatic surge of interest within this area. Moreover, the direct correlation of the polymer product (i.e., molecular weight distribution, tacticity or comonomer content) to the catalyst structure has allowed considerable scope for fine-tuning of the catalyst for a particular end use. Homogeneous catalysts offer considerable advantages over their heterogeneous counterparts such as they can be soluble in hydrocarbons, can possess only one type of active site and their chemical structures can be easily modified.

Central to the development of homogeneous catalysts was the first report in 1957 by Natta of a metallocene-mediated alkene polymerisation using a mixture of \( \text{Cp}_2\text{TiCl}_2 \) and triethyl aluminium\(^2,3\). The observed activity of this metallocene/cocatalyst combination was very low and therefore showed little commercial promise. However, the full potential of metallocenes (Figure 1: I) in general to act as olefin polymerisation catalysts was not universally appreciated until the discovery of methylaluminoxane (MAO) by Kaminsky in the 1970’s. For instance, treatment of \( \text{Cp}_2\text{ZrCl}_2 \) with MAO displayed exceptionally high activities (up to 10,000-fold increase) for ethylene polymerisation when compared with the classic aluminum alkyl cocatalyst (e.g., \( \text{AlMe}_3 \)). Since then, an appreciation that MAO can act as a weakly coordinating anion (WCA) has led to the development of a range of other WCAs [e.g., tetra(perfluorophenyl)borate anions]\(^4\)\(^-\)\(^7\).

![Figure 1 Metallocene (I), anso-metallocene (II) and constrained geometry precatalysts](image)

\[ R = \text{H, hydrocarbyl, silyl} \quad Y = \text{Me}_2\text{SiOSiMe}_2, \text{C}_2\text{H}_4, \text{Me}_2\text{Si} \]

In 1982, a further milestone was reached when Brintzinger and co-workers\(^8\) synthesised chiral-bridged metallocenes (Figure 1: II). Soon after Ewen\(^9\) and later Kaminsky demonstrated the control over tacticity of \( \alpha \)-olefin polymerisation by
employing II and were able to synthesise highly isotactic polyolefin (e.g., polypropylene). This ability to control the tacticity has fuelled an intense interest in the development of new metallocene catalysts with the result that a rich library of catalysts are now available. Metallocenes that have the capacity, to copolymerise longer olefins and cycloolefins, to produce polyolefins with narrower molecular weight distributions, to allow improved tacticity control and to generate chemically uniform copolymers unobtainable by conventional heterogeneous catalysts, have all been reported. The advent of Constrained Geometry Catalysts (CGC) (Figure 1: III) represents a further landmark in the area with these systems showing good performances for the copolymerisation of ethylene and 1-octene and for homo- and copolymerisation of styrene with ethylene. Highly branched polymers can then be accessed using III by the incorporation of long chain olefins into the growing polymer chain or novel elastomeric microstructures obtained from the polymerisation of dienes.

1.1.2 Catalytic performance

The performance of a metal-based polymerisation catalyst can be evaluated in a variety of ways. For example, the absolute activity of the catalyst can be expressed in terms of gram of polymer per millimole of precatalyst per bar of ethylene pressure per hour of polymerisation run (i.e., g.mmol⁻¹bar⁻¹h⁻¹) while the resultant polymeric material can be characterised using a various analytical techniques (e.g., DSC, ¹H and ¹³C NMR, GPC/V/LS). A glossary describing the specific terminology can be found in the appendices.

1.1.3 Generation of the active catalyst

The active catalytic species for an ethylene polymerisation reaction can be an unsaturated neutral or cationic metal alkyl species [LnMR]⁺⁺(n = 0,1) stabilised by one or more spectator ligands (L). With regard to the cationic species, three routes can be identified in order to generate the active species, all involving the action of a cocatalyst or an activator (Scheme 1).

Route (i) involves the abstraction of an alkyl anion from [LnMR]₂ by a reagent such as [Ph₃C][B(C₆F₅)₄], [Ph₃CNHMe₂][B(C₆F₅)₄], [H(OEt)₂][B(3,5-(CF₃)₂C₆H₃)₄] or B(C₆F₅)₃ to give [LnMR]⁺[WCA]⁺ [WCA = B(C₆F₅)₄, B(3,5-(CF₃)₂C₆H₃)₄, BR(C₆F₅)₃]. Route (ii) is achieved by the abstraction of an anionic ligand X from [LnMRX] followed by its replacement with a WCA (weakly coordinating anion) to give [LnMR]⁺[WCA]⁻.
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Typical reagents are salts like Na[B(3,5-(CF₃)₂C₆H₃)₄] or AgBF₄. Route (iii) combines the alkylation and abstraction steps by treating [LₙMX₂] with an alkylation reagent and then one of the aforementioned reagents in order to generate the coordinatively unsaturated species. Some reagents like methylaluminoxane (MAO) can be employed for completing both steps.

\[
\text{Scheme 1 Formation of a cationic active catalyst by three different routes: (i) alkyl abstraction; (ii) X abstraction; (iii) X abstraction and alkylation.}
\]

1.1.4 Mechanism for chain growth (propagation) and termination
The mechanism for alkene polymerisation mediated by transition metal catalysts is believed to follow the pathway first described by Cossee and Arlman to explain the polymerisation of ethylene by heterogeneous group 4 systems.²⁶ The propagation step consists of the repetition of a series of steps whereby a monomer coordinates to a metal centre followed by the migration of the chain (R) to one end of the monomer (i.e., coordination-insertion, Scheme 2). Nevertheless, while this propagation step is operational for most transition metal catalysts, subtle variations can be observed for a particular catalyst and will be discussed with reference to work in this thesis (see Chapter 6).

\[
\text{Scheme 2 Cossee-Arlman mechanism for polymerisation propagation (coordination-insertion).}
\]

The termination pathway generally involves a β-H elimination step to generate an η²-alkene-hydride complex which then can loose the α-olefin by associative displacement (Scheme 3). Depending on the type of catalyst employed the type of termination can follow alternative pathways; variations will be illustrated in Chapter 6. It is noteworthy that experimental conditions (e.g., temperature, pressure or
concentration of the monomer, solvent, catalyst concentration) influence considerably the polymerisation process, for example by affecting the kinetics, the lifetime and/or the activation of the catalysts.

\[
\begin{align*}
\text{Scheme 3 Termination by } \beta\text{-hydrogen elimination.}
\end{align*}
\]
1.2 Imino-based supports for transition metal catalysts
The following section focuses on the catalysts for olefin polymerisation incorporating imino moieties within the ligand framework as these ligands are directly related to those employed in this work. Particular emphasis will be placed on late transition metal systems while ligands combining imino units and other hetero donor atoms will not be considered in this review. The role of steric and electronic properties on the performance of the catalyst will be examined separately.

1.2.1 Overview
The field of late transition metal-mediated polymerisation catalysts was rejuvenated in 1995 with the discovery of highly active and tunable cationic group 10 catalysts.27 These new systems stimulated a great deal of interest and have resulted in a considerable research activity directed towards the development of second-generation imino-based systems. By changing either the active metal centre or the spectator ligand, these new systems have allowed access to new and specific polymeric materials. Chart 1 illustrates a selection of both early and late transition metal imino-based precatalysts that have been developed recently. The position of the precatalysts with respect to the activity-arrow attempts to give an indication of the relative performance of the system in ethylene polymerisation. Other non-cyclopentadienyl ligand sets and their application in polymerisation catalysis have been reviewed elsewhere24, 28, 29 and will not be discussed herein.

While the use of neutral nickel catalysts for the oligomerisation of ethylene is the basis of the commercially important SHOP process,30-36 the groundbreaking work of Brookhart demonstrated the great capability of cationic nickel centres, when combined with the suitable ligand architecture, to be active for oligomerisation and polymerisation applications. Specifically, the use of cationic nickel catalysts (Chart 1: IV) supported by sterically variable α-diamine ligands afforded very high activities for the polymerisation of ethylene.27 The palladium (V),27 copper (VI)37 and cobalt (VII)38, 39 analogues are, after activation, an order of magnitude less productive for ethylene polymerisation (see section 1.2.2 for details on nickel). The second breakthrough came from the simultaneous reports by three independent groups in 1998 of highly active iron (VIII) and cobalt (IX) catalysts for the polymerisation of ethylene.40-42 Later, the vanadium (X)43 and chromium (XI)44 analogues have also been reported by the Gambarotta and Esteruelas groups, respectively. All the bis(imino)pyridine-based systems have shown
very high activities with the supporting ligand allowing considerable control on catalyst performance (see section 1.2.3 for details on iron and cobalt).

Fujita et al.\textsuperscript{45, 46} followed by Bochmann\textsuperscript{47} recognised the potential of the monoanionic imino-pyrrolide ligand as a support for a group 4 metal and reported high
activities for these systems. Typically, zirconium complexes (XII) show moderate activities, whereas titanium are highly active for both the polymerisation of ethylene\(^48\) and for the living copolymerisation of ethylene and norbornene.\(^48\) The related imino-indonyl titanium complexes (XIII) allow living polymerisation of ethylene at room temperature.\(^49\), \(^50\) However, the use of other metal centres supported by an imino-pyrrolide ligand frame give much lower activities. For example, Gibson and co-workers reported that the bis(imino-pyrrolide) chromium complex (XIV), on activation by a suitable aluminium-based initiator, gave only low activity for the polymerisation of ethylene.\(^51\) On the other hand, the bis(imino)pyrrolide cobalt species (XV) exhibit very poor activity for either polymerisation or oligomerisation of ethylene.\(^47\)

The use of the monoanionic \(\beta\)-diketiminate ligand as a support for transition metal-based precatalysts related to XVI have been reported.\(^52\), \(^53\) However, the mono(\(\beta\)-diketiminate) titanium complexes show only low activity for the polymerisation of \(\alpha\)-olefins.\(^54\) An improvement in activity was observed for the bis(\(\beta\)-diketiminate) zirconium version.\(^55\) On the other hand, chromium-based complexes of type XVII allow access to higher molecular weight polymer but with only modest activity.\(^54\), \(^56\), \(^57\) More recently, Piers et al. reported moderate activity with the related scandium catalysts XVIII.\(^58\), \(^59\)

The tris(pyrazolyl)borate ligand has been employed to support titanium centres (XIX)\(^60\) which exhibit activities that can be comparable with metallocenes. The same ligand employed with a nickel centre (XX)\(^61\) also formed a highly active catalyst.

### 1.2.2 \(\alpha\)-diimine-supported catalysts

As has been appreciated in the previous section, the \(\alpha\)-diimine ligand framework has been central to the resurgence of late transition metal catalysis and has been the subject of intense research.\(^27\), \(^38\), \(^62\), \(^63\) In this section, the aim is to focus on the development of group 10 catalysts derived from the \(\alpha\)-diimine motif which have a direct connection to the content of this thesis. Advances up to the year 2000 have been reviewed by Brookhart\(^29\) and a complementary updated article has been compiled more recently by Gibson.\(^28\) Specific details concerning the polymerisation mechanism will be given in Chapter 6.
1.2.2.1 Ligand design - α-diimine

Various structural developments around the α-diimine backbone have been reported (see Chart 1 in appendices). The imino-nitrogen substituents on the α-diimine have been thoroughly investigated, with the main emphasis being placed on sterically variable aryl groups. For example, the ortho positions of the aryl groups have been decorated with alkyl, aryl, halo, silyl, and heterocycle substituents. Some alternative N-substituents include hydrazone and pyrrole. On the other hand, a range of imino-carbon substituents have been introduced including hydrogen, alkyl, aryl, and methoxy groups. The fusion of a ring system to the carbon-carbon backbone of the α-diimine with anthracenyl, phenanthrolinyl, camphor, or oxygen-, nitrogen- or sulphur-containing heterocycle represents an alternative aspect of ligand design, while unsymmetrical substituted backbones have also been reported. More recently, the ligand backbone has been employed as a site for the immobilisation onto an organic or inorganic support. Incorporation of a heterocycle in place of one of the C(R)=N imine units has also been the source of a number of studies. For example, pyridyl and related heterocycles such as pyrimidine, chinoline, imidazole or indazole derivatives have formed half of the α-diimine backbone with the remaining imino unit incorporating a variety of substituents.

1.2.2.2 Polymerisation studies - [α-diimine]M complexes

The α-diimine-based family of group 10 complexes has been screened for a range of different polymerisation applications and with different monomers (e.g., higher α-olefins, polar, unsaturated cyclic, diene, acrylamine). The active species can be generated using a variety of cocatalysts (see section 1.1.3). So far, this type of catalyst has shown its best performance for the polymerisation of ethylene and has generally produced a blend of branched and linear olefins. Furthermore, the terminal double bond of the polymer chain can be isomerised, thus a significant amount of internal and branched olefins can be obtained. This is observed for all metal centres (i.e., nickel, palladium, cobalt, copper) and is believed to be due to a process known as ‘chain walking’, in which the metal centre undergoes a series of elimination/reinsertion steps on the chain of the polymer (see section 6.4). By far, palladium-based systems have shown the best ability to undergo chain-walking and can produce hyperbranched polymers.

The use of α-diimine-based group 10 catalysts has shown limited results for the polymerisation of α-olefins higher than ethylene. Notably, studies on
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Palladium catalysts for the polymerisation of propene have demonstrated that α-olefin can only insert at primary palladium alkyl bonds.\(^{29, 100}\) An increase in the overall activity is observed with the addition of ethylene as a comonomer due to its capacity to insert at secondary palladium-alkyl bonds when not adjacent to a tertiary carbon atom.

Polar comonomers such as acrylate have been successfully incorporated within the polyethylene chain\(^{38, 63, 71, 101-109}\) with both nickel and palladium systems but the highest degrees of incorporation have been observed with palladium-based systems. A limitation to these systems comes from the progressive deactivation of the catalyst due to the blocking of the coordination site by chelating carbonyl groups thus lowering the activity. More recently, the copolymerisation of ethylene with acrylates has been reported using well-defined α-diimine-nickel precatalysts at higher temperature and pressure under the activation of B(=C\(_6\)F\(_5\))\(_3\).\(^{110, 111}\)

The tolerance to polar functional groups observed by group 10 α-diimine catalysts has also inspired a series of studies concerned with carrying out polymerisations in alternative reaction media. For instance, ethylene polymerisation in aqueous media\(^{63, 112}\) or in biphasic toluene/ionic liquid media have been reported.\(^{113}\)

1.2.3 Bis(imino)pyridine-supported catalysts

The use of the bis(imino)pyridine ligand manifold as a support for polymerisation-active metal centres (VIII-XI) has been the subject of much investigation with most studies directed towards changing the metal centre or modifying the ligand. So far, iron,\(^{40, 42}\) cobalt,\(^{40, 42}\) chromium\(^{44}\) and vanadium\(^{43}\) metal centres have shown high activity for the polymerisation of ethylene. The following sub-sections are concerned with variations to the ligand frame and its impact on the polymerisation performance.

1.2.3.1 Ligand design - bis(imino)pyridine

Various modifications of the original neutral bis(imino)pyridine ligand framework have been reported (see Chart 2 in appendices).\(^{47, 114-132}\) The central moiety of the ligand backbone consists generally of a pyridine unit or a related group such as pyrimidine\(^{121, 133}\) or pyrrolide.\(^{47, 51, 134}\) As the imino donor is highly influential on the polymerisation ability of the catalyst, both the nature of carbon and nitrogen substituents have been thoroughly investigated. For instance, hydrogen, hydrocarbyl,\(^{41, 121, 135}\) and various heteroatoms have been introduced\(^{117, 125, 128, 136, 137}\) at the imino-carbon and this site has also been used as a means of immobilising the catalyst on a heterogeneous substrate.\(^{124}\) The \(N_{\text{imine}}\) position has been also investigated mainly by changing the substituent of the
N-aryl ring,\textsuperscript{116, 131, 132} for example with a hydrazone group.\textsuperscript{75, 119, 138, 139} Additionally the entire imine unit can substituted for a heterocyclic unit such as oxazoline\textsuperscript{114, 115} or pyridine.\textsuperscript{120}

1.2.3.2 Polymerisation studies – [bis(imino)pyridine]M complexes

For iron,\textsuperscript{40, 42} cobalt,\textsuperscript{40, 42} vanadium\textsuperscript{43} and chromium\textsuperscript{44} bis(imino)pyridine-supported catalysts produce almost exclusively linear $\alpha$-olefins with very high activities. Most of the mechanistic studies have been carried out on iron-based systems and recent publications support the formation of an alkyl-iron(II) active centre.\textsuperscript{100, 140}

Experiments assessing the capacity of bis(imino)pyridine-iron complexes as catalysts for the polymerisation of higher olefins have outlined their limited capability for this application. Only propylene polymerisation has exhibited some activity at low temperature with high regioregularity resulting in low molecular weight polymers.\textsuperscript{141-143} In contrast to the $\alpha$-diimine-based family, the iron precatalysts have not shown any ability to undergo chain walking, although related cobalt complexes can produce a small amount of isomerised olefins.\textsuperscript{144} Further discussion about the polymerisation aptitude of this catalyst will be disclosed in section 6.3.

1.2.4 Influence of steric properties

The influence of steric properties on group 8-10 imino-based catalysts is now well established with the presence of bulkier groups around the metal centre leading to higher molecular weight polymers and more active systems.\textsuperscript{120, 145-147} Notably, considerable control of the molecular weight of polyethylene can be imparted by judicious choice of $o$-substituents on the N-aryl group (Figure 2).\textsuperscript{29}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure2.png}
\caption{Steric protection imparted by $o$-groups on the metal centre.}
\end{figure}

For example in $\alpha$-diimine group 10 systems, these particular substituents are ideally located to protect the active metal centre from incoming monomers and, as a result, can influence chain propagation and chain transfer.\textsuperscript{145-147} By the same token, replacement of one imino unit with a less bulky pyridine group (i.e., imino-pyridine group 10 system)
also results in reduced molecular weight polymer whilst also lowering the activity of the system.\textsuperscript{39, 84, 148-153}

1.2.5 Influence of electronic properties

The role of electronic properties on the overall performance of imino-based group 8-10 polymerisation catalysts has been investigated by modifying the electronic attributes of the ligand manifold.\textsuperscript{28} In this section, electronic effects induced by modifications of the ligand manifold are related to both the polymerisation performance and spectroscopic consequences.

1.2.5.1 Influence of the electronic properties on the polymerisation performance

Gibson and co-workers have reported the unexpectedly high activity displayed by a series of cobalt-based bis(arylimino)pyridine catalysts with ligands possessing fluoro and trifluoromethyl substituents on the N-aryl group (Figure 3).\textsuperscript{154} This effect on the activity, in addition to higher peak activities and longer catalyst lifetimes, was attributed to the enhanced electrophilicity of the metal centre due to the presence of the CF\textsubscript{3} groups. Iron is generally one order of magnitude more productive than its cobalt counterparts, nevertheless the cobalt-based (Figure 3: VIII\textsubscript{b}) system was the most active catalyst, producing almost solely solid polymer and displaying extremely high activities that surpass significantly its iron analogue (VII\textsubscript{e}).

\[
\begin{array}{cccc}
\text{R}^1 &=& \text{CF}_3; & \text{R}^2 = \text{R}^3 = \text{H}; \text{X} = \text{Br} \\
\text{R}^1 &=& \text{CF}_3; & \text{R}^2 = \text{F}; \text{R}^3 = \text{H}; \text{X} = \text{Br} \\
\text{R}^1 &=& \text{CF}_3; & \text{R}^2 = \text{H}; \text{R}^3 = \text{F}; \text{X} = \text{Br} \\
\text{R}^1 &=& \text{CH}_3; & \text{R}^2 = \text{R}^3 = \text{H}; \text{X} = \text{Cl} \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{M} = \text{Fe} & & \text{M} = \text{Co} \\
\text{VIIa} & & \text{VIIb} \\
\text{VIIe} & & \text{VII} \text{f} \\
\text{VIIg} & & \text{VII} \text{d} \\
\end{array}
\]

\textbf{Figure 3} Fluoro-substituted bis(imino)pyridine-iron and -cobalt precatalysts.

Sun and Yang have examined the influence of the bis(imino)pyridine ligand framework on the electronic properties of the active metal centre.\textsuperscript{155} The relationship between the net charge of the metal and its activity for the polymerisation of ethylene (Figure 4) was investigated by screening a series of bis(imino)pyridine-iron complexes. The net charge on the metal centre of the precatalyst was calculated by employing a combination of the charge equilibration method (QEq)\textsuperscript{156} and molecular mechanics
For the iron catalysts, VIIa, VIIb and VIIc, the correlation between net charge and activity clearly indicates a turning point in the polymerisation behaviour.

![Image](image.png)

**Figure 4** Fluoro-substituted bis(imino)pyridine-iron precatalysts.

### 1.2.5.2 Imine donor capability

In the previous section, the influence of the electronic properties of the ligand manifold was probed by examining the effect of the incorporation of various substituents on the performance of the catalyst for alkene polymerisation. As an alternative, we explore here the effect of electronic variation in imino-based ligands with regard to their spectroscopic properties. In particular, we focus on the donor capability of an imino unit by using the carbonyl stretching frequency as a guide. In addition the stretching frequency of the imine itself can be useful and will be discussed.

In principle, the donor capability of specific imine nitrogen will be determined by the nature of both the imino-carbon and the imino-nitrogen substituents. Alternatively, if the imine group is incorporated into a heterocyclic ring (e.g., pyridine), then the type of ring system will also influence the donor capability of the nitrogen atom. Table 1 lists the ν(CO) stretching bands for a series of square planar rhodium(I) carbonyl complexes bound by bidentate imino-based donor ligands. For all complexes XXI, the infrared spectra show values in a close range (i.e., 1997-1977 cm⁻¹) for the CO absorbance bands. For the α-diimine complexes XXIa-c, in which the N-aryl substituents are varied, the ν(CO) bands are found around 1993 cm⁻¹. In XXId-f, in which a pyridylimine is bound to metal centre the ν(CO) stretch is reduced to ca. 1988 cm⁻¹. The introduction of two pyridine units in the form of the bipy complex XXIg, results in much lower values at ca. 1977 cm⁻¹. The decreasing of the ν(CO) absorption band is consistent with an improvement of the donor capacity of the bidentate nitrogen donor ligand as result of an increased back donation into the π* orbitals on the CO (Scheme 4).
From this data, it is clear that the nitrogen from a pyridine is a significantly better donor than an imine. Changing the substituent of the N-aryl group seems to be far less influential as reflected by the similar values observed when varying the substituents (see complexes XXIa-c). Changing the imino-carbon substituent can also influence the donor capability of the nitrogen. A lowering of the carbonyl absorption band is observed when using a ketimine (XXIIi) instead of an aldimine (XXIh) and is consistent with the improved donor capability of a ketimine nitrogen (Table 1). This is of particular interest, as the incorporation of aldimine or ketimine moieties into the ligand frame can induce dramatic changes in activity of late transition monometallic polymerisation catalysts.

Table 1 \(v(\text{CO})\) stretching frequencies for complexes XXIa-i

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(v(\text{CO})) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXIa (R^1 = i-\text{Pr}; R^2 = R^3 = H)</td>
<td>1994</td>
</tr>
<tr>
<td>XXIb (R^1 = i-\text{Pr}; R^2 = i-\text{Pr}; R^3 = H)</td>
<td>1993</td>
</tr>
<tr>
<td>XXIc (R^1 = R^2 = R^3 = \text{Me})</td>
<td>1993</td>
</tr>
<tr>
<td>XXId (R^1 = i-\text{Pr}; R^2 = R^3 = H)</td>
<td>1987</td>
</tr>
<tr>
<td>XXIe (R^1 = i-\text{Pr}; R_2 = i-\text{Pr}; R_3 = H)</td>
<td>1988</td>
</tr>
<tr>
<td>XXIf (R^1 = R^2 = R^3 = H)</td>
<td>1989</td>
</tr>
<tr>
<td>XXIg</td>
<td>1977</td>
</tr>
<tr>
<td>XXIh (R = H)</td>
<td>1997</td>
</tr>
<tr>
<td>XXIIi (R = \text{Me})</td>
<td>1980</td>
</tr>
</tbody>
</table>

\(^a\) recorded in solid state (cm\(^{-1}\))
It is noteworthy that an imine, like a CO has the capacity to $\sigma$-donate and $\pi$-accept, though the degree of back donation is likely to be considerably less than that in a CO.\textsuperscript{160} However, the use of the $\nu$(C=N) stretching frequency as a guide to variations in the electronic properties of a complex is not found to be as sensitive as for CO. Nevertheless, its use to identify when metal coordination has occurred can be useful with differences up to 50 cm$^{-1}$ being observed on the formation of the complex.\textsuperscript{150}

1.2.6 Summary
As discussed above, homogeneous catalysts based on imino-based ligand frames are highly versatile and can be readily modified to allow access to a particular polymer type required. Central to these modifications is an appreciation of both the steric and electronic properties of the spectator ligand.
1.3 Multi-centre homogeneous catalysts for ethylene polymerisation

In recent years, the combination of more than one catalytic site in a single polymerisation reaction has been the source of considerable interest. Originally, this involved the use of two independent single-site catalysts within the same reactor with a view to modifying the properties of the polymer (viz., concurrent tandem catalysts). More recently, in order to benefit from the proximity of the metal centres, several groups have been targeting ligand manifolds that can support more than one polymerisation-active metal centre (viz., encapsulated systems). Interestingly, using either approach, evidence for unique catalytic behaviour has been presented and it seems likely to be due, in part, to cooperation between metal centres. The following section reviews new developments in both areas with particular emphasis placed on any apparent synergy exhibited between the metal centres.

1.3.1 Concurrent tandem catalysts (CTC)

In parallel with the research conducted on monometallic precatalysts, there has been numerous studies directed towards the use of homogeneous catalysts based on more than one well-defined active site. This approach, using the terminology originating in organic chemistry, is called concurrent tandem catalysis (CTC) and consists of the combination of several independent single-site catalysts operating together. To obtain an efficient CTC, each catalytic component must be compatible with substrates, intermediates and other catalysts, and in some cases, must also exhibit a specific reaction sequence selectivity. Due to the multiplicity of the parameters to be optimised, concurrent tandem catalysis constitutes a considerable challenge, but also presents a number of opportunities to improve polyolefin production. Multiple polymerisation catalysts operating simultaneously could circumvent the time and yield loss associated with the isolation and purification of intermediates in multi-step sequences, but also allow access to improved and new polymeric materials. Several examples can also be found in the industrial publications, sometimes under the name of reactor blending, and involve in some cases the immobilisation of the catalytic components on a heterogeneous support (i.e., SiO₂).

Depending on the components of the system, two types of polymeric material can be envisaged (Scheme 5). Firstly, a blend of polymer is obtained where the catalysts operate independently of each other. Secondly, through judicious choice of catalysts, one system can feed the other (e.g., when one catalyst oligomerises ethylene to short-chain olefins, the other is used to copolymerise with ethylene) so as to generate an
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The following sub-section examines these limiting polymeric cases, while also mentioning the possibility for polymeric materials being both blended and incorporated.

![Scheme 5 Limiting polymeric types using CTC.]

1.3.1.1 Polymer blending
In CTC, the simplest behaviour is observed when each separate catalyst polymerises ethylene independently, thus producing a blend of the different polymers (Scheme 6). Depending on the microstructure of the two polymeric materials, the mixture can remain homogeneous or separate into two phases.

![Scheme 6 Blending polyethylene using CTC.]

Mecking screened several dual combinations of early and late transition metal catalysts.\(^1\text{01, 102}\) For instance, use of $\text{Ia/IVa/MAO}$ (Figure 5) results in an immiscible mixture of polymers due to the significant difference of the polymer microstructures (i.e., branching content). Typically, $\text{IVa/MAO}$ produces high molecular weight branched polyethylene, which is a very oily material soluble in the solvent of polymerisation, whereas $\text{Ia/MAO}$ produces linear polyethylene that precipitates out from the polymerisation.\(^1\text{01}\) The combination involving $\text{IIb/IVb/MAO}$ (Figure 5) produces a homogeneous blend due to the similar range of MW and densities displayed
by the two polymer types.\textsuperscript{101} IVb/VIIa/MAO leads to a homogeneous mixture of polymers that possess properties related to the polyethylene produced by the separate catalysts.\textsuperscript{101} The branching content that remains constant for all the dual combinations screened in this study is indicative of the absence of incorporation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Some example of CTC components used to prepare blends.}
\end{figure}

The production of blends of polyethylene using binary CTC has been investigated mainly by combining various metallocene catalysts and have generally resulted in homogeneous blends.\textsuperscript{101,176-179} Soares and co-workers have studied similar binary systems and suggested that the active sites are not affected by the interactions between the catalysts.\textsuperscript{176} Thus, mono- or bi-modal molecular weight distributions can be correlated with the nature of the combined catalysts and the juxtaposition of their activities.\textsuperscript{176} Kaminsky and Heiland reported the influence of temperature upon the productivity of each component of a binary system; high temperature results in one catalyst dominating the polymerisation whereas low temperature inverts the tendency.\textsuperscript{177,178}

All investigations of CTC that produce polymeric blends have highlighted the importance of the nature and the relative ratio of the catalyst components. The properties of the blend are dependent on the compatibility of the polymer fractions generated during the CTC (\textit{i.e.}, molecular weight distribution, branching content). In turn, the overall performance of the CTC is based on a superposition of the actions of different catalytic components and can be adjusted by parameters such as temperature, pressure or component ratio.

\subsection*{1.3.1.2 Incorporated polymers}

CTC can be conveniently used as an effective method for the preparation of linear low density polyethylene (LLDPE). The advantage over the traditional process is that a single ethylene feed can be employed instead of ethylene and an \(
\alpha\) -olefin comonomer.\textsuperscript{161} During polymerisation, the catalysts are operating together, though not necessarily by direct interaction. One or more catalysts oligomerises ethylene to short
chain α-olefins, whereas the other catalytic site incorporates them into a growing polymer chain.

To our knowledge, Beach and Kissin reported in 1984 the first application of CTC for producing LLDPE in which the combination of an oligomerisation catalyst based on nickel and a titanium copolymerisation catalyst was employed.\textsuperscript{180, 181} These CTC systems were not perfectly balanced and as a result the total consumption of ethylene decreased while the concentration of the oligomerisation catalyst increased.

So far the best combination of catalysts reported has been developed by employing a well-defined CGC (IIIa) in combination with a nickel-based catalyst (XXII), whereby the α-olefin generated by XXII is copolymerised with ethylene using IIIa (Scheme 7).\textsuperscript{182} Under optimised conditions, the nickel catalyst exhibits a high selectivity for the dimerisation of ethylene to 1-butene. Therefore, under identical conditions, the binary system IIIa/XXII produces high molecular weight LLDPE, in which most of the α-olefins are incorporated to form ethyl branches. Significantly, the branching content of the resulting polymer depends on the ratio of the two catalysts. Another oligomerisation catalyst, (Figure 6: IVc) was added to the reaction employed above. Using this tricomponent system, branched polyethylene possessing both short (C2) and longer chains branches were accessible.\textsuperscript{183} However, the optimisation of the CTC (with regard to the molar ratio, pressure, temperature) to yield a polymer product with a monomodal MWD required considerable time and perseverance. For instance, the precatalysts possess different activation rates and each catalytic site possesses a specific rate of ethylene insertion. This is of most importance for IIIa as its copolymerisation capability depends on both the size of the growing polymer and the chain length of the incoming comonomers. The copolymerisation rate eventually stabilises after reaching a molar ratio of monomer/comonomer and results in a single type of LLDPE (i.e., constant branching level and chain length). However, the unreacted α-olefin, along with the copolymers, tends to limit the reaction by competing or preventing the monomer/comonomer coordination to the metal centre.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme7.png}
\caption{Scheme 7 CTC producing incorporated polymer (LLDPE).}
\end{figure}
As a result of the mechanistic understanding and well defined nature of the CG-type catalysts \( \text{e.g., IIIa} \),\textsuperscript{22, 184-195} most effort has been directed towards using them as the copolymerising catalysts in the CTC combination for LLDPE production. Figure 6 illustrates some examples of the oligomerisation catalysts that have been employed in combination with the CGC. For instance, Bazan \textit{et al.} used \( 1c/\text{IIIa}/\text{MAO} \) to access LLDPE with a monomodal MWD using ethylene as the sole feed.\textsuperscript{22, 194, 195} It is noteworthy that the variation of the amount of MAO, while keeping \( 1c/\text{IIIa} \) ratio constant, influences the product properties. Similar results were obtained when the same group investigated the combination of \( \text{XIXa} \) and \( 1a \) (Figure 6).\textsuperscript{61}

\begin{center}
\begin{tikzpicture}
\node[anchor=west] at (0,0) {Oligomerisation precatalysts};
\node[anchor=west] at (0,-2) {Copolymerisation precatalysts};
\node[anchor=west] at (0,-4) {Figure 6 Examples of catalytic components of CTC for polymer incorporation.};
\end{tikzpicture}
\end{center}

Temperature can also play an important role in determining the degree of incorporation. For example, ethylene-1-hexene copolymers were obtained by screening the combination of \( 1d/\text{MMAO} \) (that is known for the trimerisation of ethylene) and \( \text{IIa}/\text{MMAO} \) or \( \text{IIIa}/\text{MMAO} \) as the copolymerisation catalyst (Figure 6).\textsuperscript{196} The trimerisation catalyst\textsuperscript{197, 198} \( 1d/\text{MMAO} \) is deactivated at lower temperature whereas the copolymerisation capability of \( \text{IIa}/\text{MMAO} \)\textsuperscript{199} or \( \text{IIIa}/\text{MMAO} \)\textsuperscript{200} increases with temperature.\textsuperscript{196} Consequently, the resulting material ranges from polymer with high incorporation of 1-hexene to polymer blended with significant amounts of unreacted comonomer.

Fink \textit{et al.} investigated the use of early and late transition metal-based components. For instance, the combination of neutral nickel oligomerisation catalysts (which were
known to generate mostly 1-butene and 1-hexene) with a variety of MMAO-activated zirconocenes or with a heterogeneous mixture (e.g., MgH\textsubscript{2}/R-TiCl\textsubscript{3}/Cp\textsubscript{2}TiCl\textsubscript{2}). resulted in LLDPE from a single ethylene feed.\textsuperscript{201}

Various CTC systems have been reported in the industrial patent literature. For instance, Starzewski combined a series of nickel-ylide catalysts with a chromium/silica catalyst.\textsuperscript{202-204} In addition, a CTC formed by a bis(imino)pyridine-supported iron catalyst and a group 4 metallocene produced linear low-density polyethylene (LLDPE).\textsuperscript{101, 205, 206} However, the precise details about the experimental polymerisation conditions were not clear in these patents apart from disclosing that variation in the ratio of the catalysts was crucial to the balance of the CTC.

In summary, it would appear that the ideal combination for a CTC that is specifically designed to access incorporated polymer, should involve a highly selective oligomerisation catalyst in tandem with an efficient copolymerisation catalyst. For maximum control over the incorporation, the \(\alpha\)-olefins generated should be of a short chain length (i.e., C\textsubscript{4}-C\textsubscript{10}). As most oligomerisation catalysts available result usually in a distribution of different \(\alpha\)-olefins, the remaining unreacted olefins can later pose problems (i.e., hindered reactivity).

1.3.1.3 Simultaneous blending and incorporation

As has been already discussed, two distinct types of polymeric materials are synthesisable by CTC (i.e., blends or incorporated polymers). However, these types of polymer represent two extremes and it is likely that a combination of both behaviour can be observed. Thus, if the parameters of a CTC are not optimised properly, the resulting polymers will be effectively a blend composed of unreacted olefins and incorporated polymers. The following section outlines the difficulties that can be encountered when distinguishing between the two behaviours and highlights the importance of interpretation of findings in this area.

The CTC combinations based on IV\textsubscript{d}/III\textsubscript{a} or IV\textsubscript{d}/III\textsubscript{b} along with their immobilised versions (i.e., pyridylethylsilane-modified silica), have been reported by Spaniol et al. (Figure 7).\textsuperscript{207} Depending on the nature and the relative ratio of the catalytic components employed, differences in the MWD and the branching content were observed when using MMAO as the activator. For instance, bimodal molecular weight distributions were obtained in most cases except when using IV\textsubscript{d}/III\textsubscript{b}. For this latter combination, a monomodal distribution and an increase of branching content were observed. As for all combinations examined, the branching content increased with the concentration of IV\textsubscript{d};
both the monomodal MWD and the increase of branching content were attributed to a polymer incorporation scenario by the authors. Furthermore, a complex mechanism, in which IVd supplies olefins to be copolymerised by IIIb with ethylene was described. However, at the pressure employed, IVd/MAO is known to produce only minor amounts of short chain $\alpha$-olefins with higher molecular weight and branched polymers being the main product.\textsuperscript{149} On examination of the reported $^1$H and $^{13}$C NMR spectra reported in the Spaniol article for the polymer afforded using IVd/MMAO, it is apparent that terminal and linear olefins are only a minor product. Taking into account the above it would appear that a blend rather than an incorporation process is occurring in this work.

![Figure 7 Early and late transition metal precatalysts employed as CTC components.](image)

**Figure 7** Early and late transition metal precatalysts employed as CTC components.

1.3.1.4 **CTC performance - Synergic effects**

In rare cases, CTC systems have been reported to display unexpected behaviour for the polymerisation of ethylene. Notably, the correlation of the molar ratio of the catalysts with polymerisation features such as productivity or polymer properties can be a non-linear relationship.

Casagrande et al. investigated a binary CTC formed by an early and late transition combination IVa/IIa (Figure 8).\textsuperscript{60} At 0 $^\circ$C and 50 $^\circ$C, the productivity follows a progression almost linear with the ratio of the catalysts. However, at 30 $^\circ$C, a maximum of productivity is observed for $X_{Zr} = 0.67$ indicating some non-linear behaviour and suggesting synergic effects are operational at this temperature. One type of polymer is produced as suggested by the narrow and monomodal molecular weight distribution observed at all temperatures and the average molecular weights have similar values for intermediate $X_{Zr}$ values.

The influence of the proportion of the two precatalysts XIXa and IVa on the productivity has been screened in another study.\textsuperscript{208} The overall productivity of the system exhibits a maximum for a certain ratio ($X_{Ni} = 0.75$). Polymer properties such as the intrinsic viscosity and the melt flow indices show minimum and maximum for the same proportion Ni:Ti, respectively. The melting temperature and the crystallinity of the
polymer, which decrease with the proportion of titanium, suggest that the branching content level increases with the $X_{\text{Ni}}$.\(^{208}\)

![Figure 8](image)

**Figure 8** Examples of precatalysts combined in CTC leading to synergic effects.

In order to probe the effect of the distance between two polymerisation-active metal centres, Marks *et al.* reported a method to confine the components of a CTC by using a binuclear activator [*i.e.,* \([\text{Ph}_3\text{C}]_2[1,4-\{\text{B(}\text{C}_6\text{F}_5\}_3]\text{C}_6\text{F}_4] \) or \(\text{B2}\)] (Figure 9).\(^{209, 210}\) The precursor for the oligomerisation catalyst was IIIe and its titanium equivalent IIId was responsible for incorporating the oligomers into a growing polyethylene chain. Under stoichiometrically appropriate ratios of IIIc:IIId, and in the presence of B2, the system produced polymers having narrower molecular weight distributions than those obtained using the monofunctional activator [\(\text{Ph}_a\text{CJfB^Fs}\)]. These results show that the binuclear activator dramatically increases the efficiency of the catalysts for the production of LLDPE. In this particular example, the $\alpha$-olefins are generated in close proximity to the titanium site where incorporation into the larger polymer structure takes place. Overall, these results highlight the possibilities of enhancing the cooperativity of CTC sites by using electrostatic spatial confinement.\(^{209, 210}\)

![Figure 9](image)

**Figure 9** CTC using a binucleating activator.

### 1.3.1.5 Conclusions
As described in section 1.3.1., CTC employed for the polymerisation of alkenes can show some interesting and valuable characteristics. The flexibility of the system can be easily manipulated to produce polymeric materials (*i.e.*, blend to incorporated polymers) for various applications. Some parameters have been identified to be highly influential on the behaviour of the CTC systems described above. However, due to the number of
existing variables, the optimisation and the adjustment of all the parameters can be a
time consuming process. The nature of the catalytic components, the compatibility of
the polymer produced, the molar ratio of the catalysts and the cocatalyst, the
temperature or the pressure employed, are all key features to be considered for the
performance of the CTC.

1.3.2 Encapsulated polymerisation precatalysts/catalysts
In this subsection, the use of encapsulated polymerisation precatalysts/catalysts for the
polymerisation of olefins will be discussed.

1.3.2.1 Definition and scope
For the purpose of this work, an encapsulated polymerisation catalyst will be defined as
a species comprising two or more polymerisation-active transition metal centres (e.g,
Group 4, 5, Cr, Fe, Co, Ni, Pd, Cu) covalently bound to the same ligand framework
(i.e., polynucleating) and compartmentalised into two or more different multidentate
binding domains. In principle, these binding domains could be fused or remote (Figure
10) where remote would imply that two or more precatalysts/catalysts are joined by a
linker (inorganic or organic moiety or a chemical bond). On the other hand, a fused
encapsulated system would imply that some part of a well-defined monometallic
precatalyst/catalyst (e.g., ligand manifold) is shared in the construction of the
encapsulated system. However, in cases where the categorisation of encapsulated
systems into fused or remote is not clear, the author will highlight any ambiguity.
Reported fused encapsulated bimetallic systems will be examined in the first instance
(see sub-section 1.3.2.2) while remote systems will be discussed in the second (see sub-
section 1.3.2.3). Polymetallic systems containing one single polymerisation-active metal
centre in combination with either a cocatalyst or a non-polymerisation-active metal
centre will be also highlighted (see sub-section 1.3.2.4).

Figure 10 Fused vs. remote encapsulated catalysts.

To illustrate the definition of encapsulated systems outlined above, complex
XXIII\textsuperscript{211, 212} represents a fused encapsulated polymerisation precatalyst while XXIV a
remote encapsulated system (Figure 11). In contrast, bimetallic XXV\textsuperscript{213} is not
encapsulated as a single donor atom (*i.e.*, monodentate) is used to bridge the two metal centres.

![Image](XXIII) ![Image](XXIV M = Fe, Co) ![Image](XXV)

**Figure 11** Encapsulated precatalysts; fused (XXIII) vs. remote (XXIV); bimetallic precatalyst (XXV) will not be categorised as an encapsulated precatalyst.

In the following sections, selected examples of encapsulated catalysts will be described and the effect of having more than one polymerisation-active metal centre in close proximity on the performance of the overall catalyst outlined. To understand the effect, comparisons will be based where possible on a consideration of the performance of the most closely related monometallic precatalyst/catalyst or with that of relevant CTC will be made.

### 1.3.2.2 Fused Encapsulated precatalysts/catalysts

An example of a fused encapsulated catalyst has been reported by Jin *et al.* with the binuclear nickel complexes **XXVI** (Figure 12). These neutral, single-component catalysts contain two catalytically active sites and afford high molecular weight, moderately branched polyethylene in a similar manner to the corresponding monometallic salicylaldiminato system (*i.e.*, Grubbs-type catalyst). The N-substituents (*e.g.*, substituted phenyl; cyclohexyl) influence considerably both the activity and the molecular weight distribution. However, **XXVI**, when compared with the related single-site analogues, gives much broader MWD polymer. The authors suggest a combination of electronic effects and cooperative interactions of the two adjacent nickel centres to explain these differences. For example, the two metal centres are electronically coupled through the ligand manifold and as a result, more than one kind of active species can be generated during the polymerisation.

![Image](XXVI) Grubbs-type catalyst

**Figure 12** Fused encapsulated precatalysts vs. monometallic analogue.
Bianchini$^{219, 220}$ reported the binuclear nickel system (XXVII) in which the spacer consists of a cyclobutanyl group with one PAr$_2$ unit at each corner of the square (Figure 13). The ligand adopts a bis(bidentate) bonding mode with the nickel centres. Under activation with MAO, the binuclear catalyst produces only oligomer. However, no comparison with a related monometallic system has been reported.

![Figure 13 Encapsulated nickel catalyst.](image)

Several examples of fused group IV systems have appeared in the patent literature, one example being XXIII (Figure 11). However, the precise details of its performance as an olefin polymerisation catalyst are unclear.$^{211, 212}$

### 1.3.2.3 Remote Encapsulated precatalysts/catalysts
Remote encapsulated precatalysts/catalysts for the polymerisation of olefins have been reported for the support of various transition metal centres. In contrast with fused precatalysts, the polymerisation-active metal centres are far enough apart to be considered as totally separated (Figure 10).

#### 1.3.2.3.1 Remote group IV encapsulated systems
A number of remote group IV encapsulated bimetallic precatalysts have been synthesised by linking the ligand frameworks (e.g., metallocene and CGC). In most cases, the site of the attachment occurs at the cyclopentadienyl group. (Figure 14).

![Figure 14 Linked group IV metallocene and CG encapsulated systems.](image)

Some examples of linkers include aromatic moieties (e.g., XXVIII),$^{221-223}$ alkyl,$^{224-227}$ oxygen,$^{211}$ boryl (XXIX),$^{211, 228}$ ferrocenyl$^{229}$ (XXX) or silica (e.g., XXXI).$^{212, 223, 230-233}$ (Figure 15). Some systems have also been immobilised onto supports.$^{234, 235}$ Other
systems have been covered in the patent literature.\textsuperscript{211, 212, 236-241} Several groups have also reported encapsulated CGC linked by an alkyl unit (\textit{e.g.}, XXXII).\textsuperscript{209, 210, 225, 232, 242-245} Some encapsulated systems possessing two different catalytic sites have also been reported (\textit{e.g.}, XXXIIIa and XXXIIIb).\textsuperscript{224, 227, 231}

\[\text{XXVIII} \quad \text{XXIX} \quad \text{XXX} \quad \text{XXXI} \quad \text{XXXII} \]

\[M = M' = \text{Zr, Hf (XXXIIIa)} \quad M = \text{Zr, M'} = \text{Hf (XXXIIIb)}\]

\textbf{Figure 15} Examples of remote encapsulated systems with metallocene-based active sites.

Mühlhaupt \textit{et al.} screened XXVIII/MAO and its closest monometallic counterpart and noticed that lower molecular weight polyethylene were obtained using the encapsulated system.\textsuperscript{221-223} Interestingly, modification of the Al:Zr ratio for both the mono- and the bi-metallic species leads to converse behaviour in terms of the MWD of the polymer obtained. For instance, increasing the amount of MAO leads to a reduction of the MW of the polymer produced by XXVIII/MAO.

To date, the most complete study of encapsulated systems has been published by Marks and co-workers.\textsuperscript{246} A series of zirconium complexes of the type XXXII, which are based on methylene-linked zirconium CGC systems along with an ethylene linked analogue XXXIV and their monometallic counterpart IIIe (Figure 16), have been screened for the polymerisation of ethylene. Both mono- and di-boranes (B2) (Figure 11) along with MAO have been employed as activators for the precatalysts.

\[\text{XXXII} \quad \text{XXXIV} \quad \text{IIIe}\]

\textbf{Figure 16} CG encapsulated systems along with its monometallic counterpart.
In the case of XXXII, regardless of the cocatalyst employed, an increase in the molecular weight of the polymer is observed when compared with the performances of IIIc and XXXII. This molecular weight variation was attributed to the proximity of the two metal centres. The use of B2 instead of MAO as the cocatalyst leads for all the systems (monometallic and encapsulated) to an increase in branching (i.e., ethyl) (Scheme 8). The authors attributed that effect to the spatial confinement of the active metal centres induced by the binuclear cocatalyst. In regard to the encapsulated systems, B2 was believed to favour a spatial conformation that enhances considerably the cooperativity of the catalysts. For the authors, the proximity of the metal centres is directly responsible for this behaviour and is believed to affect considerable chain transfer rates and selectivity for comonomer enchainment.

Scheme 8 Proposed mechanism for branch formation by the encapsulated CGC XXXI and XXXII.246

The use of an encapsulated bimetallic titanium system, in combination with a mono- or di-borate activator has been screened for copolymerisation of ethylene with a series of vinyl compounds.247 For all comonomers, their incorporation into the polyethylene chain has been greatly improved by using either the binuclear activator or the dititanium encapsulated CGC. The proximity of the two polymerisation-active metal centres is believed to favour agostic interactions with one of the metal being located in such a way that its subsequent incorporation into the growing polymer is facilitated.

1.3.2.3.2 Remote late transition metal encapsulated systems
In the last few years, the use of late transition metal encapsulated precatalysts/catalysts for the polymerisation of ethylene has been reported by several groups. In each case, specific ligands have been designed to possess suitable binding domains with nitrogen, oxygen and phosphorus as the donor atoms. The different encapsulated systems will be classified according to the charge expected for the active catalyst.
1.3.2.3.2.1 Neutral precatalysts/catalysts

Encapsulated systems based on binuclear neutral species have been reported as early as 1994 by Kurtev et al. A series of symmetrical binuclear nickel complexes in which each nickel centre is chelated by a bidentate P,0 moiety have been synthesised (XXXV, Figure 17). Various tethers have been employed to link the systems (e.g., phenyl, alkyl, norbornyl, ferrocenyl). The encapsulated systems were able to oligomerise or polymerise ethylene; the precise performance being dependent on the reaction conditions. Their catalytic properties (i.e., activity, MWD and lifetime) are different when compared with the most closely related mononuclear ones and depend on the nature of the linker. The parameters controlled by the linker (e.g., substitution pattern, the distance between them, the presence of conjugation between the active centres, etc.) appear to influence considerably the performance of the systems. For instance, activation by phosphine scavenger was not necessary for all binuclear complexes unlike of their mononuclear counterparts.

Interestingly, the binuclear 3,3'-bis(salicylaldimine)-based neutral nickel complex XXXVI is capable of polymerising ethylene with high activity without any cocatalyst, whereas the monometallic equivalent (see Figure 12) possesses low activity and requires to be activated by a phosphine scavenger. The authors attributed the performance of XXXVI to the steric protection imparted on each nickel centre by the ortho-phenyl units that are used to support the other nickel centre. Temperature and pressure were found to have a dramatic effect on the catalyst activity for XXXVI, which decreases with temperature and increases with pressure, while the MWD of the polymer is slightly broader than that for the polyethylenes reported by the monometallic Grubbs catalyst (under similar conditions). In addition, the microstructure of the polyethylene produced revealed a higher level of branching than that for the monometallic equivalent.

A neutral binaphthyl-type binuclear dinickel catalyst (XXXVII) has also been reported by Li et al.; its performance for ethylene polymerisation was not disclosed.
1.3.2.3.2 Cationic catalysts

In this subsection, remote encapsulated precatalysts in which the active catalyst is expected to be cationic in nature will be reviewed. In order to clarify the reports in the area, the section has been further broken down on the basis of the linker used for the remote encapsulated bimetallic catalyst.

1.3.2.3.2.3 Use of an alkyl linker

Two groups have published in the industrial literature bi- and tri-metallic encapsulated iron systems for the polymerisation of ethylene (Figure 18). Small reported a moderately active system in which two iron centres are supported on a single ligand possessing two bis(imino)pyridine pockets connected by an methylene bridge (XXIV).251

Liu and co-workers252, 253 reported similar systems and claimed to have accessed a cyclic trimetallic complex (XXXVIII). The comparison between the trimetallic species with the monometallic counterpart for ethylene polymerisation under similar conditions (i.e., pressure, temperature and cocatalyst) reveals that the encapsulated system displays higher activity and longer lifetimes. High molecular weight polyethylene with broader MWD’s are also produced and the microstructure of the polyethylene is consistent with linear α-olefins.

![Diagrams XXIV and XXXVIII](image)

**Figure 18** Examples of bis(imino)pyridine encapsulated precatalysts (M = Fe, Co).

Novel bridged α-diimine-based nickel and palladium complexes of the type XXXIX and XXXX have been employed by Mi254 for the homo-polymerisation of styrene and the co-polymerisation of styrene with norbornene with high activities reported
Chapter One

(Figure 19). The palladium catalysts surpass their nickel counterparts in activity and result in higher molecular weight polymers with narrow MWDs.

![Figure 19 Examples of remote EB precatalysts](image)

Highly active encapsulated α-diimine nickel catalysts (XXXXI and XXXXII: Figure 20) for ethylene polymerisation, were developed successfully by Schumann and co-workers. Under activation with MAO, bi- (XXXXI) and poly-metallic (XXXXII) precatalysts were screened for ethylene polymerisation and all afforded solid polyethylene with high activities and molecular weights consistent with the ortho aryl group substitution. The authors attribute the variation of activity to a combination of steric and electronic properties of the precatalysts/catalysts.

![Figure 20 Encapsulated dinickel precatalysts](image)

Mapolie and co-workers synthesised bi-nuclear iminopyridine palladium complexes with long alkyl tethers (Figure 21: XXXXIII). XXXXIII/MAO displays lower activity than the mononuclear analogue. Surprisingly, use of both XXXXIII and its monometallic alkyl-containing counterpart result in highly linear polyethylene with high molecular weights, contrasting with the highly branched polymers reported for N-aryl iminopyridine Pd catalysts. The monomodal molecular weight distribution and the narrow MWD for the polymer afforded using XXXXIII suggests the existence of just one kind of active species. Polymerisation productivities were found to be sensitive
to temperature as well as to the amount of the cocatalyst employed. The ratio of Al to Pd was found to influence the behaviour of XXXXIII when compared to its monometallic counterpart with higher Al:Pd ratios leading to higher activities for the monometallic system. The authors explain this observation by the lower solubility of the encapsulated system when compared to the mononuclear complex.

\[ XXXXIII \]

Figure 21 Examples of an alkyl-linked iminopyridine encapsulated palladium precatalysts.

1.3.2.3.2.4 Use of a ferrocenyl linker
Gibson et al. reported the use of encapsulated bimetallic group 10 precatalysts in which each metal centre (i.e., nickel or palladium) is bound to an iminopyridine pocket with a ferrocenyl linker attached directly to the imino-nitrogen atoms (Figure 22: XXXXIV and XXXXV).\(^{258}\) Only the nickel species were active and displayed a high selectivity towards the production of very low molecular weight oligomers (C4-C8). The lack of protection at the metal centre imparted by the ferrocenyl units was used to explain the prominence of the \( \beta \)-H transfer over chain propagation.

\[ XXXXIV \]
\[ XXXXV \]

Figure 22 Encapsulated group 10 precatalysts linked by a ferrocenyl linker (M = Ni).

1.3.2.3.2.5 Use of an aryl linker
The use of an aryl group to link the backbone of \( \alpha \)-diimine has been reported in the patent literature (Figure 23: XXXXVI).\(^{259}\) For example, Li et al. claimed that naphthalene-functionalised bis(\( \alpha \)-diimine) ligand can be linked by an aromatic ether giving an active dinickel encapsulated catalyst.\(^{259}\) The details of the polymerisation performance was not, however, disclosed.
1.3.2.4 Polymetallic catalytic systems containing a single polymerisation-active metal

To simplify our discussion about encapsulated systems, we have excluded in previous sections bimetallic species in which only one of the metal centres is active for the polymerisation of an alkene. It is recognised by the author that the presence of non-polymerisation-active metal centres in close proximity to a polymerisation-active metal centre may still modify the catalytic performance. Furthermore, species where the catalyst and the cocatalyst (e.g., boron or aluminium derivatives) are held in close proximity belong to a class of species that has recently been the subject of attention. In this section, we will briefly describe some examples of bimetallic catalytic systems based on the possibilities highlighted above.

1.3.2.4.1 Precatalyst/cocatalyst combination

The activation of the catalyst generally requires the addition of a cocatalyst (see subsection 1.1.3). Most of these species are Lewis acid-containing metal atoms (e.g., boron, aluminium). Recently, the inclusion of a polymerisation-active metal centre on the same ligand manifold as the cocatalyst has been disclosed (Figure 24: XXI and IVc). For instance, XXI resulted only in short chain oligomer with moderate to high activities and can be active with and without the addition of a cocatalyst (i.e., MAO).

![Figure 23 Encapsulated dinickel precatalysts tethered by an aromatic ether (Ar = 2-R1-4-R2-6-R3-C6H2, R1 = R3 = H, Me, Et, i-Pr, t-Bu; R2 = H, CF3 = i-Pr, X = Cl, Br).](image)

![Figure 24 Example of catalysts/cocatalysts on the same ligand.](image)
1.3.2.4.2 Polymerisation-active/polymerisation-inert metal centre combination

A number of bimetallic precatalysts/catalysts have been reported by supporting two metal centres on the same binucleating ligand with one metal centre being polymerisation-active while the other is polymerisation-inert.\textsuperscript{229, 261, 262} For example, Green and co-workers described a series of heterobinuclear metallocene-based complexes (XXXXIII), in which one metal centre is based on hafnium or zirconium while other is polymerisation-inert (Co, Rh, Fe, Mn) (Figure 25).\textsuperscript{229} The performance of these early-late mixed metallocenes for ethylene or propylene polymerisation, on activation with MAO, can be best described as displaying modest activity when compared to monometallic zirconocene or hafnocene equivalents. In a separate report Hidai and co-workers have also disclosed a closely related titanium-tungsten mixed metallocene. On MAO activation this system notably shows high activity for the polymerisation of ethylene.\textsuperscript{261, 262}

![Figure 25 Heterobimetallic with one metal spectator (M = Ti, Zr, Hf; M' = Co, Rh, Fe, Mn; Z, Z' = Cp; linker = CH\(_2\)(CH\(_3\)))](image)

1.3.3 Conclusions

In principle, an EB catalyst (fused or remote) can influence the performance of an alkene polymerisation transformation in ways unreachable by conventional CTC, mainly because of the spatial confinement of the catalytic centres. EB systems lack the flexibility inherent of the CTC (e.g., systematic modification of the ratio of the catalytic components), but facilitate improved direct cooperation and interaction between the active catalytic centres to occur. The distance between the metal centres in an EB system is clearly an important parameter and has been shown to be influential on the degree of cooperation. For example, Marks et al. have demonstrated that during an EB-mediated polymerisation, increased incorporation occurs on reducing the distance between the active metal centres. Clearly this area is still in its infancy and offers great potential for further development.
1.4 Aims and objectives

1.4.1 General
As has been shown from this introduction the evolution of homogeneous polymerisation catalysis has developed along a number of different avenues. In particular, the use of more than one active site in a polymerisation reaction has highlighted the possibility for cooperative interactions. In more recent years, these type of interactions have been targeted by fixing the active catalysts on the same spectator ligand to give an encapsulated catalyst. The early results in this area have demonstrated the great potential of this approach.

In this thesis the aim is to develop the field of encapsulated polymerisation catalysts and specifically it will be directed towards late transition metal systems. In the first instance, the aim is to generate rigid and inert ligand manifolds that can support and impart the required steric and electronic properties to the metal centres. Furthermore, the design of the ligands will be adapted to form fused- and remote-type encapsulated systems which will initially incorporate two identical binding domains in order to demonstrate the feasibility of the synthetic methodology. Subsequent studies will target ligand sets that incorporate specifically designed inequivalent binding domains. In the case of the ligand sets containing a linker moiety, emphasis will be placed on its functionalisation ultimately geared towards immobilisation of the ligand frame. In the second instance, the new ligand frames will be employed as supports for homobimetallic complexes formed by selected late transition metals (e.g., iron, cobalt, nickel) and the resultant species will be fully characterised. Extension of the complexation strategy to the synthesis of heterobimetallic encapsulated systems will also be investigated. In the third instance, the new encapsulated systems will be systematically screened as ethylene polymerisation catalysts and the catalyst performance compared with each other and to their closest monometallic counterpart. Ultimately, it is hoped that the results of this thesis will shed some light on potential cooperative interactions in encapsulated late transition metal catalysts and be able to relate these interactions to steric and electronic properties.

1.4.2 Ligand design and synthetic strategy
In order to realise the objectives set, we have targeted a design strategy for the synthesis of the binucleating ligand manifold. In particular, we have targeted an imino-based multidentate chain-motif in which the imino-moieties of one binding domain (chain-
end) are separated by a hydrocarbyl group. To access the binucleating ligand frame we have identified two approaches. Firstly, through the condensation reaction of a carbonyl and a diamine (Scheme 9: Eqn. 1) or secondly through the condensation reaction of a dicarbonyl compound and a monoamine (Eqn. 1). However, in this work most emphasis will be placed on the former strategy using a variety of novel carbonyl and diamine components. Furthermore, as many of the carbonyl components targeted above have limited or no track record in the assembly of single-site late transition metal systems, we have also targeted new systems derived from the condensation reaction of a carbonyl and a monoamine (Eqn. 3). It should be noted that the dicarbonyl-diamine combination of components has not been employed so as to avoid the generation of polymeric ligand frameworks (Eqn. 4).

![Scheme 9 Synthesis strategies](image)

**Scheme 9** Synthetic strategies (1 - 3) identified for synthesis of mono- and bi-nucleating ligands to be developed in this thesis; equation 4 illustrates a possible approach to polynucleating supports.

### 1.4.3 Thesis Organisation

The following section details the breakdown of the chapters of the thesis. Chapter Two will focus on the reactivity of imino- or pyridyl-containing 2-substituted carbonyl compounds towards substituted anilines with the aim of preparing a range of novel \( C_1 \)-symmetric bi- and tri-dentate nitrogen donor ligands. The new ligands will be reacted with metal halides and the resultant complexes fully characterised. As a second aim, the role of electronic properties of the new systems will be probed with special emphasis placed on the 4-position of the N-imino aryl group; a site that has been targeted for linking the monometallic catalysts to be prepared in Chapters Three to Five.
In Chapters Three to Five, the imino- or pyridyl-containing 2-substituted carbonyl compounds prepared in Chapter Two will be reacted with a range of substituted dianilines so as to generate a range of novel binucleating ligands. Considerable emphasis will be placed on dianiline synthesis with the steric and electronic properties being systematically varied along with the nature of the linking moiety. All the new ligands will be treated with divalent metal halides and the resultant bimetallic complexes fully characterised. Specifically, Chapter Three will target fused encapsulated systems while Chapters Four and Five will target remote encapsulated systems. Chapter Five will, in addition, focus on the functionalisation of the ligand manifold towards exploring the role of electronic properties and examine the site identified as a means of tethering the encapsulated system to a support (Figure 26).

![Figure 26 Encapsulated system with functionalised linker.](image)

In Chapter Six, selected examples of both monometallic and encapsulated precatalysts will be screened for ethylene polymerisation. Particular emphasis will be placed on comparing the encapsulated systems with the closest monometallic counterparts. Conclusions about the relative performance of these systems and implications on cooperativity and electronic properties will be put forward.

Chapter Seven reports the details of the experimental procedures along with the characterisation data.
1.5 References


<table>
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<tr>
<th>Chapter One</th>
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Chapter Two

Imino-based Monometallic Iron, Cobalt and Nickel Precatalysts

Synthesis and Characterisation
Chapter Two

2.1 Introduction
As discussed in Chapter One, the use of late transition metal catalysts for ethylene polymerisation has highlighted the role of steric and electronic properties imparted by the ligand on the performance of the catalysts. While $C_2$-symmetric systems have led the way [viz., $\alpha$-di(aryl)imine, bis(arylimino)pyridine], lowering of symmetry, for example, by replacing one imino group with a pyridine unit has been widely reported for $\alpha$-diimine systems, but only to a lesser degree for bis(imino)pyridine-based ones. Moreover, an examination of the effect of electronic variation on these unsymmetrical systems has received scarcely any attention. This chapter will focus on the synthesis of a range of new $C_2$-symmetric monometallic precatalysts for olefin polymerisation. As indicated in Chapter One, monometallic systems have been targeted to complement the encapsulated systems developed in Chapters Three to Five by using the same types of chain-end groups (viz. iminophenanthroline, iminobipyridine, iminopyridine, $\alpha$-diimine).

Four classes of monometallic precatalysts have been targeted (Classes A-D) (Chart 1). With the exception of class C, the complexes of classes A, B and D all possess at least one pyridine and one imine group. In particular, we describe the synthesis of a new family of iminophenanthroline-M systems (Class A), and a more complete series of the 2-pyridyl-6-iminopyridine-M systems (Class B). Precatalysts of Class D have already been the subject of much investigation, but notably some members of the family pertinent to this thesis have not, and will be described here. Surprisingly, unsymmetrical $\alpha$-diimine-Ni systems of class C have not been, to the knowledge of author, investigated in the academic literature, although some details have been disclosed in the patent literature. To address this absence of synthetic details, we have targeted these families of complexes and the corresponding ligands.

The following sub-section illustrates the general strategy for ligand and complex synthesis while sections 2.3-2.7 show specific details relevant to each precatalyst class (A-D). Considerable emphasis will be placed on varying the electronic properties of the 4-position of the N-aryl group in classes A-C; for class C, this will be restricted to only one of the two aryl groups. Furthermore, the 4-position in some cases will serve as a potential attachment site to generate encapsulated systems for work described elsewhere in the thesis.
Chart 1 Target unsymmetrical precatalysts; $R = \text{H, Me}; R^1 = \text{Me, i-Pr}; R^2 = \text{H, Me, Br, CN, NH}_2; R^3 = \text{H, Me}; X = \text{halide.}$
2.2 General synthetic strategy
The general methodology employed to synthesise the ligands in this work involves the condensation reaction of a carbonyl substrate with an aniline to afford a Schiff base product (Scheme 1).

\[
\text{R}^\text{N}H + \text{R}'^\text{Ar} \xrightarrow{\text{cat. } H^+} \text{R}^\text{N} = \text{R}'^\text{Ar} + \text{H}_2\text{O}
\]

Scheme 1 Generic scheme for ligand synthesis; R = H, Me; R' = imine, pyridinyl, bipyridinyl, phenanthroinyl.

To drive the reaction to the right hand side of the equilibrium (i.e., to remove the water), a number of approaches have been employed, notably by using azeotropic distillation (e.g., Dean-Stark apparatus), different acid catalysts (e.g., p-toluene sulfonic acid, formic acid, glacial acetic acid), drying agents (e.g., molecular sieves, magnesium sulfate), the aniline as the solvent, and to run the reaction under rigorously dry conditions. In general, the reactions were performed in alcoholic solvents; the products were conveniently precipitated, filtered and collected as either off-white, yellow or red solids. More specific details associated with a particular condensation reaction will be outlined in the individual sections.

The precatalysts targeted (Classes A-D) in this work are to be prepared by the reaction of the corresponding ligand with a metal dihalide (i.e., NiCl₂, [DME]NiBr₂, FeCl₂, CoCl₂: Scheme 2) (DME = 1,2-dimethoxyethane) in n-BuOH at elevated temperature. On cooling to room temperature, the products generally precipitated and can be conveniently collected.

\[
\text{R}^\text{N} = \text{R}'^\text{Ar} + \text{MX}_2 \xrightarrow{n-\text{BuOH}/\text{Heat}} \left[ \begin{array}{c} \text{R}^\text{N} = \text{R}'^\text{Ar} \\ \text{MX}_2 \end{array} \right]
\]

Scheme 2 Generic scheme for complexation reaction; R = H, Me; R' = imine, pyridinyl, bipyridinyl, phenanthroinyl.
Chapter Two

2.3 Synthesis of [2-iminophenanthroline]MCl₂ (M = Fe, Co) (Class A)

Use of [1,10]-phenanthroline or ligands incorporating the phenanthroline motif (phen) are well known in coordination chemistry and have been employed in a number of applications.²⁻⁷ However, in the arena of olefin polymerisation catalysis, examples of their use remain scarce. For example, Wang and co-workers⁸ have described the synthesis and the screening of late-transition metal-based complexes in which a bis(imino)phenanthroline ligand has been used to support the active catalysts (Figure 1).

At best, the nickel systems result in moderate to low activities under 20 bar ethylene pressure, while the cobalt analogues were less active and the iron versions inactive.

![Figure 1](image1.png)

Figure 1 M = Fe, Co, Ni; X = Br, Cl; Ar = (2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl).⁸

It is likely that the low activity observed in these systems is due to the presence of an imino pendant arm, which can potentially coordinate and deactivate the active catalyst. In order to probe this theory, we decided to develop cobalt and iron systems supported by the tridentate aryl-iminophenanthrolinyl ligand.

This subsection will be concerned with the preparation of a series of complexes based on class A (Figure 2). Firstly, the preparation of aryl-iminophenanthrolinyl ligands will be discussed and secondly the complexation reactions will be outlined.

![Figure 2](image2.png)

Figure 2 Target system [2-iminophen]; MCl₂ (M = Fe, Co, Ni); R₁ = Me, i-Pr; R₂ = H, Me, Br, CN, NH₂; X = halide (Class A).

2.3.1 Synthesis of [1,10]-phenanthroline-2-carboxaldehyde

The precursor [1,10]-phenanthroline-2-carboxaldehyde can be made in 5 steps using a methodology that has previously been reported (Scheme 3).⁹⁻¹² The oxidation of the [1,10]-phenanthroline precursor leads to the 1-oxime-[1,10]-phenanthroline that can undergo a cyanation reaction at the 2-position. The cyano-phenanthroline compound can be oxidised to the ester and subsequently reduced to give the corresponding hydroxyl compound. After oxidation, [1,10]-phenanthroline-2-carboxaldehyde is
afforded in good to moderate overall yield. In spite of the number of steps, the overall yield was good and the method has been scaled up to access up to 5 grams of the target aldehyde. Although no conditions for the oxidation employing SeO$_2$ were previously reported, we found that treatment of alcohol with SeO$_2$ in dioxane at elevated temperature gave the product in high yield.

Scheme 3 Reagents and conditions: (i) H$_2$O$_2$, CH$_3$COOH, 80 °C; (ii) KCN, H$_2$O, C$_6$H$_5$COCl, rt; (iii) cat. Na, MeOH, 90 °C; (iv) NaBH$_4$, EtOH, rt; (v) SeO$_2$, dioxane, 110 °C.

2.3.2 Synthesis of ligands L1-L5
 Treatment of [1,10]-phenanthroline-2-carboxaldehyde with one equivalent of 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diisopropylaniline, 4-bromo-2,6-diisopropylaniline$^{13}$ and 4-cyano-2,6-diisopropylaniline$^{13}$ in ethanol at 50 °C, in the presence of a catalytic amount of acetic acid, afforded [([2-[1,10]-C$_{12}$H$_7$N$_2$]HCN)(2,6-R$_1$4-R$_2$-C$_6$H$_2$)] [R$_1$ = Me; R$_2$ = H (L1), R$_1$ = R$_2$ = Me; (L2), R$_1$ = i-Pr; R$_2$ = H (L3), R$_1$ = i-Pr; R$_2$ = Br (L4); R$_1$ = i-Pr; R$_2$ = CN (L5)] in good yield, respectively (Scheme 4). L1-L5 have been characterised by $^1$H NMR, $^{13}$C NMR and IR spectroscopy and ElectroSpray Mass Spectrometry (ESMS) (see experimental section). In addition, L4 has been the subject of a single crystal X-ray diffraction study.

Scheme 4 Reagents and conditions: (i) [1,10]-C$_{12}$H$_7$N$_3$CHO, EtOH, cat. H*, 50 °C.
All the compounds (L1-L5) gave peaks corresponding to their molecular ions in their ES-Mass spectra. In their infrared spectra, the absorption bands observed at ca. 1634 cm<sup>-1</sup> were consistent with the presence of an aldimine group. In the <sup>1</sup>H NMR spectra, the singlet at ca. δ 8.75 and the signal at ca. δ 163.5 in their <sup>13</sup>C NMR spectra confirmed the presence of the CH=N proton and the CH=N carbon, respectively. In the case of L5, a band at 2224 cm<sup>-1</sup>, characteristic of ν(CN<sub>nitrile</sub>), was seen. The symmetric ligands, 2,9-bis(arylimino)phenanthroline, reported by Wang showed similar spectroscopic data to L1-L5.

![Molecular structure of L4](image)

**Figure 3** Molecular structure of L4; all the hydrogen atoms, apart from H11, have been omitted for clarity.

Slow evaporation of a solution of L4 in ethanol afforded red crystals suitable for an X-ray determination. The molecular structure of L4 is depicted in Figure 3; selected bonds lengths and angles are shown in Table 1.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
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<tr>
<td>N(1)-C(1)</td>
<td>1.341(5) N(3)-C(11) 1.265(4)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.346(4) N(3)-C(14) 1.433(4)</td>
</tr>
<tr>
<td>N(2)-C(10)</td>
<td>1.339(4) Br(1)-C(17) 1.911(4)</td>
</tr>
<tr>
<td>N(2)-C(6)</td>
<td>1.359(4)</td>
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<tr>
<td>C(1)-N(1)-C(5)</td>
<td>117.0(4) C(11)-N(3)-C(14) 118.5(3)</td>
</tr>
<tr>
<td>C(10)-N(2)-C(6)</td>
<td>117.1(3)</td>
</tr>
</tbody>
</table>

This structure consists of a phenanthroline moiety linked to an arylimino group at the 2-position with the imino nitrogen [N(3)] atom adopting a transoid configuration with
Chapter Two

respect to the nitrogen donors of the phenanthroline unit [N(2)]. The iminophenanthroline unit is almost planar [tors. N(3)-C(11)-C(10)-N(2) 2.0°] with the N-aryl groups almost orthogonal to this plane. The short length of the N(3)-C(11) [1.265(4) Å] bond is consistent with double bond character and the C-Br distance [C(17)-Br(1) 1.911(4) Å] falls in the range found for single bonds between these elements.

2.3.3 Synthesis of complexes 1a-2b
All the 2-(imino)-[1,10]-phenanthrolinyl ligands, L1-L5, were reacted with one equivalent of iron(II) or cobalt(II) dichloride in n-butanol at 90 °C for one hour to afford [(Lx)FeCl2] [Lx = L1 (1a), L2 (1b), L3 (1c), L4 (1d), L5 (1e)] as pale green to brown solids and [(Lx)CoCl2] [Lx = L3 (2a), L5 (2b)] as blue solids in good yield (Scheme 5).

All the complexes have been characterised by FAB-MS, IR spectroscopy and by magnetic susceptibility measurements (see Table 3). In addition, 2a and 2b have been the subject of single crystal X-ray diffraction studies.

Crystals of complexes 2a and 2b suitable for the X-ray determinations were grown by slow cooling of hot acetonitrile solutions containing the corresponding complex. The molecular structures of 2a and 2b are shown in Figures 4 and 5, respectively; selected bonds and angles are displayed in Table 2.

The structures of 2a and 2b are essentially similar and will be discussed together. In each structure, a single cobalt atom is surrounded by an iminophen ligand, L3 (for 2a) or L5 (for 2b), and two terminally bound chloride ligands. The geometry of the five-coordinate complexes can be best described as distorted square pyramidal as indicated by the low values of their structural index parameters [τ = 0.179 for 2a] and [τ = 0.283 for 2b] (see appendices). However, the apical site of 2a is occupied by Cl(1) while
N(1), N(2), N(3) and Cl(2) form the square base. In 2b, the apex is attributed to Cl(2) with the basal plane being defined by N(1), N(2), N(3) and Cl(1).

The Co-N distances are inequivalent with the central Co(1)-N(2) being the shortest [at 2.0448(18) Å for 2a and at 2.018(6) Å for 2b], while the external cobalt nitrogen distances are longer with Co(1)-N(3)_{imine} being the longest [at 2.2939(18) Å for 2a and at 2.353(6) Å for 2b]. In both structures, the reason for the asymmetry between the external metal nitrogen distances [N(1)_{imine} vs. N(3)_{phen}] is likely to be due to the improved donor capability of a pyridine nitrogen over an imine nitrogen (see 1.2.5.2).

The Co-Cl distances are inequivalent for both complexes, with the distance involving the apical chloride Cl(1) in 2a being longer [at 2.2612(7) Å] than that for the basal chloride [at 2.2393(7) Å]. In the case of 2b, the difference in distance between the cobalt chloride bond lengths is less significant [Co(1)-Cl(2) 2.247(2) Å vs. Co(1)-Cl(1) 2.251(2) Å]. A further subtle difference can be identified on inspection of the cobalt-nitrogen distances in each structure. In 2a, the Co-N_{phen} distances are longer than the corresponding distances in 2b, while the Co-N_{imine} distance in 2a is shorter than the corresponding distance in 2b. The origin of this apparent variation in position of the CoCl₂ unit within the iminophen cavity is uncertain but could be due to the changes in electronic properties of the aryl 4-position substitution pattern (H vs. CN). As expected the aryl groups in each structure adopt an orthogonal disposition with respect to the plane formed by the iminophen unit. The short length of the N(4)-C(23) bond [1.103(11) Å] bond is consistent with triple bond character for the nitrile functionality in 2b.¹⁴ Inspection of the packing diagram for 2b shows no evidence for any short intermolecular distances.

The apparent relative reorganisation of the chloride ligands between basal and apical sites in 2a and 2b would seem to suggest that some mobility could be operational within each structure in solution.

To the knowledge of the author, complexes 2a and 2b are the first crystallographically characterised examples of complexes containing iminophen ligands. The most closely related example has been reported by Wang et al. for [2,9-bis(2,6-diisopropylphenyl)imine][1,10]-phenanthroline]CoCl₂ (Figure 1), in which one metal dihalide unit is bound in the iminophen cavity and the second imine group is non-coordinated. It is worthy of note that the external metal coordinated nitrogen distances are more elongated in this structure than in closely related 2a.
Table 2 Selected bond distances (Å) and angles (°) for 2a and 2b; for comparison purposes the data for 2,9-bis(arylimino)phen|CoCl₂ is also included

<table>
<thead>
<tr>
<th></th>
<th>2a</th>
<th>2b</th>
<th>[2,9-bis(arylimino)phen]CoCl₂</th>
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<tr>
<td>Co(1)-N(1)</td>
<td>2.2138(18)</td>
<td>2.189(6)</td>
<td>2.2503(18)</td>
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<tr>
<td>Co(1)-N(2)</td>
<td>2.0448(18)</td>
<td>2.018(6)</td>
<td>2.0428(17)</td>
</tr>
<tr>
<td>Co(1)-N(3)</td>
<td>2.2939(18)</td>
<td>2.353(6)</td>
<td>2.4352(18)</td>
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<tr>
<td>Co(1)-Cl(1)</td>
<td>2.2612(7)</td>
<td>2.251(2)</td>
<td>2.2503(18)</td>
</tr>
<tr>
<td>Co(1)-Cl(2)</td>
<td>2.2393(7)</td>
<td>2.247(2)</td>
<td>2.2501(8)</td>
</tr>
<tr>
<td>N(4)-C(23)</td>
<td>-</td>
<td>1.103(11)</td>
<td>-</td>
</tr>
<tr>
<td>N(1)-Co(1)-N(2)</td>
<td>75.95(7)</td>
<td>77.7(3)</td>
<td>76.82(7)</td>
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<tr>
<td>N(1)-Co(1)-N(3)</td>
<td>148.23(7)</td>
<td>149.6(2)</td>
<td>149.83(6)</td>
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<tr>
<td>N(1)-Co(1)-Cl(1)</td>
<td>94.64(5)</td>
<td>94.91(18)</td>
<td>97.14(5)</td>
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<tr>
<td>N(1)-Co(1)-Cl(2)</td>
<td>99.29(5)</td>
<td>100.12(18)</td>
<td>97.82(5)</td>
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<tr>
<td>N(2)-Co(1)-N(3)</td>
<td>73.67(7)</td>
<td>72.3(2)</td>
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<tr>
<td>N(2)-Co(1)-Cl(1)</td>
<td>104.94(5)</td>
<td>132.58(19)</td>
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<tr>
<td>N(2)-Co(1)-Cl(2)</td>
<td>137.49(5)</td>
<td>112.61(19)</td>
<td>121.37(5)</td>
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<tr>
<td>N(3)-Co(1)-Cl(1)</td>
<td>101.88(5)</td>
<td>101.34(16)</td>
<td>100.93(5)</td>
</tr>
<tr>
<td>N(3)-Co(1)-Cl(2)</td>
<td>96.81(5)</td>
<td>96.19(16)</td>
<td>95.97(5)</td>
</tr>
<tr>
<td>Cl(2)-Co(1)-Cl(1)</td>
<td>117.57(3)</td>
<td>114.79(9)</td>
<td>115.42(3)</td>
</tr>
</tbody>
</table>
Figure 4 Molecular structure of [(L3)CoCl2] (2a). All the hydrogen atoms, apart from H11, have been omitted for clarity.
Figure 5 Molecular structure of [(L5)CoCl2] (2b). All the hydrogen atoms, apart from H11, have been omitted for clarity.
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The FAB mass spectrometric data for 1a-1e, 2a and 2b exhibit characteristic mass and isotope distributions consistent with the molecular ion along with fragmentation peaks corresponding to the loss of one or two chloride ions. The magnetic moments (measured on an Evans balance at ambient temperature) for the iron complexes (1a-1e) display magnetic moments ranging from 4.3 \( \mu_B \) to 5.5 \( \mu_B \), their magnitude being consistent with the presence of four unpaired electrons (\( S = 2 \)). On the other hand, the cobalt complexes exhibit lower values ca. 4.0 \( \mu_B \) in accordance with the presence of three unpaired electrons (\( S = 3/2 \)). The IR spectra for 1a-2b show absorption bands between 1601-1612 cm\(^{-1}\) which correspond to the \( \nu(C=N) \) stretching frequencies for a coordinated imine and are shifted by ca. 30 cm\(^{-1}\) in comparison with the free ligands.

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>( \nu(C=N) ) ( ^a )</th>
<th>Magnetic moment ( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Pale green 402 [M-Cl]^+</td>
<td>1604</td>
<td>5.5</td>
</tr>
<tr>
<td>1b</td>
<td>Green 416 [M-Cl]^+</td>
<td>1604</td>
<td>4.6</td>
</tr>
<tr>
<td>1d</td>
<td>Brown 573 [M]^+, 538 [M-Cl]^+</td>
<td>1605</td>
<td>5.0</td>
</tr>
<tr>
<td>1e</td>
<td>Brown 518 [M]^+, 483 [M-Cl]^+</td>
<td>1605</td>
<td>5.0</td>
</tr>
<tr>
<td>2a</td>
<td>Blue 541 [M-Cl]^+, 504 [M-2Cl]^+</td>
<td>1612</td>
<td>4.0</td>
</tr>
</tbody>
</table>

\(^a\) recorded in the solid-state (cm\(^{-1}\)); \(^b\) recorded on an Evans balance at ambient temperature (\( \mu_B \))
2.4 Synthesis of [2-pyridyl-6-iminopyridine]MX₂ (M = Fe, Ni) (Class B)

Following the discovery of bis(imino)pyridine-iron catalysts for ethylene polymerisation, Gibson and co-workers shortly after reported the synthesis of [2-(2,6-diisopropylphenyl)imino-6-pyridyl-pyridine]iron(II)dichloride and showed that this system, on treatment of MAO, was active for the formation of low molecular weight oligomers (i.e., mainly C6 and C8). The aldimine version was claimed in a patent, although no synthetic details were reported. However, studies of this family of precatalysts did not go further, and notably single crystal X-ray diffraction studies have not been reported. It is likely that difficulties associated with ligand synthesis precluded a more extensive development of systems of this type.

In this subsection, the preparation of a series of complexes of class B will be described (Figure 6). The discussion will be focused firstly on the synthesis and characterisation of imino(bipyridine) ligands (both aldimine and ketimine) which will then be developed to cover their use as supports for a single iron or nickel dihalide unit.

![Figure 7 Target [2-pyridyl-6-iminopyridine]MX₂ or [iminobipy]MX₂ (Class B).](image)

2.4.1 Synthesis of 2,2'-bipyridine-6-carboxaldehyde and 6-acetyl-2,2'-bipyridine

After probing different synthetic methodologies, the 2,2'-bipyridine-carbonyl precursors required for the formation of the ligands, 2,2'-bipyridine-6-carboxaldehyde [2-CHO-6-(2-C₅H₄N)C₅H₃N] and 6-acetyl-2,2'-bipyridine [2-MeCO-6-(2'-C₅H₄N)C₅H₃N] were conveniently synthesised by using a Stille-type methodology (Scheme 6).

The 6-carbonyl-2-bromo-pyridines were prepared using previously reported procedures. Following the protection of the carbonyl functionality, the tin reagent, [6-tributylstannyl-2-(1,3-dioxolan-2-yl)pyridine], was accessed through lithium halogen exchange and stannylation with tributyltin chloride. Treatment of the tin reagents with 2-bromo-pyridine in the presence of a palladium(0) catalyst followed by acid-mediated deprotection gave the 2,2'-bipyridine-6-carboxaldehyde and 6-acetyl-2,2'-bipyridine in moderate yield, respectively. The synthesis of the 2,2'-bipyridine-6-carboxaldehyde was harder to realise and the yield was considerably lower than for 2,2'-bipyridine-6-acetyl. Nevertheless, the characterisation data for the compounds and the yield of the reaction were consistent with the preparations reported by Constable et al.
Scheme 6 Reagents and conditions: (i) n-BuLi, (CH₃)₂NCRO (R = H, Me); (ii) HOCH₂CH₂OH, C₆H₆, p-TsSO₄, reflux; (iii) n-BuLi, Et₂O, ClSn(n-Bu)₃, -78 °C; (iv) 2-Br-(C₆H₄N), cat. Pd(PPh₃)₄, C₇H₈, reflux; (v) H₂O, H⁺, 70 °C.

2.4.2 Synthesis of ligands L₆ and L₇
The reaction of 2,2'-bipyridine-6-carboxaldehyde with 2,6-diisopropylaniline in ethanol was performed at reflux in the presence of a catalytic amount of acetic acid to afford [2-(2'-C₅H₄N)-6-((2,6-i-Pr₂C₆H₃)HCN)-C₅H₃N] (L₆) in good yield (Scheme 7). More forcing conditions were required to obtain the ketimine counterparts. The reactions of 6-acetyl-2,2'-bipyridine with 2,4,6-trimethylaniline or 2,6-diisopropylaniline to afford [2-(2'-C₅H₄N)-6-((2,6-i-Pr₂C₆H₃)NMeC)-C₅H₃N] (L₇) were carried out successfully in n-butanol at high temperature (Scheme 7). L₆ and L₇ have been characterised by ¹H NMR, ¹³C NMR and IR spectroscopy and ES Mass Spectrometry (see experimental section).

The ES mass spectrum of L₆ showed a peak corresponding to the molecular ion while the absorption band at 1639 cm⁻¹ confirmed the presence of the aldimine moiety. In the ¹H NMR spectra, the singlet observed at δ 8.34 and the signal at δ 164.3 in the ¹³C NMR were in accordance with the formation of L₆. Comparison of the spectroscopic data for L₆ with those of L₁-L₅ revealed some notable differences. For example, in L₁-L₅, the proton of the aldimine group is seen typically more downfield ca. δ 8.75 in their ¹H NMR spectra. This variation highlights the electronic effect imparted by the presence of a phenanthroline over a bipyridine unit.

Compound L₇ displayed a peak corresponding to the molecular ion in its ES mass spectrum. The singlet observed at δ 2.23 in the ¹H NMR spectrum along with the signal at δ 166.55 in the ¹³C NMR spectrum confirmed the presence of the ketimine group. The IR spectrum revealed an absorption band at 1644 cm⁻¹ consistent with the presence of the imine. The previous data reported for the preparation of L₇ were consistent with that found in this work.
2.4.3 Synthesis of complexes 3a-4

The reaction of one equivalent of iron(II) dichloride with L6 and L7 in n-butanol at 110 °C for one hour afforded [(Lx)FeCl2] [Lx = L6 (3a), L7 (3b)] in moderate yield (Scheme 8). Likewise, treatment of L7 with 1,2-dimethoxyethanenickel(II)dibromide in n-butanol at 110 °C gave [(L7)NiBr2] (4) in moderate yield (Scheme 8). The complexes 3a-3c and 4 have been characterised by FAB-MS, IR spectroscopy and magnetic susceptibility measurements (see Table 5). In addition, crystals of 4 were subject to a single crystal X-ray diffraction study.

Crystals of complex 4 suitable for the X-ray determination were grown by slow cooling of a hot acetonitrile solution containing the complex. The molecular structure of 4 is presented in Figure 8; selected bonds and angles are listed in Table 4.

The structure of 4 consists of a single nickel atom surrounded by one tridentate L7 and two terminally bound bromide ligands. The geometry of the five-coordinate complex can be best described as slightly distorted square pyramidal (τ = 0.063)\(^{15}\) with Br(1)
occupying the apical site and N(1), N(2), N(3) and Br(2) forming the square base. The Ni(1)-Br distances are inequivalent with the distance involving the apical bromide being longer [at 2.4555(6) Å] than that for the basal bromide [at 2.3520(6) Å]. Similarly, the Ni-N distances are inequivalent with the central Ni(1)-N(2) being the shortest [at 1.978(3) Å] while the external nickel nitrogen distances are longer with Ni(1)-N(3)_{imine} the longest [at 2.147(3) Å]. The reason for this asymmetry is uncertain but could be a consequence of satisfying the tridentate chelating constraint of the ligand or could be attributed to the relative donor capacity of a nitrogen from a pyridine vs. that from an imine. The 2,6-diisopropylphenyl substituents adopt an orthogonal disposition with respect to the plane formed by the nickel centre and the three nitrogen atoms.

| Table 4 Selected bond distances (Å) and angles (°) for 4 |
|---------------------------------|---------------------------------|---------------------------------|
| Ni(1)-N(1)                      | 2.103(3)                        | Ni(1)-Br(1)                     | 2.4555(6)                        |
| Ni(1)-N(2)                      | 1.978(3)                        | Ni(1)-Br(2)                     | 2.3520(6)                        |
| Ni(1)-N(3)                      | 2.147(3)                        | -                               | -                               |
| N(1)-Ni(1)-N(2)                 | 77.71(12)                       | N(2)-Ni(1)-Br(1)                | 91.76(8)                         |
| N(1)-Ni(1)-N(3)                 | 151.12(11)                      | N(2)-Ni(1)-Br(2)                | 154.88(9)                        |
| N(1)-Ni(1)-Br(1)                | 94.81(8)                        | N(3)-Ni(1)-Br(1)                | 100.25(8)                        |
| N(1)-Ni(1)-Br(2)                | 96.72(8)                        | N(3)-Ni(1)-Br(2)                | 99.71(8)                         |
| N(2)-Ni(1)-N(3)                 | 77.34(11)                       | Br(1)-Ni(1)-Br(2)               | 113.21(2)                        |

Comparing the geometry index parameters for 4 with those of 2a and 2b suggests that 4 is the least distorted \([2b > 2a > 4]\).\(^\text{15}\) This is likely due to the increased flexibility possessed by the bipyridine skeleton compared to the fused phenanthroline unit.

To the knowledge of the author, and after inspection of the CCD, only a few examples could be found possessing a related structure motif. A close example has been reported by Goodwin et al.,\(^\text{24}\) in which a nickel centre is bis-ligated by two 2,2'-bipyridine-6-carbaldehyde phenylhydrazone ligands to give an octahedral geometry. The sterically bulky nature of L7 is clearly impeding bis(igation) in 4.

The FAB mass spectrometric data for 3a, 3b and 4 exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one halide ion from the corresponding molecular ion. The magnetic moments (measured on an Evans balance at ambient temperature) are at 4.9 \(\mu_b\) and 5.0 \(\mu_b\) for the iron complexes (3a and 3b, respectively), their magnitude being consistent with the presence of four unpaired electrons \((S = 2)\). On the other hand, the nickel complex 4 exhibits a lower value at 2.8 \(\mu_b\)
Chapter Two

in accordance with the presence of two unpaired electrons (S = 1). The IR spectra for 3a-4 show absorption bands around 1595 cm⁻¹, which correspond to \(\nu(C=\text{N})\) stretching frequencies for a coordinated imine and are shifted by ca. 40 cm⁻¹ in comparison with the free ligands.

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>(\nu(C=\text{N})) (^a)</th>
<th>Magnetic moment (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>Dark blue</td>
<td>434 [M-Cl](^+)</td>
<td>1595</td>
</tr>
<tr>
<td>3b</td>
<td>Dark blue</td>
<td>448 [M-Cl](^+)</td>
<td>1595</td>
</tr>
<tr>
<td>4</td>
<td>Dark red</td>
<td>499 [M-Br](^+)</td>
<td>1596</td>
</tr>
</tbody>
</table>

\(^a\) recorded in the solid-state (cm⁻¹); \(^b\) recorded on an Evans balance at ambient temperature (\(\mu_\text{B}\))
Figure 8 Molecular structure of [(L7)NiBr₂]₄. All the hydrogen atoms have been omitted for clarity.
2.5 Synthesis of unsymmetrical [α-diimine]NiBr₂ (Class C)

In this subsection, the preparation of complexes in which a nickel centre is bound to an unsymmetrical α-diimine ligand will be disclosed. Special emphasis will be placed on the development of α-di(aryl)imines incorporating two different types of aryl group. Among the comprehensive collection of α-diimine-based group 10 precatalysts reported,²⁵,²⁶ there are few examples of C₁-symmetric α-diimines in which the N-substituents are differently substituted (Figure 9).²⁷-³⁰

![Figure 9](image_url)

This subsection will be concerned with the preparation of a series of complexes based on the motif C (Figure 9). Firstly, strategies will be investigated in order to attempt to generate unsymmetrical α-diimines. Where successful, complexation reactions with 1,2-dimethoxyethanenickel(II)dibromide will be probed.

2.5.1 Synthesis of 3-(2,6-diisopropyl-phenylimino)-butan-2-one

In order to access unsymmetrical α-diimines we have targeted the imine-ketone compound 3-(2,6-diisopropyl-phenylimino)-butan-2-one as a starting material for subsequent condensation reactions. It is noteworthy that during the course of this work, 3-(2,6-diisopropyl-phenylimino)-butan-2-one, has been employed in a related fashion, although experimental details were limited.²⁸-³⁰ 3-(2,6-diisopropyl-phenylimino)-butan-2-one could be conveniently prepared in high spectroscopic purity by the treatment of 2,6-diisopropylaniline with an excess of 2,3-butanedione in toluene over 24 hours, with the excess 2,3-butanedione readily removed by distillation (Scheme 9).

![Scheme 9](image_url)

**Scheme 9** Reagents and conditions: (i) xs. C₂Me₂O₂, C₇H₈, cat. H⁺, 50 °C.

[2,6-i-Pr₂C₆H₃]NC(Me)C(Me)O] was identified by the presence of a molecular ion peak in the ES mass spectrum. The presence of both the ketone and the ketimine
functionalities was supported by the observation of two singlets of integration 3 at δ 2.50 and δ 1.74 in its ¹H NMR spectrum, respectively. Furthermore, the ¹³C NMR spectrum revealed peaks at δ 167.0 and δ 200.6 for the corresponding carbon atoms.

2.5.2 Synthesis of ligand L8
In order to investigate the viability of forming unsymmetrical α-di(aryl)imines we have explored the reaction of 3-(2,6-diisopropyl-phenylimino)-butan-2-one with a range of anilines (viz., 2,3,5,6-tetramethylphenyl-1,4-diamine, 2,6-dimethylaniline or 2,4,6-dimethylaniline). Firstly, the reaction of 3-(2,6-diisopropyl-phenylimino)-butan-2-one with an excess of 2,3,5,6-tetramethylphenyl-1,4-diamine, in the presence of a catalytic amount of formic acid, in toluene gave [N-(N-(2,6-i-Pr₂C₆H₃)-1,2-Me₂-2-NC₂)₄-N(2,3,5,6-Me₄C₆NH₂) (L8) (Scheme 10). The excess 2,3,5,6-tetramethylphenyl-1,4-diamine could conveniently be removed by filtration from chloroform giving (L8) as a black oily solid in moderate yield.

However, this approach when employed with the monoanilines, 2,6-dimethylaniline or 2,4,6-dimethylaniline led to a mixture of different products including the desired material. Typically, a distribution of α-diimine compounds was observed with a significant amount of the corresponding symmetrical products present [1,2-Me₂-1,2-(2,6-Me₂-N-C₆H₃)-₂-C₂], [1,2-Me₂-1,2-(2,4,6-Me₃-N-C₆H₂)-₂-C₂], [1,2-Me₂-1,2-(2,6-i-Pr₂-N-C₆H₃)-₂-C₂]]. Further optimisation attempts failed to improve neither the selectivity of this synthesis nor the following purification procedure.

Compound L8 showed a peak in its ES mass spectrum corresponding to the molecular ion. In the ¹H NMR spectrum, two singlets of equal intensity observed at δ 1.96 and δ 2.02 are attributed to the two types of proton from the methyl group of the distinct ketimine functionalities. In the ¹³C NMR spectrum, the two signals at δ 167.4 and δ 167.7 confirm the presence of the two ketimine groups. The absorption band at 1639 cm⁻¹ in the IR spectrum revealed the presence of overlapping imine groups. The broad singlet at δ 3.40 (¹H NMR) and the broad absorption band at 3398 cm⁻¹ are consistent with the presence of a free amine.
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Scheme 10 Reagents and conditions: (i) H₂N(2,3,5,6-Me₄C₆)NH₂, C₇H₈, cat. H⁺, 50 °C; (ii) 2,6-R₁-4-R₂-C₆H₃ (R₁ = Me, R₂ = H; R₁ = R₂ = Me), C₇H₈, cat. H⁺, 20 °C.

This short study revealed that the unsymmetrical α-diimine backbone can be particularly unstable and is susceptible to re-distribution reactions. For the synthesis of L₈, the experimental conditions are crucial for the selectivity of the reaction. Unless the various parameters (i.e., the nature of the acid used, the nature of the solvent, the temperature) are optimised, substantial amounts of byproducts are obtained.

2.5.3 Synthesis of complex 5

The reaction of one equivalent of 1,2-dimethoxyethanenickel(II)dibromide with L₈ in dichloromethane at ambient temperature for one day gave [(L₈)NiBr₂] (5) in moderate yield (Scheme 11). Complex 5 have been characterised by FAB-MS, IR spectroscopy and magnetic susceptibility measurements (see Table 5).

Scheme 11 Reagents and conditions: (i) [DME]NiBr₂ > CH₂C₁₂, rt.

The FAB mass spectrometric data exhibit characteristic mass and isotope distributions for 5 with fragmentation peaks consistent with the loss of one bromine at m/z 530. The magnetic moment (measured on an Evans balance at ambient temperature) at 3.5 μ₀ is consistent with the presence of two unpaired electrons (S = 1). The IR spectrum for 5 shows a strong absorption band around 1595 cm⁻¹, which corresponds to the ν(C=N)
stretches for a coordinated imine and is shifted by ca. 40 cm\(^{-1}\) in comparison with that of L8. Furthermore, microanalytical data of these black crystals are consistent with composition described.

In order to fully elucidate the structure we targeted single crystals of 5 that could be employed for a single crystal X-ray diffraction study. Black crystals of 5 were grown by slow evaporation of a solution of dichloromethane containing the complex. The molecular structure is shown in Figure 10; selected bond distances and angles are listed in Table 6.

The complex consists of a single nickel centre bound by two nitrogen donors from L8 and by two terminally bound bromide ligands. The geometry of the nickel is best described as a slightly distorted tetrahedron. The 5-membered metalloring [Ni(1)-C(1)-C(2)-N(1)-N(2)] is almost planar [max. dev. is (Ni) = 0.211 Å]. The plane containing Br(1), Br(2) and Ni(1) forms a quasi-orthogonal dihedral angle (90.4°) with that of the \(\alpha\)-diimine framework. The Ni-N bond lengths are relatively close [at 1.981(4) Å and 2.003(4) Å] but still showing a slight difference that is likely due to the differing donor properties of the inequivalent imine nitrogen atoms.

The structure to 5 is the first of its type but shows some resemblance to \([1R,7,7\text{-trimethylbicyclo[2.2.1]heptan-2,3-bis(2,6-diisopropylphen-1-yl)imine}]\text{NiBr}_2\) reported by Wurtz and co-workers.\(^{31}\) Comparison of the structural parameters of this structure with those of 5 does not highlight any significant variations.

<table>
<thead>
<tr>
<th>Table 6 Selected bond distances (Å) and angles (°) for 5</th>
</tr>
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<tbody>
<tr>
<td>Ni(1)-N(1)</td>
</tr>
<tr>
<td>Ni(1)-N(2)</td>
</tr>
<tr>
<td>N(1)-Ni(1)-N(2)</td>
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<td>N(1)-Ni(1)-Br(1)</td>
</tr>
<tr>
<td>N(1)-Ni(1)-Br(2)</td>
</tr>
</tbody>
</table>
Figure 10 Molecular structure of 5. All the hydrogen atoms, apart from H3B and H3A, have been omitted for clarity.
2.6 Synthesis of [2-iminopyridine]NiX₂ (X = Cl, Br) (Class D)
This research direction has been initiated by Laine\textsuperscript{32} and reviewed later by Alt\textsuperscript{33} (Figure 11). A number of patents have also appeared in this area.\textsuperscript{19,34} Under MAO activation, iminoarypyridine-Ni catalysts polymerise ethylene to afford branched low molecular weight polyethylene with activities lower than that reported for their \(\alpha\)-di(aryl)imine-Ni counterparts. This difference of behaviour has been attributed to the lack of steric protection imparted by the ligand to the metal centre (see section 1.2.4).
This subsection will be concerned with the preparation of a series of complexes based on the class D (Figure 11). Despite the considerable body of work reported in this area there are a number of exceptions with regard to aryl substitution pattern. The following sections address these absentees by synthesising and characterising the corresponding ligands and nickel complexes. For the purposes of our catalytic screening (see later) a number of previously reported systems are also described.

![Figure 11][2-iminopyridine]NiX₂  \(R = H, Me; R^1 = Me, i-Pr; R^2 = H, Me, NH₂; R^3 = H, Me; X = \text{halide}\) (Class D).\textsuperscript{33}

2.6.1 Synthesis of ligands L9-L13
The reaction of 2-pyridinecarboxaldehyde with 2,6-dimethylaniline, 2,4,6-trimethylaniline or 2,6-diisopropylaniline in ethanol at room temperature furnished [2-[(2,6-Me₂C₆H₃)HNC]C₅H₄N] (L9), [2-((2,4,6-Me₂C₆H₃)HNC)C₅H₄N] (L10) and [2-[(2,6-i-Pr₂C₆H₃)HNC]C₅H₄N] (L11) in good yield. Harsher conditions were required in order to obtain the ketimine versions L12-L13. In particular, a higher boiling alcoholic solvent was required (\textit{i.e.}, \(n\)-propanol or \(n\)-butanol) in order to allow the reaction to proceed. Thus, treatment of 2,6-dimethylaniline, 2,4,6-trimethylaniline or 2,6-diisopropylaniline with 2-acetylpyridine in \(n\)-BuOH at reflux allowed access to [2-((2,6-Me₂C₆H₃)MeNC]C₅H₄N] (L12) and [2-((2,6-i-Pr₂C₆H₃)MeNC]C₅H₄N] (L13) in good yield. The preparation of L9, L11 and L13 has been previously reported by Laine\textsuperscript{32,35-37} (Scheme 12). The compounds have been characterised by \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and IR spectroscopy and ES Mass Spectrometry and are consistent with that previously reported.\textsuperscript{32,33}
The new compounds L10 and L12 were identified by peaks corresponding to their respective molecular ions (ESMS). The absorption bands around 1640-1650 cm\(^{-1}\) confirmed the formation of the aldimine for L10 and the ketimine for L12. The singlet observed at ca. \(\delta 8.26\) in the \(^1\)H NMR spectrum and the signal at \(\delta 163.4\) in the \(^{13}\)C NMR spectra for L9-L11 were consistent with the proton and the carbon of an aldimine. The spectroscopic characterisation of L12-L13 revealed a singlet of integration 3 at ca. \(\delta 2.05\) in the \(^1\)H NMR spectra and the signals at ca. \(\delta 167.4\) in the \(^{13}\)C NMR spectra that indicate the presence of the ketimine carbon and methyl.

In order to extend the above condensation reactions to dianilines with the intent of preparing an iminopyridine ligands with a pendant imino group (see L8 for comparison) we have examined the reaction of 2-acetyl-pyridine with 2,3,5,6-tetramethylphenyl-1,4-diamine. Thus, the reaction of 2-acetyl-pyridine with 1.4 equivalents of 2,3,5,6-tetramethylphenyl-1,4-diamine in toluene at 50 °C, in the presence of a catalytic amount of formic acid, afforded [1-(2'-(C\(_5\)H\(_4\)N)MeNC)(2,3,5,6-Me\(_4\)C\(_6\)NH\(_2\))] (L14) in moderate yield (Scheme 13). The compound has been characterised by \(^1\)H NMR, \(^{13}\)C NMR and IR spectroscopy and ElectroSpray Mass Spectrometry (ESMS).

**Scheme 13 Reagents and conditions:** (i) 2,3,5,6-Me\(_4\)C\(_6\)NH\(_2\), toluene, 50 °C, cat. H\(^+\).

Compound L14 showed a peak corresponding to the molecular ion in its ES mass spectrum. The singlet observed at 2.11 (\(^1\)H NMR), the signal at \(\delta 168.1\) (\(^{13}\)C NMR) and the absorption band at 1632 cm\(^{-1}\) confirmed the presence of the (Me)C=N functionality.
Chapter Two

The broad signal at 3.40 (1H NMR) and the broad signal at 3378 cm⁻¹ indicate the presence of a free amine group.

2.6.2 Synthesis of complexes 6a-6f

The reaction of one equivalent of nickel(II)dichloride with L9 – L13 in n-butanol at 110 °C overnight gave [(Lx)NiCl₂] [Lx = L9 (6a), L10 (6b), L11 (6c), L12 (6d), L13 (6e)] in good yield (Scheme 14), respectively. On the other hand, treatment of one equivalent of [DME]nickel(II)dibromide with L14 in n-butanol at 110 °C for one hour gave 6f in good yield (Scheme 14). Complexes 6a-6f have been characterised by FAB-MS, IR spectroscopy and magnetic susceptibility measurements; the results can be found in Table 7.

![Scheme 14 Reagents and conditions: (i) NiX₂ [NiX₂ = NiCl₂, [DME]NiBr₂], n-BuOH, 110 °C.]

The FAB mass spectrometric data for 6a–6f exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one or two halide ions. The magnetic moments (measured on an Evans balance at ambient temperature) range from 2.7 to 3.3 μB and are consistent with the presence of two unpaired electrons (S = 1). The IR spectra for 6a–6f show absorption bands between 1590-1595 cm⁻¹, which correspond to a coordinated imine and are shifted by ca. 40 cm⁻¹ in comparison with the free ligands. In the case of 6c, the FAB mass spectrometric data suggests the formation of a dimeric species. Interestingly, 6c demonstrated an ability to bind two ligands as the only peak observed in FAB was at m/z 626 and was interpreted as one-nickel atom coordinated to two ligands L11 and one chlorine. This is consistent with the report by Mi and co-workers of a related dimeric species in which two units L11-nickel are bridged by two chlorine ions. Laine et al. also mentioned a comparable dimeric form of iminoarylpine supported complexes.
<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>IR $\nu$(C=N)$^a$</th>
<th>Magnetic moment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a Orange</td>
<td>303 [M-Cl]$^+$</td>
<td>1591</td>
<td>2.8</td>
</tr>
<tr>
<td>6c Green</td>
<td>626 [2L+Ni+Cl]$^+$</td>
<td>1595</td>
<td>3.1</td>
</tr>
<tr>
<td>6d Green</td>
<td>331 [M-Cl]$^+$, 296 [M-2Cl]$^+$</td>
<td>1591</td>
<td>2.8</td>
</tr>
<tr>
<td>6f Brown</td>
<td>405 [M-Br]$^+$</td>
<td>1595</td>
<td>3.3</td>
</tr>
</tbody>
</table>

$^a$ recorded in the solid-state (cm$^{-1}$); $^b$ recorded on an Evans balance at ambient temperature ($\mu_b$)
2.7 Conclusions
The objective set for this chapter was to develop a series of late transition metal monometallic dihalide complexes that would not only behave as potential olefin polymerisation catalysts but would also serve as valid comparitors for the EB systems to be developed in later chapters. Four classes of complexes (A-D) were synthesised, each based on multidentate nitrogen donor ligands, the precise binding domain dictating the metal centre to be employed [viz. phenanthroline-imine (Class A), bipyridine-imine (Class B), \(\alpha\)-diimine (Class C), pyridine-imine (Class D)]. The synthetic methodology employed was successful to produce ten novel ligands (L1-L14) and eighteen new complexes (1a-6f: Chart 2). All complexes 1a-6f have been characterised using a range of techniques, and a number have been the subject of single crystal X-ray diffraction studies (2a and 2b, 4 and 5).

The preparation of complexes based on the unsymmetrical \(\alpha\)-diimine ligands (Class D) encountered some synthetic difficulties. For instance, the imine function of the ligand was prone to rearrangement reactions. Nevertheless, one example of this type of ligand could be synthesised and successfully complexed, with the structure of the nickel dibromide species being determined by single crystal X-ray diffraction.

The performance of these complexes for the polymerisation of ethylene will be discussed in Chapter Six.
Chart 2 List of ligands and complexes prepared in Chapter Two.
2.8 References


3.1 Introduction

In parallel with the development of single-site catalysis for the polymerisation of olefins, the combination of multiple polymerisation-active metal centres in the same reaction has emerged as a way of producing novel polyolefins with improved microstructures (see subsection 1.3). The development of concurrent tandem catalysts (CTC), in which a combination of several independent single-site catalysts operates together, has seen a surge of interest (see subsection 1.3.1). On the other hand, the use of a binucleating ligand manifold to constrain the two catalysts into close proximity [encapsulated bimetallic (EB)] (see 1.3.2) remains a field in its relative infancy. To some extent, the advantages expected from this type of system can be related to those observed for CTC systems, but the inherent close proximity of the metal centres is likely to enhance the probability of synergic interactions.

In Chapters Three to Five, we are interested in probing the effect of proximity on the catalytic performance of EB systems. In this particular chapter, we are concerned with the synthesis of fused encapsulated systems (see sub-section 1.3.2.2), in which some part of a well-defined monometallic catalyst/precatalyst (e.g., an aryl group on the ligand manifold) is shared in the construction of the encapsulated system (Figure 1). In principle, this type of system would allow the metal centres to be held at their closest proximity.

![Figure 1 Generic scheme for fused encapsulated bimetallic precatalysts/catalysts.](image)

Using the chain-end groups discussed in Chapter Two (viz. iminophenanthroline, iminobipyridine, iminopyridine, α-diimine), we aim to assemble a series of fused bimetallic complexes (Classes E-H), in which the metal centres are separated by a single 1,4-aryl group. Some effort will also be directed towards making encapsulated fused precatalysts containing inequivalent binding domains. Some of our preliminary attempts at preparing encapsulated trimetallic systems are also mentioned. The generic synthetic approach is described in the following sub-section, while sections 3.3-3.7 outline specific details connected with the preparation and characterisation of the complexes of classes E-H (Chart 1).
It is noteworthy that during the time between the design of these targets and the writing of this thesis, several groups have published related works (see 1.3.2). Where appropriate, a comparison between the EB systems prepared in our study with the results determined independently will be given.
3.2 General synthesis strategy

The general methodology employed to synthesise the ligands in this chapter involves the condensation reaction of two equivalents of a carbonyl-containing substrate with a monoaryl dianiline compound (Scheme 1).

\[
2 \text{R}\text{O} + \text{H}_{2}\text{N-}\text{Ar-}\text{NH}_{2} \xrightarrow{\text{cat. H}^+} \text{R}\text{N}-\text{Ar-}\text{N-R'} + 2 \text{H}_{2}\text{O}
\]

Scheme 1 Generic scheme for ligand synthesis (R = H, Me; R' = pyridyl, bipyridyl, phenanthroinyl or iminyl).

Optimisation of the ligand synthesis has been achieved by using the same approaches described in Chapter Two, mainly by driving the reaction to the right hand side of the equilibrium (i.e., to remove the water). For instance, various techniques have been employed including the use of azeotropic distillation (e.g., Dean-Stark apparatus), use of different acid catalysts (e.g., p-toluene sulfonic acid, formic acid, glacial acetic acid), use of drying agents (e.g., molecular sieves, magnesium sulfate), using the aniline as the solvent, and to run the reaction under rigorously dry conditions. In general, the reactions are performed in alcoholic solvents and the products conveniently precipitated, filtered and collected as either off-white, yellow or red solids.

The precatalysts targeted (Classes E-H) in this work are to be prepared by the reaction of the corresponding ligand with two equivalents of the corresponding metal dihalide. Typically, the reactions are performed in anhydrous n-BuOH at elevated temperatures and the product precipitated on cooling to room temperature or induced to precipitate by the addition of hexane (Scheme 2).

\[
\text{R}'\text{N-}\text{Ar-}\text{N-R'} + 2 \text{MX}_2 \xrightarrow{n\text{-BuOH/Heat}} \left[ \text{R}'\text{N-}\text{Ar-}\text{N-R'} \right] \xrightarrow{\text{M}_2\text{X}_4}
\]

Scheme 2 Generic scheme for complexation reaction (R = H, Me; R' = pyridyl, bipyridyl, phenanthroinyl or iminyl).
3.3 Preparation of \([1,4\text{-bis}(2\text{-iminopyridine})\text{aryl}]\text{Ni}_2\text{X}_4\) (Class E)

Examples of ligands possessing two iminopyridine pockets tethered by a 1,4-monoaryl moiety have been reported for a variety of applications. For example, bimetallic complexes (e.g., Ru, Ag, Pd) featuring this ligand family have been applied in catalysis\(^1\)\(^{-}\)\(^4\) (i.e., oxidation of alkenes),\(^4\) new materials design\(^5\) and for biological applications.\(^6\) 1,4-Bis(iminopyridine)aryl ligands possess low lying \(\pi^*\) orbitals that have been found to exhibit interesting photophysical and photochemical properties.\(^1\)\(^^{-}\)\(^3\) In some cases, electrochemical studies have been employed to investigate metal-metal communication in polynuclear metal arrays based on this ligand frame.\(^4\)\(^,\)\(^6\)\(^\text{\(\ldots\)}\)\(^{10}\) This type of ligand has also been employed for the assembly of polymeric inorganic supramolecular materials.\(^5\) An example of the use of the ligand frame to support two polymerisation-active metal centres has been reported recently by Murray. In order to generate ligands suitable for polymerisation applications, we have targeted ligand sets that have sterically bulky groups on the central N-aryl unit (see section 1.2.4 for background).

In this section, dinickel halide complexes containing 1,4-bis(iminopyridine)aryl ligands will be targeted. In the first instance, ligands containing two identical bidentate binding domains will be synthesised (Figure 2). In the second instance, an unsymmetrical 1,4-bis(iminopyridine)aryl ligand (i.e., with inequivalent bidentate binding domains) will be synthesised. In the third instance, the resulting ligands will be reacted with two equivalents of nickel dihalide to form the target dinickel encapsulated compounds.

![Figure 2](image)

**Figure 2** Encapsulated precatalysts of type \([1,4\text{-bis}(2\text{-iminopyridine})\text{phenyl}]\text{M}_2\text{X}_4\); \(R = H, \text{Me} \) \(R' = H \) or \(\text{Me} \); \(X = \text{Cl}, \text{Br} \) (Class E).

### 3.3.1 Synthesis of ligands L15-L17

The reaction of 2,3,5,6-tetramethylphenyl-1,4-diamine with 2-pyridine carboxaldehyde in ethanol at 50 °C or with 2-acetyl-pyridine in ethanol at 90 °C, in the presence of a catalytic amount of formic acid, gave \([1,4\text{-}(\text{2-C}_5\text{H}_4\text{N})\text{HCN})_2\text{-2,3,5,6-Me}_4\text{C}_6\] (L15) and \([1,4\text{-}(\text{2-C}_5\text{H}_4\text{N})\text{MeCN})_2\text{-2,3,5,6-Me}_4\text{C}_6\] (L16) in good yield as yellow solids (Scheme 3). The compounds have been characterised by ElectroSpray mass spectrometry (ESMS) and \(^1\)H NMR, \(^{13}\)C NMR and IR spectroscopy. In addition, L15 has been the subject of a single crystal X-ray diffraction study (see experimental section).
Chapter Three

Scheme 3 Reagents and conditions: (i) 2 eq. (2-C₅H₄N)CHO, EtOH; (ii) 2 eq. (2-C₅H₄N)C(CH₃)O, EtOH, cat. H⁺, 90 °C.

Yellow crystals of L15 suitable for a single crystal X-ray diffraction study were grown by the slow cooling of a hot ethanol solution containing L15. The molecular structure is shown in Figure 3; selected bond lengths and angles are listed in Table 1.

The structure of L15 consists of two terminal iminopyridyl units bridged by a 2,3,5,6-tetramethylphenyl moiety. The molecule possesses a centre of symmetry located at the centre of the aryl section. Each pyridyl-imine section is nearly planar [tors. N(1)-C(5)-C(6)-N(2) 11.9°] with the imine and pyridine nitrogen atoms adopting a mutually transoid configuration. The central ring is quasi-orthogonal to the plane containing the imino-pyridyl units [ca. 100.1°]; this configuration is similar to that reported by Chanda et al.⁸ for [(1,4-((2-C₅H₄N)HCN)₂C₆H₄].

Figure 3 Molecular structure of L15. All the hydrogen atoms, apart for H6, have been omitted for clarity.

<table>
<thead>
<tr>
<th>Table 1 Selected bond lengths (Å) and angles (°) for L15</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
</tr>
<tr>
<td>N(2)-C(6)</td>
</tr>
<tr>
<td>C(6)-N(2)-C(7)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)</td>
</tr>
<tr>
<td>Symmetric atoms are generated by the transformation (1-x,-y, 2-z).</td>
</tr>
</tbody>
</table>

82
Both L15 and L16 gave peaks corresponding to their molecular ions in their ES-mass spectra, respectively. The C=N stretches for the imine units were observed at 1641 cm\(^{-1}\) and 1631 cm\(^{-1}\) in their spectrum, respectively. For L15, the singlet at \(\delta\) 8.28 in the \(^1\)H NMR spectrum and the signal at \(\delta\) 163.8 in the \(^{13}\)C NMR spectrum were consistent with the presence of the CH=N proton and the CH=N carbon. Yoshida and co-workers reported the synthesis of [(1,4-((2-C\(_5\)H\(_4\)N)HCN)\(_2\)-C\(_6\)H\(_4\))], which possesses a related identical backbone to that in L15.\(^{11}\) L16, the ketimine counterpart of L15, was identified by the singlet at ca. \(\delta\) 2.19 in its \(^1\)H NMR spectrum while the signal at \(\delta\) 168.3 in its \(^{13}\)C NMR spectra confirmed the presence of the CMe=N proton and the CMe=N carbon, respectively.

In order to access a ligand frame containing two distinct bidentate binding domains, L14 was employed as a reactive building block (Scheme 4). Thus, the reaction of 2,3,5,6-tetramethyl-N-(pyridin-2-ylethylidene)-phenyl-1,4-diamine (L14) with 2-pyridine carboxaldehyde in toluene at 50 °C, in the presence of catalytic amount of formic acid, furnished [1-((2-C\(_5\)H\(_4\)N)H(ACN))-4-((2'-C\(_5\)H\(_4\)N)MeCN)-2,3,5,6-Me\(_4\)C\(_6\)) (L17) in good yield.

![Scheme 4](image-url)

**Scheme 4 Reagents and conditions:** (i) (2-C\(_5\)H\(_4\)N)CHO, C\(_7\)H\(_8\), cat. H\(^+\) 50 °C.

L17 gave a peak corresponding to its molecular ion in its ES-mass spectrum. The presence of the CH=N proton and the CH=N carbon corresponding to the aldimine unit was confirmed with signals at \(\delta\) 8.30 in the \(^1\)H NMR spectrum and \(\delta\) 166.6 in the \(^{13}\)C NMR spectrum, respectively. The ketimine unit, on the other hand, was identified by the presence of signals at \(\delta\) 2.11 in the \(^1\)H NMR spectrum [CMe=N proton] and \(\delta\) 168.3 [CMe=N carbon] in its \(^{13}\)C NMR spectrum. In the IR spectrum, a broad absorption band was evident at 1632 cm\(^{-1}\) which was ascribed to a C=N stretch for both aldimine and ketimine bands being superimposed. In the \(^1\)H NMR spectrum, the integration of the aldimine CH=N and the ketimine CMe=N signals reveals a relative 1:3 ratio, consistent with the structure of L17.
3.3.2 Synthesis of complexes 7a-7d

The reaction of two equivalents of 1,2-dimethoxyethanenickel(II)dibromide with L15, L16 and L17 in n-butanol at 110 °C overnight gave [(Lx)Ni2Br4] (Lx = L15 (7a), L16 (7b), L17 (7c)) in good yield, respectively (Scheme 5). Similarly, treatment of nickel(II)dichloride with L15 in n-butanol at 120 °C overnight gave [(L15)Ni2Cl4] (7d) in good yield. Complexes 7a-7d have been characterised by FAB-MS, IR spectroscopy and by magnetic susceptibility measurements (see Table 2). Furthermore, the DMF adducts of 7a, 7b, 7c and 7d (7a', 7b', 7c' and 7d') have been characterised by single crystal X-ray diffraction (see later).

Scheme 5 Reagents and conditions: (i) [DME]NiBr2, w-BuOH, 110 °C; (ii) NiCl2, w-BuOH, 120 °C.

The FAB mass spectrometric data for 7a-7d exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one or more halide ions. The magnetic susceptibility measurements (Evans balance at ambient temperature) reveal magnetic moments ranging from 3.9 to 4.2 μb for the nickel complexes which are consistent with the presence of two non-interacting high spin Ni(II) centres (using μ2 = Σμi2, where μi is the magnetic moment of the individual metal centres). The IR spectra for 7a-7d show absorption bands around 1595 cm⁻¹ which correspond to ν(C=N) stretching frequencies for coordinated imines and are shifted by ca. 40 cm⁻¹ in comparison with the free ligands L15-L16.

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>ν(C=N)</th>
<th>Magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7d</td>
<td>Green</td>
<td>566 [M-Cl]+, 530 [M-2Cl]+, 495 [M-3Cl]+</td>
<td>1595</td>
</tr>
</tbody>
</table>

* recorded in the solid-state (cm⁻¹); † recorded on an Evans balance at ambient temperature (μb)
Treatment of 7a-7d with hot DMF followed by layering the cooled solution with diethylether gave, for all reactions, red crystals corresponding to the adducts 7a'-7d' in moderate to low yield (Scheme 6). The FAB mass spectra for 7a'-7d' gave peaks similar to that observed for precursor complexes 7a-7d. In the IR spectra, the imine bands could be seen at ca. 1595 cm\(^{-1}\) while a strong additional band at 1644 cm\(^{-1}\) was observed for C=O absorption bands suggesting the presence of coordinated DMF ligands. In each case, the crystals of 7a'-7d' were of a quality suitable for X-ray determination. The molecular structures of 7a'-7d' are shown in Figures 4, 5, 6 and 7; selected bond lengths and angles are listed in Tables 3 (7a' and 7b'), 4 and 5, whereas Table 6 contains complementary structural data.

The molecular structures of 7a' and 7b' are similar and are based on centrosymmetric dimers in which the charge of the di-cationic nickel-containing units are balanced by two non-coordinating bromide anions. Each nickel centre is bound to two nitrogen atoms [N(1) and N(2) from L15 (for 7a') or L16 (for 7b')], three oxygen atoms [O(1), O(2), O(3) from three molecules of dimethylformamide] and one bromide ligand to complete a distorted octahedral geometry at each metal atom. The square plane of the octahedron is defined by N(1), N(2), O(1) and O(3) while the apical sites are occupied by Br(1) and O(2). The trans configuration of Br(1) and O(2) is indicated by their almost linear disposition [O(2)-Ni(1)-Br(1) 175.84(8)° for 7a' and O(2)-Ni(1)-Br(1) 174.64(8)° for 7b'].

In both structures, the N-metal bond distances show similar characteristics with the Ni-N\(_{pyridine}\) bond being shorter [Ni(1)-N(1) 2.040(3) Å (7a'), 2.042(3) Å (7b')] than the corresponding Ni-N\(_{imine}\) bond [Ni(1)-N(2) 2.119(3) Å (7a') and 2.115(2) Å (7b')] and
consistent with the better donor capability of a pyridine over an imine (see 1.2.5.2). This relative donor capability is also reflected in the \textit{trans} metal-oxygen bonds distances with Ni(1)-O(3) for 7a' [2.149(6) Å] being longer than Ni(1)-O(1) [2.023(3) Å]. A similar trend is also observed for 7b' but the variation of the distance is less significant [Ni(1)-O(3) 2.043(2) Å vs. Ni(1)-O(1) 2.038(2) Å]. This may be due to a ketimine being a better donor than an aldimine (see 1.2.5.2). The metal-bromine bond distances in 7a' and 7b' are the longest within both structures with the Ni-Br(1) distance for 7b' being longer than that for 7a' [2.5313(5) Å for 7b' vs. 2.4956(8) Å for 7a'].

| Table 3 Selected bond lengths (Å) and angles (°) for 7a' and 7b' |
|-----------------|-----------------|
|                 | 7a'             | 7b'             |
| Ni(1)-N(1)      | 2.040(3)        | 2.042(3)        |
| Ni(1)-N(2)      | 2.119(3)        | 2.115(2)        |
| Ni(1)-Br(1)     | 2.4956(8)       | 2.5314(5)       |
| Ni(1)-O(1)      | 2.023(3)        | 2.038(2)        |
| Ni(1)-O(2)      | 2.103(3)        | 2.122(2)        |
| Ni(1)-O(3)      | 2.149(6)        | 2.043(2)        |
| C(6)-C(21)      | -               | 1.489(4)        |
| N(1)-Ni(1)-N(2) | 79.06(13)       | 78.66(10)       |
| N(1)-Ni(1)-Br(1)| 94.00(9)        | 96.21(7)        |
| N(1)-Ni(1)-O(1) | 92.06(13)       | 91.73(10)       |
| N(1)-Ni(1)-O(2) | 87.25(13)       | 85.71(9)        |
| N(1)-Ni(1)-O(3) | 167.62(16)      | 168.33(9)       |
| N(2)-Ni(1)-O(1) | 169.53(13)      | 169.27(9)       |
| N(2)-Ni(1)-O(2) | 90.81(12)       | 91.41(9)        |
| N(2)-Ni(1)-O(3) | 100.13(15)      | 97.26(9)        |
| N(2)-Ni(1)-Br(1)| 93.33(9)        | 93.88(7)        |
| O(1)-Ni(1)-O(2) | 83.17(12)       | 83.04(9)        |
| O(1)-Ni(1)-O(3) | 87.35(16)       | 91.25(9)        |
| O(1)-Ni(1)-Br(1)| 92.82(10)       | 91.88(6)        |
| O(2)-Ni(1)-O(3) | 80.40(16)       | 83.46(9)        |
| O(2)-Ni(1)-Br(1)| 175.84(8)       | 174.64(6)       |
| O(3)-Ni(1)-Br(1)| 8.38(13)        | 94.97(6)        |

The symmetric atoms are generated using the transformation (1-x, 1-y, z) for 7a' and (-x+1, y+1, -z+1) for 7b'.

The distribution of the bond angles for 7a' and 7b' are similar, though there are some subtle differences. In both cases, the angles formed by the metal centre and the
equatorial ligands display the largest distortions. For instance, the angles exhibited by N(1)-Ni(1)-N(2) are the smallest [at 79.06(13)° for 7a' and 78.66(10)° for 7b'], probably due to the constraints of the ligand framework. In contrast, the N(2)-Ni(1)-O(3) bond angles are the largest [at 100.13(15)° for 7a' and at 97.26(9)° for 7b'], whereas the remaining angles N(1)-Ni(1)-O(1) [at 92.06(13)° for 7a' and at 91.73(10)° for 7b'] and O(1)-Ni(1)-O(3) [at 87.35(16)° for 7a' and 91.25(9)° for 7b'] exhibit reduced distortions. In 7a', the two nickel centres are located slightly closer in 7b' [at 8.786 Å when compared to 7a' [at 8.897 Å]. In both cases, the five-membered metallocyclic rings, formed by the pyridyl-imine unit and the nickel centre, are quasi-planar [max. dev. from plane is Ni(II) = 0.1158 Å 7a', 0.1011 Å 7b']. In the two structures, the substituted aryl groups are almost orthogonal to this metallocyclic ring plane as indicated by their respective torsion angles [tors. Ni(1)-N(2)-C(7)-C(8) 106.5° (7a'), Ni(1)-N(2)-C(7)-C(8) 103.3° (7b')]. The difference of substituent pattern on the imine carbon (i.e., from a hydrogen to a methyl) appears to have little effect on the geometry of the metal centres.

As with the molecular structures of 7a' and 7b', complex 7c' also consists of a dicationic dinickel unit and two bromide counter anions (Figure 6). However, due to the inequivalent bidentate binding domains, the complex is not generated through symmetry. Nevertheless, the mixed aldimine-ketimine binucleating L16 ligand binds to the two nickel centres in a bis(bidentate) fashion with each metal centre being additionally bound by three oxygen-bound DMF ligands and a bromide ligand in a relative disposition identical to that seen in 7a' and 7b'. The geometry at each nickel centre can be best described as distorted octahedral. On inspection of the N-metal bond distances similar characteristics for both nickel centres are revealed; the Ni-N_{pyridine} bonds are shorter [Ni(1)-N(1) 2.122(13) Å, Ni(2)-N(4) 1.997(11) Å] than the Ni-N_{imine} [Ni(1)-N(2) 2.159(11) Å, Ni(1)-N(2) 2.089(12) Å] ones. This is again consistent with better donor capability of a pyridine over an imine (see 1.2.5.2). The metal-bromine bonds [Ni(1)-Br(1) 2.530(3) Å, Ni(2)-Br(2) 2.520(2) Å] are longer than any other metal-ligand bond and vary slightly between the two metal centres. Inspection of the metal-oxygen lengths suggests a comparable distortion between the two metals. For Ni(1) and Ni(2), the longest bonds are with the apical oxygen atoms [Ni(1)-O(1) 2.120(10) Å, Ni(2)-O(4) 2.112(11)], whereas the distance involving the equatorial oxygen would appear to be equivalent within error [Ni(1)-O(2) 2.047(12) Å, Ni(2)-O(5) 2.030(11) Å or Ni(1)-O(3) 2.028(9) Å, Ni(2)-O(6) 2.052(11) Å].
Figure 4 Molecular structure of the dicationic unit in \{(L15)(DMF)_{6}\text{NiBr}_2\text{Br}_2\} (7a'). All the hydrogen atoms, apart from H6, have been omitted for clarity.
Figure 5 Molecular structure of the dicationic unit in \(\{(L16)(DMF)_6\}Ni_2Br_2\)Br_2 (7b'). All the hydrogen atoms have been omitted for clarity.
Chapter Three

For both nickel centres, the chelate bite angles for L17 are different with the aldimine N-Ni-N angle being substantially bigger than the ketimine angle [N(3)-Ni(2)-N(4) 81.5(5)° vs. N(1)-Ni(1)-N(2) 78.66(10)°]; a feature that is also evident when comparing symmetrical 7a' against 7b' but to a lesser degree.

Table 4 Selected bond lengths (Å) and angles (°) for 7c'

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>Ni(1)-N(1)</td>
<td>2.122(13)</td>
<td>Ni(2)-N(3) 2.089(12)</td>
</tr>
<tr>
<td>Ni(1)-N(2)</td>
<td>2.159(11)</td>
<td>Ni(2)-N(4) 1.997(11)</td>
</tr>
<tr>
<td>Ni(1)-Br(1)</td>
<td>2.530(3)</td>
<td>Ni(2)-Br(2) 2.520(2)</td>
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<tr>
<td>Ni(1)-O(1)</td>
<td>2.120(10)</td>
<td>Ni(2)-O(4) 2.112(11)</td>
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<tr>
<td>Ni(1)-O(2)</td>
<td>2.047(12)</td>
<td>Ni(2)-O(5) 2.030(11)</td>
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<td>Ni(1)-O(3)</td>
<td>2.028(9)</td>
<td>Ni(2)-O(6) 2.052(12)</td>
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<td>C(7)-C(8)</td>
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<tr>
<td>N(1)-N(1)-N(2)</td>
<td>76.0(5)</td>
<td>N(3)-N(2)-N(4) 81.5(5)</td>
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<td>N(1)-N(1)-Br(1)</td>
<td>96.8(4)</td>
<td>N(3)-N(2)-Br(2) 94.3(4)</td>
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<td>N(3)-N(2)-O(4) 91.1(4)</td>
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<td>N(3)-N(2)-O(5) 167.3(5)</td>
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<tr>
<td>N(1)-N(1)-O(3)</td>
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<td>N(4)-N(2)-Br(2) 95.1(3)</td>
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<td>O(5)-N(2)-Br(2) 90.5(3)</td>
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<tr>
<td>O(3)-N(1)-Br(1)</td>
<td>94.5(3)</td>
<td>O(6)-N(2)-Br(2) 94.3(4)</td>
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</table>
Figure 6 Molecular structure of the dicationic unit in \{[(L17)(DMF)_6]Ni_2Br_2\}_2Br_2 (7c'). All the hydrogen atoms, apart from H19, have been omitted for clarity.
The two nickel centres in 7c' are separated by 8.903 Å; a distance similar to 7a' but longer than in 7b'. The two five-membered metallocyclic rings formed by the pyridyl-imines and the metal centres are almost planar with the maximum deviation from planarity being more significant for pyridyl-aldimine-Ni(2) than for pyridyl-ketimine-Ni(1) [max. dev. for plane Ni(1) = 0.3049 Å vs. max. dev. for plane Ni(2) = 0.1071 Å]. As with 7a' and 7b', the aryl groups in 7c' are disposed almost orthogonally to the metallocyclic rings as shown by the corresponding torsion angles [tors. Ni(1)-N(2)-C(9)-C(10) 106.3°, tors. Ni(2)-N(3)-C(12)-C(11) 103.3°].

The molecular structure of 7d' differs from 7a'-7c' in that the complex is a neutral species (Figure 7). In 7d', the symmetrical 1,4-bis(iminopyridine)aryl ligand L15 again acts as a bis(bidentate) ligand but the nature of the monodentate ligands coordinated to each nickel centre varies when compared to 7a'-7c'. Thus, each nickel centre is bound to two chlorides and two oxygen-bound DMF ligands with each pair being disposed mutually cis. One DMF-oxygen atom [O(2)] is trans to a chloride [Cl(1)] while the other oxygen [O(1)] is trans to a pyridine nitrogen atom [N(1)] so as to complete a distorted octahedral geometry.

<table>
<thead>
<tr>
<th>Table 5 Selected bond lengths (Å) and angles (°) for 7d'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)-N(1) 2.039(2)</td>
</tr>
<tr>
<td>Ni(1)-N(2) 2.150(2)</td>
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<td>Ni(1)-Cl(1) 2.4081(10)</td>
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<td>N(1)-Ni(1)-N(2) 79.49(9)</td>
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<td>N(1)-Ni(1)-Cl(1) 89.02(8)</td>
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<td>N(1)-Ni(1)-Cl(2) 95.17(7)</td>
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<td>N(1)-Ni(1)-O(1) 168.95(9)</td>
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<td>N(2)-Ni(1)-O(1) 90.06(8)</td>
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<tr>
<td>N(2)-Ni(1)-O(2) 84.63(9)</td>
</tr>
<tr>
<td>Cl(1)-Ni(1)-Cl(2) 95.65(4)</td>
</tr>
</tbody>
</table>

The symmetric atoms are generated by using the transformation (1.5-x, 0.5-y, 2-z).

The metal-chlorine distances in 7d' are different with Ni(1)-Cl(1) being longer than Ni(1)-Cl(2) [2.4081(10) Å vs. 2.3812(9) Å], presumably due to the nature of the ligand trans to each. As with 7a'-7c' the Ni-Npyridine bond lengths are shorter than the Ni-Nimine distances [Ni(1)-N(1) 2.039(2) Å vs. Ni(1)-N(2) 2.150(2) Å] due to the better donor capability of a pyridine over an imine. The chelate bite angle N(1)-Ni(1)-N(2) [at 79.49(9)°] in 7d' is slightly bigger than the corresponding angle in 7a' [at 79.06(13)°].
Of the four dinickel complexes 7a'-7d', the metal-metal distance in neutral 7d' is the longest [at ca. 8.934 Å] but remains close to that observed in cationic 7a' [at ca. 8.897 Å] which contains the same 1,4-bis(iminopyridine)aryl ligand L15. The two equivalent five-membered metalallocyclic rings formed by the pyridyl-imines and the metal centres as with 7a'-7c' are almost planar [max. dev. from plane Ni = 0.1807 Å]. As with 7a'-7c', the metalallocyclic ring plane and the central aryl group are inclined almost orthogonally [tors. Ni(1)-N(2)-C(7)-C(8) 101.4°]. The slight variation from orthogonality would appear to explain the difference in M...M distance exhibited in 7a'-7d' (see Table 6).

It is noteworthy that Yoshida et al. reported the related 1-D Zn-containing polymer, [Zn(1,4-bis(iminopyridine)phenyl)(DMF)2]n-(DMF)n.(ClO4)2n, in which a 1,4-bis(iminopyridine)phenyl ligand bridges the metal centres with each metal centre being bound by two oxygen-bound DMF ligands. Notably, in 7a'-7d' the presence of the substituted aryl groups would appear to prevent the formation of a polymeric network. It is unclear why the treatment of the bromide-containing complexes 7a'-7c with DMF give salts, while neutral species were obtained when employing the chloride complex 7d.

| Table 6 Torsion angle variation and effect on the Ni...Ni distance in 7a'-7d'. |
|---------------------------------|-----|-----|-----|-----|
| Torsion angle (°), C\text{im}-N_{\text{im}}-C_{\text{ar}}-C_{\text{ar}} | 63.4 | 70.2 | 68.7 Ni(1) | 71.9 |
| Torsion angle (°), Ni-N_{\text{im}}-C_{\text{ar}}-C_{\text{ar}} | 106.5 | 103.3 | 106.3 Ni(1) | 101.4 |
| Ni...Ni distance (Å) | 8.897 | 8.786 | 8.903 | 8.934 |
Figure 7 Molecular structure of neutral [(L15)(DMF)$_4$Ni$_2$Cl$_4$] (7d$^+\text{). All the hydrogen atoms, apart from H6, have been omitted for clarity.}
3.4 Synthesis of [1,4-bis(α-diimine)aryl]Ni₂X₄ (Class F)
In this section, dinickel halide complexes containing 1,4-bis(α-diimine)aryl ligands will be targeted. In Chapter Two, it was noted that the preparation of unsymmetrical α-diimine ligands can prove problematic with re-distribution and side-reactions being a common feature. Nevertheless, it was observed that the unsymmetrical ligand [(2,6-i-Pr₂C₆H₃)NC(Me)C(Me)N(2,3,5,6-Me₄C₆NH₂)] (L9) and the corresponding complex [(2,6-i-Pr₂C₆H₃)NC(Me)C(Me)N(2,3,5,6-Me₄C₆NH₂]NiBr₂ (5) can be isolated in good yield. With this result in mind, we decided to target symmetrically disposed 1,4-bis(α-diimine)tetramethylaryl ligands with the intent of preparing the corresponding dinickel complexes (Class F, Figure 8).

![Figure 8](image)

Figure 8 Target encapsulated precatalyst (Class F) supported by 1,4-bis(α-diimine)aryl ligands; X = halide.

3.4.1 Attempted synthesis of ligand L18
Treatment of two equivalents of 3-(2,6-diisopropyl-phenylimino)-butan-2-one with 2,3,5,6-tetramethylphenyl-1,4-diamine in ethanol at 50 °C, in the presence of a catalytic amount of glacial acetic acid, for 12 hours afforded a mixture of products including [(1,4-((2,6-i-Pr₂C₆H₃ )N(Me)C(Me)CN)r 2,3,5,6-Me₄C₆ )] (L18) (Scheme 7). ¹H NMR spectroscopy and ESMS confirmed the presence of L18 along with symmetrical (2,6-i-Pr₂C₆H₃)N=CC(Me)=N(2,6-i-Pr₂-C₆H₃)¹² and, although not characterised, it was assumed that a polymeric species of the type (1,4-{N(Me)C(Me)CN)-2,3,5,6-Me₄C₆)n was also present. The ESMS for L18 revealed a molecular ion peak at 619 m/z along with a pair of signals at δ 169.3 and 169.6 in the ¹³C NMR spectrum corresponding to the inequivalent imine carbon atoms. Several attempts at varying the solvent, temperature and reaction duration were carried out. Reaction of [(2,6-i-Pr₂C₆H₃)N(Me)C(Me)CN(2,3,5,6-Me₄C₆NH₂)] (L9) with one equivalent of 3-(2,6-diisopropyl-phenylimino)-butan-2-one in ethanol also gave a similar product distribution using the conditions described above. In all cases a similar range of products was observed.
3.4.2 Attempted synthesis of complex 8
As an alternative strategy, complex 5 was viewed as an ideal precursor to generate the targeted encapsulated precatalysts (class F). The unsymmetrical diimine unit, by virtue of being incorporated into a five-membered metallocycle was considered a more stable moiety and more likely to remain intact during subsequent reactions. Thus, 5 was treated firstly with 3-(2,6-diisopropyl-phenylimino)-butan-2-one in ethanol and then reacting the resultant residue with 1,2-dimethoxyethanenickel(II)dibromide in dichloromethane at 50 °C (Scheme 8).

Inspection of the ν(C=N) stretches in the IR spectrum of the resulting black powder indicated metal coordination had occurred. However, the FAB-MS displayed fragmentation peak corresponding to 5 along with significant peaks corresponding to the symmetrical monometallic species [(2,6-i-Pr2C6H3)NC(Me)C(Me)(2,6-i-Pr2C6H3)].
Crystallisation of the residue was unsuccessful and this direction of the work was not pursued.
3.5 **Synthesis of [1,4-bis(iminobipry)aryl]Fe₂Cl₄ (Class G)**

Given the fragility of the 1,4-bis(α-diamine)aryl ligand system observed in section 3.4, we decided to return to nitrogen donor fragments containing a single carbonyl functionality. In Chapter Two, the bipy-carbonyl precursor was successfully employed to make monometallic precatalysts of class B based on iron and nickel metal centres and with a range of aryl groups. In this section, we explore the use of the bipy-carbonyl compound as a reactive chain-end precursor for the assembly of 1,4-bis(iminobipyrindine)aryl ligands. These ligands are designed to act as bis(tridentate) ligands and their coordination chemistry with divalent iron halides will be investigated (Figure 9). To our knowledge, neither this type of ligand nor coordination complexes have been examined before.

![Figure 9 Target encapsulated precatalysts supported on 1,4-bis(iminobipyrindine)aryl ligands; R = H, Me (Class G).](image)

### 3.5.1 Synthesis of ligands L19 and L20

The reaction of 2,3,5,6-tetramethylphenyl-1,4-diamine with two equivalents of 2,2'-bipyridine-6-carboxaldehyde in diethyl ether at 50 °C or with 6-acetyl-2,2'-bipyridine in n-butanol at 80 °C, in the presence of a catalytic amount of glacial acetic acid, furnished

\[
[1,4-(6''-(2''-C₅H₄N)(2'-C₅H₃N)CHN)₂(2,3,5,6-Me₄C₆)] (L19) \quad \text{and} \quad [1,4-(6''-(2''-C₅H₄N)(2'-C₅H₃N)CMeN)₂(2,3,5,6-Me₄C₆)] (L20)
\]

in moderate to low yield (Scheme 9). The compounds have been characterised by ES mass spectrometry and \(^1\)H NMR, \(^13\)C NMR and IR spectroscopy.

![Scheme 9 Reagents and conditions: (i) 2 eq. \([2-(CCH₃=O)-6-(2''-C₅H₄N)-C₅H₃N])\), Et₂O, cat. H⁺, 50 °C; (ii) 2 eq. \([2-(CH=O)-6-(2''-C₅H₄N)-C₅H₃N])\), n-BuOH, cat. H⁺, 80 °C.](image)
Both L19 and L20 gave peaks corresponding to their molecular ions in their ES-mass spectra. For L19, the signals at δ 8.34 in the ¹H NMR spectrum, δ 163.3 in the ¹³C NMR spectrum along with an absorption band at 1635 cm⁻¹ in its IR spectrum, confirmed the presence of the CH=N proton, the CH=N carbon and the C=N stretch of the aldimine unit, respectively.

The spectral data of L20 support the formation of the ketimine as indicated by the absorption band at 1645 cm⁻¹ (IR) while the signals at δ 2.26 (¹H NMR), at δ 168.6 (¹³C NMR) are consistent with the MeC=N unit. All the spectral data of L19 and L20 are close to that of L6 and L7, which also possess the iminylbipyridine motif (see 2.4.2).

3.5.2 Synthesis of complexes 9a and 9b

Reaction of two equivalents of iron(II)dichloride with L19 and L20 in n-butanol at 120 °C overnight gave [(Lx)Fe₂Cl₄] [Lx = L19 (9a), L20 (9b)] as brown/blue solids in good yield, respectively (Scheme 10). Complexes 9a and 9b have been characterised by FAB-MS, IR spectroscopy and magnetic susceptibility measurements. Unfortunately, single crystals of 9a and 9b could not be obtained to fully elucidate the structure.

The FAB mass spectrometric data for 9a and 9b exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of more than one halide ion {at 716 [M-Cl]⁺ and 680 [M-2Cl]⁺ for 9a} and {at 743 [M-Cl]⁺, 707 [M-2Cl]⁺ for 9b}. The magnitude of the magnetic moments (Evans balance at ambient temperature) at 6.0 and 6.5 μb were consistent with the presence of two high spin (S = 2) non-interacting iron centres (using μ² = Σμᵢ², where μᵢ is the magnetic moment of the individual metal centres). The IR spectra for 9a and 9b show ν(C=N) absorption bands around 1591 cm⁻¹, which are shifted by ca. 50 cm⁻¹ when compared with the spectra of the corresponding free ligands L19 and L20, and thus are consistent with the imine moiety being bound in 9a and 9b. In addition, the spectral data of 9a and 9b compare favourably with the data reported for the monometallic complexes of class B (see 2.4.3).
3.6 Synthesis of [1,4-bis(2-iminophenanthroline)aryl]Fe₂Cl₄ (Class H)

The ready reactivity of 1,10-phenanthroline carboxaldehyde towards a range of sterically and electronically variable monoanilines in Chapter Two indicated that a similar investigation of its capacity to undergo di-condensation reactions with 1,4-dianilines should be worthy of study. In this section, we target 1,4-bis(iminophenanthroline)aryl-based ligands with a view to preparing diiron complexes. As with 1,4-bis(iminopyridine)aryl ligands (L₁₉, L₂₀), these ligand frames should have the ability to bind the metal dihalide units in a bis(tridentate) fashion to give bimetallic species of class H (Figure 10). Complexes of class H and their corresponding free ligands have not been the subject of a synthetic study to the knowledge of the author. The details of ligand synthesis and complexation reactions are outlined below.

![Figure 10 Target encapsulated precatalysts supported on a 1,4-bis(iminophenanthroline)aryl ligand (Class H).](image)

3.6.1 Synthesis of ligand L₂₁

The reaction of two equivalents of [1,10]-phenanthroline-2-carboxaldehyde with 2,3,5,6-tetramethyl-benzene-1,4-diamine in toluene at 50 °C overnight, in the presence of a catalytic amount of glacial acetic acid, afforded pale yellow [1,4-(([(1,10]-C₁₂H₁₁N₂)HCN)₂(2,3,5,6-Me₄C₆)] (L₂₁) in good yield (Scheme 11). L₂₁ has been characterised by ES mass spectrometry and ¹H NMR, ¹³C NMR and IR spectroscopy.

![Scheme 11 Reagents and conditions: (i) 2 eq. [1,10]-(C₁₂H₁₁N₂)CHO, EtOH, 50 °C, cat. H⁺.](image)

Compound L₂₁ showed a peak corresponding to the molecular ion in its ESMS. In the ¹H NMR spectrum a singlet at δ 8.78 could be seen for the CH=N proton. It is noteworthy that the limited solubility of L₂₁ in deuterated chloroform precluded
identification of all seventeen carbon atoms in its $^{13}$C NMR spectrum. The characteristic $\nu$(C=N) absorption band for the imine was clearly visible at 1639 cm$^{-1}$.

3.6.2 Synthesis of complex 10

The reaction of two equivalents of iron(II)dichloride with L21 in $n$-butanol at 120 °C overnight gave blue [(L21)Fe$_2$Cl$_4$] (10) in good yield (Scheme 12). Complex 10 has been characterised by FAB-MS, IR spectroscopy and by magnetic measurements.

![Scheme 12](image)

Scheme 12 Reagents and conditions: (i) 2 eq. FeCl$_2$, $n$-BuOH, 120 °C.

The FAB mass spectrometric data for 10 exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one chloride ion. The magnetic susceptibility measurement (Evans balance at ambient temperature) revealed a magnetic moment of 6.0 $\mu_b$, the value being consistent with the presence of two non-interacting high spin ($S = 2$) iron centres. The IR spectrum for 10 shows an absorption band a 1603 cm$^{-1}$ similar to that observed for monometallic complexes 1a-le. As with 1a-le it is difficult to say unequivocally that this band corresponds to uniquely a $\nu$(C=N) stretch as coordinated imines in this work tend to be seen at ca. 1591-1595 cm$^{-1}$. It is likely that there may be some superposition of the $\nu$(C=C) bands of the fused aromatic ring within the phen moiety. Nevertheless, the shift to lower wavenumber (at least 36 cm$^{-1}$) by the imine in 10 compared with free L21 is consistent with the imine coordination to the iron centre.
3.7 Attempted synthesis of alternative fused precatalysts

3.7.1 General synthetic methodology

In section 3.3, we have shown the pendant amine-containing species, L14, can undergo a smooth reaction with 2-pyridine carboxaldehyde to afford the unsymmetrical bis(iminopyridine)aryl species L17. The use of a pre-coordinated pendant amine-containing species offers an alternative attractive means of accessing directly metal-based products. However, we have shown that the reaction of 5 towards the imine-ketone, 3-(2,6-diisopropyl-phenylimino)-butan-2-one, can be problematic with side products apparent (see section 3.4). We reasoned that a carboxaldehyde-containing organo-substrate may lead to cleaner reactions. In this section we explore the reactivity of the pendant amine-containing complexes 5 and 6f towards the aldehyde-containing reagents, 2-pyridinecarboxaldehyde, glyoxal and 2,6-diformylpyridine. It was viewed that this approach could allow access to fused bimetallic and trimetallic precatalysts containing at least one inequivalent binding domain.

3.7.2 Derivatisation of 5

Treatment of 5 with 2-pyridinecarboxaldehyde in dichloromethane at ambient temperature for one hour afforded \([1-((2,6-i-Pr_2C_6H_3)NC(Me)C(Me)N)-4-((2-C_5H_4N)MeCN))(2,3,5,6-Me_4C_6)]NiBr_2\) (11a) along with a number of other uncharacterised species (Scheme 13). Thus, the FAB-MS of the mixture revealed a range of peaks including fragmentation peaks consistent with the lost of one and two bromides \({[M-Br] \text{ at } m/z \, 619 \text{ and } [M-2Br] \text{ at } m/z \, 538}\) from the molecular ion pertaining to 11a. The infrared spectra of the mixture revealed two absorptions bands at 1630 and 1597 cm\(^{-1}\) consistent with both a coordinated and an uncoordinated imine present in 11a. As recrystallisation proved unsuccessful, crude 11a was reacted with one equivalent of 1,2-dimethoxyethanenickel(II)dibromide in dichloromethane at room temperature to afford \([1-((2,6-i-Pr_2C_6H_3)NC(Me)C(Me)N)-4-((2-C_5H_4N)MeCN))(2,3,5,6-Me_4C_6H_2)]Ni_2Br_4\) (11b) along with a number of other uncharacterised species (Scheme 13). The resulting dark brown powder displayed several peaks in the FAB mass spectrum that could be attributed to the fragmentation of 11b \({[M-2Br] \text{ at } m/z \, 758 \text{ and } [M-3Br] \text{ at } m/z \, 677}\). Unfortunately single crystals of 11b suitable for an X-ray diffraction study could not be obtained.
The use of 5 as a building block to form encapsulated precatalysts/catalysts was attempted by reacting 5 with 2,6-diformylpyridine at 20 °C in dichloromethane to yield \([2,6-((4-((2,6-i-Pr_2C_6H_3)NC(Me)C(Me)N))(2,3,5,6-Me_4C_6)HCN)2C_5H_3N]Ni_2Br_4\) 12a as a blue dark powder (see Scheme 14). The condensation reaction between two units of 5 and one carboxaldehyde was supported by the FAB MS and infrared analysis performed on \([2,6-((4-((2,6-i-Pr_2C_6H_3)NC(Me)C(Me)N))(2,3,5,6-Me_4C_6)HCN)2C_5H_3N]Ni_2Br_4FeCl_2\) 12b that showed fragmentation peaks and isotopic distribution consistent with the loss of one and more bromide ions at \([M-Br] at m/z 1178\) \([M-2Br] at m/z 1100\), \([M-3Br] at m/z 1020\) and \([M-4Br] at m/z 939\). The infrared spectra contained two absorption bands corresponding to two types of imine; at the band at 1595 cm\(^{-1}\) was attributed to imine coordinated to a metal whereas that at 1623 cm\(^{-1}\) would be consistent with that of a free imine.
3.7.3 Derivatisation of 6f

Treatment of two equivalents of 6f with either glyoxal or 2,6-diformylpyridine was carried out in dichloromethane at 50 °C (Scheme 15). However in each case, the FAB mass spectrum of the reaction products did reveal peaks consistent with a mixture of products. The poor solubility of 6f in dichloromethane might explain the lack of success of the reaction.

Scheme 15 Reagents and conditions: (i) CH(O)CH(O), CH₂Cl₂, 20 °C; (ii) [DME]FeCl₂, CH₂Cl₂, 20 °C; (iii) C₅H₃N(CHO)₂, CH₂Cl₂; (iv) FeCl₂, THF, 20 °C.
3.7.4 Conclusions

Six new aryl-linked imino-containing binucleating ligands [L15-L17 {1,4-bis(2-iminopyridine)aryl}, L19 and L20{1,4-bis(iminobipyridine)aryl}, L21 {1,4-bis(iminophenanthroline)aryl}] have been synthesised and characterised. The necessity to employ a rigid pyridyl-monocarbonyl-containing precursor over an imine-carbonyl in the condensation reaction has been recognised. The ligands L15-L17 have been employed as bis(bidentate) supports for two nickel dihalide units affording bimetallic (Lx)Ni2X4 [X = Br; Lx = L15 (7a), L16 (7b), L17 (7c); X = Cl; Lx = L15 (7d)] in good yields. The amenability of 7a-7d to derivatisation has been demonstrated by their reactions with DMF leading to the X-ray characterised salts [[(Lx)(DMF)6]Ni2Br2]Br2 (Lx = L15 (7a'), L16 (7b'), L17 (7c')) and the neutral species [(L15)(DMF)4]Ni2Cl4 (7d'). The reactions of the bis(tridentate) ligands, L19-L21, with iron dichloride have been investigated affording the diferrous complexes (Lx)Fe2Cl4 [Lx = L19 (9a), L20 (9b), L21 (10)] in good yield. Some effort was also directed towards preparing fused imino-containing trinucleating ligands and complexes; however, the results were inconclusive. All the new complexes have been characterised by a variety of techniques including FAB-mass spectrometry, IR spectroscopy and magnetic susceptibility measurements (all complexes are high spin) and in some cases by single crystal X-ray diffraction (Chart 2).

The performance of these new fused bimetallic complexes as precatalysts for ethylene polymerisation will be discussed in Chapter Six.
Chart 2 Lists of ligands and complexes synthesised in Chapter 3
3.8 References


Chapter Four

Imino-based Remote Encapsulated Bimetallic Nickel and Iron Precatalysts

Synthesis and Characterisation
4.1 Introduction
As established previously (see 1.4), one of the main objectives of this thesis is an investigation of the influence of the proximity between several catalytic components on the performance of the overall system for the polymerisation of ethylene. The approach employed for our studies consists of designing specific binucleating ligands for the generation of encapsulated bimetallic systems in which the two polymerisation-active metal centres are compartmentalised in close proximity (see 1.3.2). In this particular chapter, we are concerned with the preparation of remote EB systems (see 1.3.4) whereby a linker group (e.g., inorganic, organic moiety or a chemical bond) is positioned between two well-defined monometallic precatalysts/catalysts (Figure 1). The development of remote EB systems in this thesis is of a three-fold interest: firstly, it will allow an examination of the effect of a linker unit on the polymerisation performance of the catalytic components, secondly it will allow a comparison between fused (Chapter Three: Classes E-H) and remote EB systems (present Chapter: Classes I-M) and thirdly it will allow a comparison with the corresponding monometallic systems (Chapter Two: Classes A-D).

Figure 1 Generic representation of a remote EB system.

In a remote EB system, the role of the linker is to define and to separate the monometallic precatalysts/catalysts while mediating any potential interactions between the catalytic sites (see 1.3.4). As a result, both the nature of the linker and its attachment sites on the catalytic components are important parameters to be considered when designing the system. For our study, the N-aryl group was selected as the attachment site so as to allow continuity with the strategy employed for the fused EB systems (Chapter Three: Classes E-H). Specifically, the 4-position of the N-aryl ring was chosen to connect the linker because it was considered to have least effect on the steric properties at each of the catalytic sites and would also allow a comparison of the targeted EB systems with the most closely related monometallic precatalysts/catalysts (Chapter Two: Classes A-D; where considerable emphasis has been placed on modifying the electronic properties of the 4-position).

Five classes of complexes (Chart 1: Classes I-M) have been identified for development in this chapter, each possessing two discrete binding domains on their ligand frames (viz. iminophen, iminobipyridine, iminopyridine, α-diiimine). Complexes
belonging to classes I, K, L and M possess at least one pyridine and one imine donor group, whereas J is composed of solely imino groups. Systems of class M differ from that of classes I-L in that the aryl group 4-positions are directly linked by a single C-C bond while in I-L a CH$_2$ group facilitates the linkage. With regard to system I, complexes incorporating both symmetric and unsymmetric methylene diaryl units will be described. It is noteworthy that some examples of EB precatalysts/catalysts of the class I and J have been reported during the writing of this thesis (see below) whereas K, L and M are novel to the knowledge of the author.

![Chemical structures](image)

**Chart 1** Target remote encapsulated bimetallic precatalysts; R = H, Me; $R^1$ = Me, i-Pr; $R^2$ = Me, i-Pr; X = Cl or Br.
4.2 General synthetic strategy

The general methodology employed to synthesise the ligands and complexes in this work was similar to the one described in Chapter Three. The preparation of the ligands was obtained by a condensation reaction of two equivalents of a carbonyl substrate and a dianiline (Scheme 1). However, many of the dianiline reactants are not commercially available or have not been previously reported and so synthetic procedures for their synthesis is outlined in the next section (see section 4.3). The complexes can be obtained by reaction of the corresponding ligand with two equivalents of the appropriate metal dihalide in a high boiling point alcoholic solvent.

$$2R-O + H_2N-Ar-(CH_2)_n-Ar-NH_2 \xrightarrow{\text{cat. H}^+} \frac{R-N-Ar-(CH_2)_n-Ar-N}{R'} + 2H_2O$$

$$2MX_2|n-BuOH/Heat$$

$$\left[ \begin{array}{c}
R-N-Ar-(CH_2)_n-Ar-N \\
R'
\end{array} \right] \xrightarrow{n-BuOH/Heat} M_2X_4$$

Scheme 1 Generic scheme for synthesis of ligands and complexes; $R = H$ or $Me$, $R' = pyridyl, iminyl,$ bipyridyl or phenanthrolinyl
4.3 Synthesis of the dianilines

4.3.1 Symmetrical and unsymmetrical 4,4'-diaminodiphenylmethanes

Symmetrical 4,4'-diaminodiphenylmethanes have been used in large quantities as polymer additives by the polymer industry\(^1\) or as yellow dyes.\(^2\) In addition, they have a track record as precursors to generate ligands for the assembly of supramolecular architectures.\(^3\)\(^-\)\(^5\) In general, the synthesis of symmetrical 4,4'-diaminodiphenylmethanes involves the condensation of two molecules of an aniline with one molecule of formaldehyde under acidic conditions.\(^1\) To our knowledge, the only examples of unsymmetrical 4,4'-diaminodiphenylmethanes have been mentioned in the patent literature.\(^6\)\(^-\)\(^7\)

In the first instance, 4,4'-diaminodiphenylmethanes have been targeted with a range of substitution patterns at the 3- and 5-positions. A typical procedure comprises the treatment of an aqueous solution of the substituted aniline (e.g., 2,6-dimethylaniline or 2,6-diisopropylaniline) with formaldehyde in the presence of concentrated hydrochloric acid to give, following neutralisation, \([(4-\text{NH}_2-3,5-R^1_2 \text{C}_6\text{H}_2)\text{CH}_2]\) \((R^1 = \text{Me, i-Pr})\) (Scheme 2). For a given substitution pattern the temperature employed proved to be an important parameter to be optimised in order to obtain good yields of the products. For instance, a temperature of 70 °C was found to be optimal for the synthesis of \([(4-\text{NH}_2-3,5-\text{Me}_2 \text{C}_6\text{H}_2)\text{CH}_2]\), whereas that of \([(4-\text{NH}_2-3,5-\text{i-Pr}_2 \text{C}_6\text{H}_2)\text{CH}_2]\) required higher temperature (at 110 °C).

![Scheme 2](image)

**Scheme 2** Reagents and conditions: (i) H\(_2\)CO, H\(_2\)O, conc. H\(^+\), 70 - 110 °C; (ii) NaOH, CHCl\(_3\).

The unsymmetrical versions of the 4,4'-diaminodiphenylmethanes were obtained by employing an equimolar combination of two different anilines under the same experimental conditions as described above. For example, an aqueous mixture of 2,6-dimethylaniline and 2,6-diisopropylaniline or 2-methylaniline and 2,6-diisopropylaniline produced the unsymmetrical compounds \([(4-\text{NH}_2-3,5-\text{Me}_2 \text{C}_6\text{H}_2)\text{CH}_2]\) or \([(4-\text{NH}_2-3-\text{Me} \text{C}_6\text{H}_3)(4-\text{NH}_2-3,5-\text{i-Pr}_2 \text{C}_6\text{H}_2)\text{CH}_2]\) (Scheme 3), respectively. In all cases, these reactions lead to statistical distributions of the product along with the corresponding symmetrical 4,4'-diaminodiphenylmethanes.
The pure unsymmetrical compound \[\{(4-NH_2-3,5-Me_2C_6H_2)(4-NH_2-3,5-i-Pr_2C_6H_2)\}CH_2\] could be isolated following a series of fractional recrystallisations (or sublimation) while the purification of \[\{(4-NH_2-3-Me-C_6H_3)(4-NH_2-3,5-i-Pr_2C_6H_2)\}CH_2\] proved more problematic.

All symmetrical and unsymmetrical 4,4'-diaminodiphenylmethanes have been characterised by ElectroSpray Mass spectrometry (ESMS) and \(^1\)H NMR, \(^{13}\)C NMR and IR spectroscopy. In addition, a crystal of 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyldiphenylmethane has been the subject of a single crystal X-ray diffraction study.

![Scheme 3 Reagents and conditions:](image)

White crystals of unsymmetrical \[\{(4-NH_2-3,5-Me_2C_6H_2)(4-NH_2-3,5-i-Pr_2C_6H_2)\}CH_2\] suitable for the X-ray determination were obtained by slow evaporation of a solution containing the compound in hexane. The molecular structure of \[\{(4-NH_2-3,5-Me_2C_6H_2)(4-NH_2-3,5-i-Pr_2C_6H_2)\}CH_2\] is depicted in Figure 2; selected bond lengths and angles are listed in Table 1. The molecular structure of \[\{(4-NH_2-3,5-Me_2C_6H_2)(4-NH_2-3,5-i-Pr_2C_6H_2)\}CH_2\] consists of two aromatic rings bridged at their 4-positions by a methylene unit. For each of the two rings, a primary amine is located in the \textit{para} position and two alkyl substituents in the \textit{meta}; one ring possesses two methyl groups whereas two isopropyl groups occupy the other. The aryl rings on the central CH\textsubscript{2} group are disposed at an angle of 115.87(17)° [C(6)-C(7)-C(8)]; a value slightly larger than expected for a sp\textsuperscript{3} carbon, probably due to the presence of the two sterically bulky rings.
Figure 2 Molecular structure of \[(4\text{-NH}_2\text{-3,5-Me}_2\text{C}_6\text{H}_2)(4\text{-NH}_2\text{-3,5-i-Pr}_2\text{C}_6\text{H}_2)\text{CH}_2\]. All the hydrogen atoms, apart from H1A, H1B, H2A and H2B, have been omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for \[(4\text{-H}_2\text{N-2,6-Me}_2\text{C}_6\text{H}_2)(4\text{-NH}_2\text{-2,6-i-Pr}_2\text{C}_6\text{H}_2)\text{CH}_2\]

<table>
<thead>
<tr>
<th>Bond Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(3)</td>
<td>1.387(2)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.507(3)</td>
</tr>
<tr>
<td>N(2)-C(11)</td>
<td>1.399(3)</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.497(3)</td>
</tr>
<tr>
<td>C(6)-C(7)-C(8)</td>
<td>115.87(17)</td>
</tr>
</tbody>
</table>

All the dianilines prepared, \([(4\text{-NH}_2\text{-3,5-R}_1\text{2C}_6\text{H}_2)\text{2CH}_2]\) (R = Me, i-Pr) and \([(4\text{-NH}_2\text{-3-R}_1\text{-5-R}_2\text{-C}_6\text{H}_2})(4\text{-NH}_2\text{-3,5-i-Pr}_2\text{C}_6\text{H}_2)\text{CH}_2]\) (R\(^1\) = R\(^2\) = Me; R\(^1\) = Me, R\(^2\) = H), were identified by peaks corresponding to their molecular ions in their respective ES-mass spectra \(i.e., \ 4,4'\text{-diamino-3,5,3',5'-tetramethylidiphenylmethane at 255 m/z, 4,4'-diamino-3,5,3',5'-tetraisopropylidiphenylmethane at 366 m/z, 4,4'-diamino-3-isopropyl-3',5'-dimethyldiphenylmethane at 297 m/z, and 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyldiphenylmethane at 311 m/z}\). For all compounds, the signals at ca. δ 3.70 in their \(^1\)H NMR spectra and at ca. δ 40.0 in their \(^13\)C NMR spectra were consistent with the formation of the methylene bridge. On the other hand, the singlets around δ 6.80 in their \(^1\)H NMR spectra for \([(4\text{-NH}_2\text{-3,5-R}_1\text{2C}_6\text{H}_2)\text{2CH}_2]\) (R = Me, i-Pr) and \([(4\text{-NH}_2\text{-3,5-Me}_2\text{C}_6\text{H}_2})(4\text{-NH}_2\text{-3,5-i-Pr}_2\text{C}_6\text{H}_2)\text{CH}_2]\) instead of the multiplets observed in the corresponding aniline precursor, supports the presence of the bridge at the para position.
4.3.2 Symmetrical biphenyl-4,4'-diamines

The lack of any commercially available compounds apart from 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine, required that other substituted biphenyl-4,4-diamines had to be synthesised prior to ligand synthesis. For example, the experimental protocol reported by Bamfield\(^8\) was used to synthesise 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine (Scheme 4).

\[
\begin{align*}
\text{Scheme 4 & Reagents and conditions:} & & \text{(i) Pd/C paste (5%), NaOH, NaOOCH, CTAB, H}_2\text{O, 110 °C; (ii) NaOOCH.} \\
\end{align*}
\]

In spite of various attempts to optimise parameters such as temperature, base, co-solvent or phase transfer reagent, the yield remained low. Nevertheless, 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine was characterised by ES mass spectrometry and \(^1\)H NMR, \(^{13}\)C NMR and IR spectroscopy. In addition, red crystals of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine suitable for X-ray diffractometry studies were grown by recrystallisation from hexane. The molecular structure of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine is depicted in Figure 3; selected bond lengths and angles are listed on Table 2.

\[
\text{Figure 3 Molecular structure of [} (4-NH}_2\text{-3,5-}\text{-i-Pr}_2\text{C}_6\text{H}_2\text{)] All the hydrogen atoms, apart from H1A, H1B, H2A and H2B, have been omitted for clarity.} 
\]
Chapter Four

Table 2 Selected bond distances (Å) and angles (°) for 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
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<tbody>
<tr>
<td>C(6)-C(7)</td>
<td>1.490(3)</td>
<td>N(1)-C(3)</td>
<td>1.405(3)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.392(3)</td>
<td>N(2)-C(10)</td>
<td>1.392(3)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.394(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)-C(6)-C(7)</td>
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<td>C(8)-C(7)-C(6)</td>
<td>121.9(2)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
<td>122.2(2)</td>
<td>C(12)-C(7)-C(6)</td>
<td>121.5(2)</td>
</tr>
</tbody>
</table>

The structure consists of two aniline rings linked by a single carbon-carbon bond at their para positions. The ortho positions of each ring are substituted with isopropyl groups. Curiously, the two rings adopt a conformation intermediate between eclipsed and staggered [tors. C(1)-C(6)-C(7)-C(8) 19.6°]. This may be partly due to some conjugation occurring between the two rings. Interestingly, in 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine the corresponding rings are quasi-planar, as indicated by the corresponding torsion angle (0.515°). On the other hand, the length of the central carbon-carbon bond of 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine [1.488(8) Å] is almost equivalent to that found in 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine [C(6)-C(7) 1.490(3) Å].
4.4 Synthesis of [4,4′-bis(2-iminopyridine)diphenylmethane]Ni₂X₄ (Class I)

Ligands of the type bis(4-(2-iminopyridine)phenyl)methane have been used to generate supramolecular architectures. More recently, related ligands have been used as supports for group 10 catalysts for the polymerisation of olefins (Figure 4). For example, Sun and Chen have investigated the EB nickel and palladium catalysts XXXIX for the polymerisation of ethylene, but notably omitted to make the comparison with related monometallic counterparts. In particular, they have investigated the effect of changing the substituents on the ligand backbone (viz. imino-carbon and aryl group substituents) on the catalytic performance of XXXIX. Similar EB systems XXXX based on palladium or nickel have been employed by Hu and co-workers for the polymerisation of norbornene and the copolymerisation of norbornene with styrene. Both the palladium and the nickel catalysts demonstrated some activity for the polymerisation of ethylene, although the palladium systems performed generally better.

![Figure 4 Examples of remote EB precatalysts: R = H, Ph; R¹ = Me, Et, i-Pr; R² = Me, Et, i-Pr.](image)

This section will be focused on the preparation and characterisation of a series of bis(iminopyridine)phenylmethane-based ligands and their corresponding di-nickel complexes (Figure 5: Class I). With the exception of 13a and 13b, all the systems are new and possess a range of different imino-carbon and imino-nitrogen substituents.

![Figure 5 Target system (Class I); R¹ = Me, i-Pr R² = Me, i-Pr.](image)
4.4.1 Synthesis of ligands L22-L26

Reaction of 4,4’-diamino-3,5,3’,5’-tetramethyldiphenylmethane, 4,4’-diamino-3,5,3’,5’-tetraisopropyldiphenylmethane or 4,4’-diamino-3,5,3’,5’-dimethylidiphenylmethane with 2-pyridine carboxaldehyde in ethanol at 45 °C, in presence of catalytic amount of formic acid, afforded \[((4-(2-C₅H₄N)HCN)-3,5-R₁C₆H₂)((4-(2-C₅H₄N)HCN)-3,5-R₂C₆H₂)CH₂]\ [R₁ = R₂ = Me (L22), R₁ = R₂ = i-Pr (L23), R₁ = i-Pr; R₂ = Me (L24)] in good yield (Scheme 5). Similarly, treatment of 2-acetyl-pyridine with 4,4’-diamino-3,5,3’,5’-tetramethyldiphenylmethane, 4,4’-diamino-3,5-diisopropylphenyl-3’,5’-dimethyldiphenylmethane in ethanol at 90 °C, in the presence of catalytic amount of glacial acetic acid, furnished \[((4-(2-C₅H₄N)MeCN)-3,5-R₁C₆H₂)((4-(2-C₅H₄N)MeCN)-3,5-R₂C₆H₂)CH₂]\ [R₁ = R₂ = Me (L25), R₁ = R₂ = i-Pr (L26)] in moderate yield. L22-L26 were characterised by a combination of ES mass spectrometry and ¹H NMR, ¹³C NMR and IR spectroscopy. In addition crystals of L22 were subject of a single crystal X-ray diffraction study.

Scheme 5 Reagents and conditions: (i) 2 eq. (2-C₅H₄N)CHO, EtOH, cat. H⁺, 45 °C; (ii) 2 eq. (2-C₅H₄N)CCH₃O, EtOH, cat. H⁺, 90 °C.

Yellow crystals of L22 suitable for the X-ray determination were grown by slow evaporation of a solution of L22 in ethanol. The molecular structure of L22 is depicted in Figure 6; selected bonds lengths and angles are shown in Table 3.
Figure 6 Molecular structure of L22. All the hydrogen atoms, apart from H6 and H24, have been omitted for clarity.

The molecular structure of L22 is based on two identical aryliminopyridine units bridged by a central methylene moiety [C(15)] with a methyl substituent on each of the 3,3,5,5' positions of the diphenylmethane unit. The angle formed by the two rings [C(10)-C(15)-C(16) 114.66(13)°] is slightly larger than that expected for a sp3-hybridised carbon. The imino nitrogen atoms [N(2), N(3)] adopt a transoid configuration with respect to the nitrogen donors [N(1), N(4)] of the pyridine unit [tors. N(1)-C(6)-C(5)-N(2) = 6.3° and tors. N(3)-C(24)-C(25)-N(4) = 5.5°]. The aryl rings are inclined at an angle less than 90° with respect to each of the pyridyl-imine units [tors. C(6)-N(2)-C(7)-C(8) = 61.8° and tors. C(18)-C(19)-N(3)-C(24) = 66.9°]. Sun and Chen have reported the structure of a closely related ligand, (((4-(2-C₅H₄N)CHN)-3-Me-5-i-PrC₆H₂CH₂), that differs only by the substituents located at the 3,3,5,5' positions. This difference seems to have little consequence, as both structures are remarkably similar. For instance, the value of the angle formed by the two aryl rings with the central methylene unit is similar to that for L22 at ca. 114.3(4)°. The imine and pyridine nitrogen atoms adopt a similar transoid disposition to that observed in L22.

All the ligands, L22-L26, were identified by peaks corresponding to their molecular ions in their ES-mass spectra. The formation of the aldimine and the ketimine units in L22-L26 was confirmed by absorption bands in the 1635-1639 cm⁻¹ region corresponding to the υ(C=N)imine stretches. In the NMR spectra of L22-L24, the singlets at ca. δ 8.22 (¹H NMR) and the signals centred around δ 163.3 (¹³C NMR) confirmed the presence of the CH=N proton and the CH=N carbon, respectively. On the other hand, the singlets at ca. δ 2.17 in the ¹H NMR spectra for L25 and L26 and the signals at ca. δ 167.3 in their ¹³C NMR spectra were consistent with the methyl and carbonyl carbon atom of the ketimine units, respectively. Furthermore, comparison of
the spectral data for L22-L24 with that of other ligands containing iminopyridine units developed in this work (e.g., L15-L18) showed similar characteristics (see 3.3).

Table 3 Selected bond distances (Å) and angles (°) for L22.

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>Values</th>
</tr>
</thead>
<tbody>
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<td>1.335(2)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.340(2)</td>
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<tr>
<td>N(2)-C(6)</td>
<td>1.265(2)</td>
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<tr>
<td>N(2)-C(7)</td>
<td>1.4248(19)</td>
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<td>C(10)-C(15)</td>
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<td>C(6)-N(2)-C(7)</td>
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<tr>
<td>N(1)-C(5)-C(6)</td>
<td>114.93(15)</td>
</tr>
<tr>
<td>N(2)-C(6)-C(5)</td>
<td>121.90(16)</td>
</tr>
<tr>
<td>C(10)-C(15)-C(16)</td>
<td>114.66(13)</td>
</tr>
<tr>
<td>N(3)-C(19)</td>
<td>1.423(2)</td>
</tr>
<tr>
<td>N(3)-C(24)</td>
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</tr>
<tr>
<td>N(4)-C(25)</td>
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<td>C(15)-C(16)</td>
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<tr>
<td>C(24)-N(3)-C(19)</td>
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</tr>
<tr>
<td>N(4)-C(25)-C(24)</td>
<td>114.62(15)</td>
</tr>
<tr>
<td>N(3)-C(24)-C(29)</td>
<td>121.48(16)</td>
</tr>
</tbody>
</table>

4.4.2 Synthesis of complexes 13a-13f

Reaction of two equivalents of nickel(II)dichloride with L22-L26 in n-butanol at 120 °C overnight gave [(Lx)Ni2Cl4] \([Lx = L22 (13a), L23 (13b), L24 (13c), L25 (13d), L26 (13e)]\) in good yield, respectively (Scheme 6). Under milder conditions, treatment of L24 by two equivalents of 1,2-dimethoxyethanenickel(II)dibromide in dichloromethane at 50 °C overnight gave [(L24)Ni2Br4] (13f) in good yield (Scheme 6). Complexes 13a-13f have been characterised by FAB-MS, IR spectroscopy and magnetic measurements (see Table 4).

For complexes 13a-13f, the FAB mass spectrometric data exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one or more halides (chloride for 13a-13e and bromide for 13f). The coordination of the imine to the metal in 13a-13f was confirmed by comparison of the IR spectra for the free ligands with 13a-13f. In all cases, the complexes showed strong absorption bands for
\(\nu(C=\text{N})_{\text{mine}}\) between 1591 cm\(^{-1}\) and 1597 cm\(^{-1}\) that were shifted by ca. 40 cm\(^{-1}\) when compared to L22-L26. The magnitude of the magnetic moments for 13a-13f, 3.9 \(\mu_b\) to 4.1 \(\mu_b\), (measured on an Evans balance at ambient temperature), are consistent with the presence of two non-interacting high spin Ni(II) centres (using \(\mu^2 = \Sigma \mu_i^2\), where \(\mu_i\) is the magnetic moment of the individual metal centres). These values fall in a comparable range to those found for other dinickel complexes prepared in this work (e.g., 7a-7d; see 3.3).

**Table 4 Selected characterisation data for 13a - 13f**

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>(\nu(C=\text{N})^a)</th>
<th>Magnetic moment (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>Brown</td>
<td>-</td>
<td>1592</td>
</tr>
<tr>
<td>13d</td>
<td>Green</td>
<td>797 [M-Cl]^+ , 760 [M-2Cl]^+ , 723 [M-3Cl]^+</td>
<td>1596</td>
</tr>
<tr>
<td>13f</td>
<td>Green</td>
<td>901 [M-Br]^+</td>
<td>1596</td>
</tr>
</tbody>
</table>

*a recorded in the solid-state (cm\(^{-1}\)); \(^b\) recorded on an Evans balance at ambient temperature (\(\mu_b\))

Attempts to derivatise 13a-13f have been carried out by treating the complexes with acetonitrile at elevated temperatures (Scheme 7). In the cases of 13b and 13e green crystals of \([(L23)_2Ni_4Cl_8(CH_3CN)_4]\ (13b') and \([(L26)_2Ni_4Cl_8(CH_3CN)_2]\ (13e') suitable for X-ray determinations were obtained. The molecular structures of 13b' and 13e' are illustrated in Figures 7 and 8; Tables 5 and 6 contain selected bond lengths and angles for 13b' and 13e', respectively while Table 7 lists additional data.

**Scheme 7 Reagents and conditions:** (i) CH\(_3\)CN, heat.
Chapter Four

The molecular structure of 13b' consists of a symmetry generated cyclic species (approximately $C_2$-symmetric), in which two $[(L23)(NCMe)_2]Ni_2Cl_4$ units have effectively dimerised by bridging of two chlorides on each unit. Each nickel centre is bound by two nitrogen atoms belonging to the iminopyridine fragment in L23, one nitrogen from a molecule of acetonitrile, two bridging chlorides, and one terminal chloride ligand so as to complete a distorted octahedral geometry. For each nickel centre, the imino nitrogen atom is located $trans$ to one of the two bridging chlorides, whereas the nitrogen atom of the pyridine unit is $trans$ to the molecule of acetonitrile. The two remaining coordination sites are occupied by one bridging and one terminal chloride. The N-Ni-N chelate bite angle for the two bidentate binding domains in L23 is acute [N(1)-Ni(1)-N(2) 78.5(4)°, N(3)-Ni(2)-N(4) 78.2(4)°].

The central cavity of the metallacycle is 13.789 Å in length [C(1A)...C(1AA)] and 8.988 Å in width [Ni(1)...Ni(2A)], whereas the distance between the metal centres in a particular Ni(μ-Cl)$_2$Ni unit [Ni(1)...Ni(2)] is ca. 3.582 Å. As for 7a' and 7d', the Ni-N$_{pyridine}$ distances in 13b' [Ni(1)-N(1) 2.025(9) Å, Ni(2)-N(3) 2.049(11) Å] are significantly shorter than the Ni-N$_{imine}$ ones [Ni(1)-N(2) 2.133(10) Å, Ni(2)-N(4) 2.120(10) Å]; this is likely to be due to the relative donor capacity of a pyridyl nitrogen versus an imino nitrogen (see 1.2.5.2). Surprisingly, the Ni-N$_{MeCN}$ bond distances vary considerably between the two nickel, [Ni(1)-N(5) 2.022(12) Å, Ni(2)-N(6) 2.141(15) Å]; the origin of this variation is uncertain.

As a general observation, the Ni-Cl$_{bridging}$ distances in 13b' [Ni-Cl(1) 2.408(4) Å, Ni(1)-Cl(2) 2.459(4) Å, Ni(2)-Cl(1) 2.367(4) Å, Ni(2)-Cl(2) 2.410(4) Å] are more elongated than Ni-Cl$_{terminal}$ distances [Ni(1)-Cl(3) 2.338(4) Å, Ni(2)-Cl(4) 2.314(5) Å] as has been observed in a number of related complexes. For example, Laine and co-workers reported the X-ray structure of $\{[L11]NiCl_2\}_2$ (6c, see chapter 2), in which two pentacoordinate nickel centres are bound to both terminal and bridging chlorides. As with 13b' Ni-Cl$_{terminal}$ distances in 6c are shorter than the Ni-Cl$_{bridging}$ distances [Ni-Cl$_{terminal}$ 2.273 Å, Ni-Cl$_{bridging}$ 2.337 Å, 2.397 Å].
Table 5 Selected bond distance (Å) and angles (°) for 13b′

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Distance/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)-N(1)</td>
<td>2.025(9)</td>
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<tr>
<td>Ni(1)-N(2)</td>
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<td>Ni(1)-Cl(1)</td>
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<tr>
<td>Ni(1)-Cl(2)</td>
<td>2.459(4)</td>
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<td>Ni(1)-Cl(3)</td>
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<td>Ni(2)-N(3)</td>
<td>2.049(11)</td>
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<td>Ni(2)-N(6)</td>
<td>2.141(15)</td>
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<td>2.367(4)</td>
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<tr>
<td>Ni(2)-Cl(2)</td>
<td>2.410(4)</td>
</tr>
<tr>
<td>Ni(2)-Cl(4)</td>
<td>2.314(5)</td>
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<td>N(1)-Ni(1)-Ni(2)-Cl(2)</td>
<td>89.0(3)</td>
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<td>N(1)-Ni(1)-Ni(2)-Cl(4)</td>
<td>103.5(3)</td>
</tr>
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<td>N(1)-Ni(1)-Ni(2)-Cl(3)</td>
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<td>N(2)-Ni(1)-N(5)</td>
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<td>N(2)-Ni(1)-Ni(2)-Cl(4)</td>
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<td>N(2)-Ni(1)-Cl(1)</td>
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<td>N(2)-Ni(1)-Cl(2)</td>
<td>89.27(15)</td>
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<td>N(2)-Ni(1)-Cl(3)</td>
<td>166.51(16)</td>
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<td>N(2)-Ni(1)-Cl(4)</td>
<td>94.71(13)</td>
</tr>
<tr>
<td>C(10)-C(1A)-C(28A)</td>
<td>112.9(13)</td>
</tr>
</tbody>
</table>

The transformation employed to generate all atoms by symmetry is 1-x, 1-y, 1-z.
Figure 7 Molecular structure of [(L23)₂(NCMe)₄]Ni₄Cl₈ (13b'). All hydrogen atoms, apart from H6 and H24, have been omitted for clarity.
In comparison with related dinickel complexes prepared in this work, the distance found between the two metal centres in a [(L23)(NCMe)2]Ni2Cl4 unit in 13b' is comparable [e.g., Ni...Ni distances range from 8.786 (7b) to 8.934 Å (7d')]. However, in previous reports where less sterically demanding analogues of L22-L26 are employed for supramolecular assembly the corresponding M...M distance [M = Zn(II), Cu(II)] is found to be considerably elongated (up to 11.576 Å).5,13 It is likely that the variation in M...M distance can, in part, be attributed to distortions of the (4-(2-iminopyridine)phenyl)methane ligand backbone that occurs as a result of multiple coordination in these supramolecular species.

The molecular structure of 13e' consists of a centrosymmetric dimeric species adopting an overall chain-like structure, in which four nickel atoms are bound by two L26 ligands (i.e., two Ni atoms per L26). In contrast with 13e', only two nickel centres are connected to each other via bridging chlorides [Ni(1), Ni(1A)]. The central nickel Ni(1) is bound to two nitrogen atoms [N(1), N(2)] from L26, two bridging chlorides [Cl(1) and Cl(1A)] and one terminal chloride ligand [Cl(2)] to give a five-coordinate nickel centre. The geometry at Ni(1) can be best described as an intermediate between distorted square pyramidal and trigonal bipyramid as indicated by the value of its structural index parameter [τ = 0.508].14 On the other hand, the chain-end nickel Ni(2) is bound to two nitrogen atoms [N(3), N(4)] from L26, one nitrogen atom from a molecule of acetonitrile [N(5)] and two terminal chlorides [Cl(3) and Cl(4)]. In this case the geometry of the five-coordinate nickel Ni(2) can be best described as a severely distorted trigonal bipyramid [τ = 0.682]14 with N(3) and N(5) occupying the axial sites and Cl(3), Cl(4) and N(4) the equatorial sites.

For both Ni(1) and Ni(2), the metal-nitrogen distances involving L26 are similar [Ni(1)-N(1) 2.032(2) Å, Ni(1)-N(2) 2.065(2) Å, Ni(2)-N(3) 2.035(2) Å, Ni(2)-N(4) 2.035(2) Å] which is in contrast to that observed for 13b', 7a'-7d', where the Ni-N distances featuring the pyridine donor are significantly shorter than those with the imine. As with 13b' the Ni-Clbridging distances are longer than the Ni-Clterminal ones [Ni(1)-Cl(1) 2.3540(8) Å, Ni(1)-Cl(1A) 2.4412(8) Å vs. Ni(1)-Cl(2) 2.2745(9) Å, Ni(2)-Cl(3) 2.2838(9), Ni(2)-Cl(4) 2.2815(10) Å]. The N-Ni-N bite angles featuring L26 are similar [N(1)-Ni(1)-N(2) 79.19(9)°, N(3)-Ni(2)-N(4) 79.03(9)°] and compare well to those observed in 13b' and 7a'-7d'. The metal-nitrogen distance for the coordinated acetonitrile molecule [Ni(2)-N(3) 2.058(3) Å] is intermediate between the two distances in 13b'.
In 13e', the distance between the two bridged nickel atoms [Ni(1)...Ni(1A)] 3.616 Å is slightly longer than that found in 13b'. The distance between the two chain-end nickel atoms [Ni(2)...Ni(2A)] is 17.397 Å, whereas the two nickel atoms bound on the same ligand [Ni(1), Ni(2)] are positioned at a distance of 8.410 Å apart.

Table 6 Selected bond angles (°) and bond distances (Å) for 13e'

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(1)-N(1)</td>
<td>2.032(2)</td>
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<tr>
<td>Ni(1)-N(2)</td>
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</tr>
<tr>
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<tr>
<td>N(2)-Ni(1)-Cl(1)</td>
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<td>Cl(2)-Ni(1)-Cl(1A)</td>
<td>137.34(3)</td>
</tr>
<tr>
<td>Ni(1)-Cl(1)-Ni(1A)</td>
<td>97.73(3)</td>
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</tbody>
</table>

The transformation employed to generate all atoms by symmetry is 1 -x+1,-y,-z+2.

It is uncertain why aldimine-containing 13b' forms a cyclic structure while the ketimine-containing counterpart 13e' forms a chain structure. However, it could be argued that the variation of structural type (wheel vs. polymer) is due, in part, to the relative donor capability of a ketimine nitrogen versus an aldimine nitrogen (see section 1.2.5).

Sun and Chen reported the X-ray structures of two similar dinickel complexes, [(4-(2-C₅H₄N)(RCN)(3,5-RC₆H₄)₂CH₂)₂Ni₂Br₄ (R = H; R¹ = Me, R = Ph; R¹ = i-Pr) belonging to class I, in which two nickel dibromide units are supported on a single bis(4-(2-iminopyridine)phenyl)methane ligand. Notably neither of these complexes are found to dimerise in the solid state c.f. 13b' and 13e' (Scheme 5). It is possible that this difference in behaviour might be due to the difference of the ligand substituent,
either on the imino function or on the central aryl rings. On another hand, the use of bromide instead of chloride ligand is also likely to be influential.

Table 7 Torsion angle variation and effect on the Ni...Ni distance in 13b' and 13e'.

<table>
<thead>
<tr>
<th>Torsion angle (°)</th>
<th>13b'</th>
<th>13e'</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni-Ni—C=C-C=]</td>
<td>94.5 [Ni(1)-N(2)-C(7)-C(8)], 98.5 [Ni(1)-N(2)-C(8)-C(10)],</td>
<td>85.2 [Ni(2)-N(4)-C(25)-C(26)], 102.4 [Ni(2)-N(4)-C(24)-C(23)]</td>
</tr>
<tr>
<td>Ni...Ni distance (Å)</td>
<td>3.582 [Ni(1)...N(2)], 3.616 [Ni(1)...N(1A)], 8.988 Å [Ni(1)...Ni(1A)], 8.410 [Ni(1)...Ni(2)], 17.397 [Ni(2)...Ni(2A)]</td>
<td></td>
</tr>
</tbody>
</table>
Figure 8 Molecular structure of [(L26)(NCMe)2]Ni4Cl8 (13e'). All the hydrogen atoms have been omitted for clarity.
4.5 Synthesis of [4,4'-bis(α-diimine)diphenylmethane]Ni₂Br₄ (Class J)

In this section, the attempted step-wise preparation of bimetallic nickel complexes (Figure 9: Class J) based on the potentially binucleating ligand, bis((2-(2,6-diisopropylphenyl)imino)-1-methyl-propylidene)diaminodiphenylmethane (L27), will be discussed. By analogy with the well-studied monometallic (α-diimine)Ni systems, precatalysts of class J are expected to behave as polymerisation catalysts but due to the proximity of the two polymerisation-active metal centres some differences in performances may be expected. However, given our experience with facile rearrangement reactions that can occur on making unsymmetrical α-di(aryl)imines (see sections 2.5 and 3.4), synthetic difficulties were anticipated at the ligand synthesis step. Interestingly, during the writing of this work, a report by Schumann et al. indicated that this family of ligands are readily accessible using routine condensation chemistry. Indeed, the resultant nickel complexes have shown high activity for ethylene polymerisation. Nonetheless, we report our own efforts at preparing complexes of class J and compare and contrast our observations with this recent literature report.

![Figure 9 Target system (Class J)](image)

4.5.1 Synthesis of the ligand L27

The reaction of 4,4'-diamino-3,5,3',5'-tetraisopropydiphenylmethane with two equivalents of pure 3-(2,6-diisopropylphenylimino)-butan-2-one in toluene at 50 °C (Scheme 6) overnight leads to an oily mixture of products composed of the target compound L27 and bis(2,6-diisopropylphenylimine) along with starting materials and partially condensed products. Using more extended reaction times did not drive the reaction further. Attempted purification of the reaction mixture by selective precipitation, recrystallisation or column chromatography proved unsuccessful. Moreover, carrying out the reaction in an alternative solvent (e.g., ethanol) or performing the reaction at lower temperature did result in an improvement of the efficiency of the reaction. Surprisingly, Schumann et al. reported that L27 can be prepared using a route related but subtly different to method described above. That is, 3-
(2,6-diisopropyl-phenylimino)-butan-2-one was prepared \textit{in situ} from 2,3-butanedione and treated directly with half an equivalent of the diamine in ethanol for one week at room temperature giving L27 as a yellow powder in moderate yield. It is noteworthy that we have found that the acid catalysed reaction of 2,3-butanedione with one equivalent of 2,6-diisopropylaniline in ethanol at room temperature for 24 hours gives (i.e., conditions employed by Schumann), before work-up, a mixture of starting materials along with a small amount of bis(2,6-diisopropylphenylimine). As a result (and consistent with the approach applied in Chapters Two and Three), we have employed pure 3-(2,6-diisopropyl-phenylimino)-butan-2-one in all subsequent reactions. Nevertheless, rearrangement reactions (to give symmetrical \( \alpha \)-diimines) were prevalent as also observed in Chapters Two and Three. Consequently, given this poor reactivity and inability to purify L27, this direction of the project was not pursued.

\begin{center}
\textbf{Scheme 6 Reagents and conditions:} (i) toluene, cat. H\(^+\), 50 °C.
\end{center}
4.6 Synthesis of [4,4′-bis(iminobipy)diphenylmethane]Fe₂Cl₄ (Class K)

While monometallic iron precatalysts based on a bipyridylimine framework have been developed (see section 2.3), the related bimetallic species, to our knowledge, have not been disclosed. In this section, we target bimetallic diiron complexes of class K based on a bis(2-pyridyl-6-iminopyridine)phenylmethane ligand frame (Figure 10). Both the ligand synthesis and the complexes characterisation will be discussed.

![Figure 10 Target EB systems (Class K); R¹ = Me, i-Pr; R = H, Me.](image)

A related example of a multi-metallic iron precatalyst has been published by Liu and co-workers. The triiron complex XXXVIII (Figure 11) self assembles in the presence of 2,6-diacetylpyridine, 4,4′-diamino-3,5,3′,5′-tetraisopropylidiphenylmethane and iron(II)dichloride.¹⁷,¹⁸ This precatalyst, on activation with MAO, was found to be highly active for ethylene polymerisation and afforded higher MW polymers when compared with the corresponding monometallic bis(iminopyridine)-iron system. On the other hand, Small patented the use of XXIV for the polymerisation of ethylene (Figure 11).¹⁹
4.6.1 Synthesis of ligands L28-L30
The reaction of 4,4'-diamino-3,5,3',5'-tetraisopropydiphenylmethane with 2,2'-bipyridine-6-carboxaldehyde in absolute ethanol at reflux, in the presence of a catalytic amount of formic acid, furnished \([(6-(2'-\text{C}_5\text{H}_4\text{N})(\text{C}_5\text{H}_3\text{N})\text{HCN}(2,6-i-\text{Pr}_2\text{C}_6\text{H}_2))_2\text{CH}_2]\) (L28) in good yield (Scheme 7). Similarly, the reaction of 6-acetyl-2,2'-bipyridine with 4,4'-diamino-3,5,3',5'-tetramethyldiphenylmethane or 4,4'-diamino-3,5,3',5'-tetraisopropydiphenylmethane in ethanol at reflux, in the presence of a catalytic amount of acetic acid, allowed access to \([(6-(2'-\text{C}_5\text{H}_4\text{N})(\text{C}_5\text{H}_3\text{N})\text{MeCN}(2,6-R^1\text{C}_6\text{H}_2))_2\text{CH}_2]\) [R1 = Me (L29); i-Pr (L30)] in moderate to good yield. All the ligands have been characterised by a combination of ESMS, HR mass spectrometry (FAB), IR, ^1H NMR and ^13C NMR spectroscopy.

L28 showed a peak corresponding to its molecular ion (ESMS) at 699 m/z while the IR spectrum revealed an absorption band at 1644 cm\(^{-1}\) corresponding to the imine unit. In the ^1H NMR spectrum of L28, the CH=N signal was seen as a singlet at \(\delta\) 8.34, whereas the CH=N carbon atom was assigned to the signal at \(\delta\) 163.6 in the ^13C NMR spectrum. For L29 and L30 peaks corresponding to their molecular ion (ESMS) were seen at m/z 614 and m/z 727 with the absorption band for the imine unit being observed at 1644 cm\(^{-1}\). Further support for ligand formation (in L29 and L30) was provided by the ^1H NMR and ^13C NMR spectra which show singlets for both the CMe=N methyls (at ca. \(\delta\) 2.25) and the CMe=N carbon atoms (at \(\delta\) 167.3), respectively.

Scheme 7 Reagents and conditions: (i) 2 eq. 6-(2'-\text{C}_5\text{H}_4\text{N})(\text{C}_5\text{H}_3\text{N})\text{CHO}, EtOH, H\(^+\), reflux; (ii) 2 eq 6-(2'-\text{C}_5\text{H}_4\text{N})(\text{C}_5\text{H}_3\text{N})\text{CCH}_3\text{O}, EtOH, reflux.

4.6.2 Synthesis of complexes 14a-14c
The reaction of two equivalents of iron(II)dichloride with L28-L30 in n-butanol at 120 °C overnight gave dark blue \([\text{LxFe}_2\text{Cl}_4]\) [Lx = L28 (14a), L29 (14b), L30 (14c)], respectively in good yield (Scheme 8). Complexes 14a-14c have been characterised by FAB-MS, IR spectroscopy and by magnetic measurements (see Table 8).
In the FAB mass spectra for 14a-14c characteristic mass and isotope distributions for fragmentation peaks consistent with the loss of one chloride ion from their molecular ions were observed. The IR spectra for 14a-14c show absorption bands at ca. 1595 cm\(^{-1}\) for the \(\nu(\text{C=N})\) stretches and support coordination of the imine by being shifted by ca. 40 cm\(^{-1}\) when compared with the free ligands (L28-L30). The magnitude of the magnetic moments (Evans balance at ambient temperature) range from 5.7 to 6.2 \(\mu_b\) and are consistent with the presence of two high spin (\(S = 2\)) non-interacting iron centres (using \(\mu^2 = \Sigma \mu_i^2\), where \(\mu_i\) is the magnetic moment of the individual metal centres). Furthermore, these values are comparable with those determined for the diiron complexes of the class of G (see 3.3; complexes 9a and 9b).

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>(\nu(\text{C=N})^a)</th>
<th>Magnetic moment (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14a</td>
<td>Dark blue</td>
<td>917 [M-Cl]^+</td>
<td>1595</td>
</tr>
<tr>
<td>14b</td>
<td>Dark blue</td>
<td>833 [M-Cl]^+</td>
<td>1593</td>
</tr>
<tr>
<td>14c</td>
<td>Dark blue</td>
<td>945 [M-Cl], 908 [M-2Cl],</td>
<td>1595</td>
</tr>
</tbody>
</table>

\(^a\) recorded in the solid-state (cm\(^{-1}\)); \(^b\) recorded on an Evans balance at ambient temperature (\(\mu_b\))
4.7 Synthesis of [4,4'-bis(2-iminophen) diphenylmethane]M₂Cl₄ (M = Fe, Co) (Class L)

This section will focus on the preparation of bimetallic based on bis(phenanthroline)phenyl methane ligands complexes (class L; Figure 12). As described in Chapter 2 (see section 2.3), the first application of a phenanthroline-imine moiety as a support for a single polymerisation-active metal centre was described. The potential effect of a fused arene ring on the performance of a bipy-imine-supported iron catalyst (Class G) was identified as a reason to develop monometallic iron precatalysts (Class B). Similarly, in this section, we target bis(phenanthroline)-containing diiron systems with view to compare their catalytic performance with the corresponding bis(bipyimine)-containing diiron systems.

![Figure 12](image)

**Figure 12** Target EB systems (Class L): M = Fe, Co; R₁ = Me, i-Pr

### 4.7.1 Synthesis of ligands L₃₁ and L₃₂

The reaction of [1,10]-phenanthroline-2-carboxaldehyde with 4,4'-diamino-3,5,3',5'-tetramethyldiphenylmethane or 4,4'-diamino-3,5,3',5'-tetraisopropyl diphenylmethane in ethanol at 50 °C, in the presence of a catalytic amount of acetic acid, afforded [(4-((2-C₁₂H₁₇N₂)HCN)-3,5-R₁C₆H₂)₂CH₂] [R₁ = Me (L₃₁), i-Pr (L₃₂)] in moderate yield, respectively (Scheme 9). Both L₃₁ and L₃₂ have been characterised by a combination of ES mass spectrometry, IR, ¹H NMR and ¹³C NMR spectroscopy.

![Scheme 9](image)

**Scheme 9** Reagents and conditions: (i) (2-C₁₂H₁₇N₂)CHO, ethanol, 50 °C, cat. H⁺.

In the ES mass spectra of L₃₁ and L₃₂, peaks corresponding to their molecular ions were observed. The formation of an imine in both compounds was confirmed by the
presence of absorption bands in the 1627-1643 cm\(^{-1}\) region corresponding to the \(v(\text{CN})\) stretches. In the \(^1\)H NMR spectra of L31 and L32, the singlets seen at ca. 8.78 were consistent with the protons on the CH=N unit. Due to the poor solubility of L31 and L34 in deuterated chloroform, the \(^{13}\)C NMR spectra gave signals less than predicted for a molecule with \(C_2\) symmetry although the imino-carbon resonances could be observed.

### 4.7.2 Synthesis of complexes 15 and 16

The reaction of two equivalents of iron(II)dichloride with L31 or L32 in \(n\)-butanol at 100 °C overnight gave blue [(Lx)Fe\(_2\)Cl\(_4\)] \(\text{[Lx} = \text{L31 (15a), L32 (15b)]}\) in good yield (Scheme 10). Similarly, the reaction of two equivalents of cobalt(II)dichloride with L32 in \(n\)-butanol at 100 °C overnight gave dark green [(L32)Co\(_2\)Cl\(_4\)] (16) in good yield (Scheme 10). Complexes 15a, 15b and 16 have been characterised by FAB-MS, IR spectroscopy and by magnetic measurements (see Table 9).

![Scheme 10 Reagents and conditions: (i) 2 eq. MCl\(_2\), \(n\)-BuOH, 100 °C (M = Fe, Co).](image)

The FAB mass spectra for 15a, 15b and 16 exhibit characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one or two chloride ions from their molecular ions. The IR spectra for 15a, 15b and 16 reflect the coordination of the two tridentate ligands to the two metal centres with C=Nimine absorption bands being observed between 1605 and 1610 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>(v(\text{C=N})^a)</th>
<th>Magnetic moment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>Blue 852 [M-Cl](^+), 816 [M-2Cl](^+)</td>
<td>1605</td>
<td>5.8</td>
</tr>
<tr>
<td>15b</td>
<td>Blue 965 [M-Cl](^+)</td>
<td>1607</td>
<td>5.6</td>
</tr>
<tr>
<td>16</td>
<td>Dark green 971 [M-Cl](^+)</td>
<td>1610</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\) recorded in the solid-state (cm\(^{-1}\)); \(^b\) recorded on an Evans balance at ambient temperature (\(\mu_b\))
The magnetic moments (Evans balance at ambient temperature) for 15a and 15b are 5.6 and 5.8 $\mu_b$, respectively with their magnitudes being consistent with the presence of two high spin ($S = 2$) non-interacting iron centres (using $\mu^2 = \Sigma \mu_i^2$, where $\mu_i$ is the magnetic moment of the individual metal centres). These values are close to those determined for the fused diiron complexes of class G and H (see 3.5 and 3.6). The magnetic moment determined for 16 is consistent with two high spin ($S = 3/2$) non-interacting cobalt centres.
4.8 Synthesis of [4,4'-bis(2-iminopyridine)diphenyl]Ni₂Cl₄ (Class M)

To pursue our investigation of the effect of proximity on the overall catalytic performance of two closely located active sites a second type of remote encapsulated system was identified. Specifically, precatalysts of class M were targeted in which two aryliminopyridine-nickel units are tethered directly at the 4-position of the aryl group (Figure 13). To the knowledge of the author, this class of EB has no track record for use in olefin polymerisation catalysis. Nevertheless, transition metal complexes have been prepared containing ligands belonging to this family and, in particular, those in which the aryl rings contain no hydrocarbyl substituents.

![Figure 13 Target dinickel EB precatalysts (Class M).](image)

4.8.1 Synthesis of ligands L33-L35

Treatment of 3,5,3',5'-tetramethylbiphenyl-4,4'-diamine or 3,5,3',5'-tetraisopropylbiphenyl-4,4'-diamine with an excess of 2-pyridine carboxaldehyde in absolute ethanol at 50 °C, in the presence of a catalytic amount of formic acid, furnished \[\{(4-(2-C₅H₅N)HCN)₃Cl,5-R₁₂C₆H₂\}\] \[R₁ = Me (L33) and i-Pr (L34)\] in moderate yield (Scheme 11). On the other hand, treatment of 3,5,3',5'-tetramethylbiphenyl-4,4'-diamine or 3,5,3',5'-tetramethylbiphenyl-4,4'-diamine with 2-acetyl-pyridine in absolute ethanol at reflux, in the presence of a catalytic amount of formic acid, gave \[\{(4-(2-C₅H₅N)HCN(3,5-R₂C₆H₂)₂\]\ [R = Me (L35) and i-Pr (L35)] in good yield (Scheme 11). Compounds L33-L35 have been characterised by \(^1\)H NMR, \(^{13}\)C NMR and IR spectroscopy and ES mass spectrometry. In addition, L33 has been the subject of a single crystal X-ray diffraction study (see experimental section).
Slow evaporation of a solution of L33 in ethanol afforded yellow crystals suitable for the X-ray determination. The molecular structure is depicted in Figure 14; selected bond lengths and angles are given in Table 10. The structure of L33 is symmetry generated and consists of two pyridyl-(2,6-dimethylphenyl)imine units linked through the 4-position of the aryl substituent. The imino nitrogen atoms and the pyridine units are quasi planar and adopt a trans configuration [tors. N(1)-C(6)-C(5)-N(2) 179.7°] as has already been seen in the structures of L15 and L22 (see 3.3.1 and 4.3.1). The arrangement of the aryl groups in L33 can be regarded as slightly twisted from the orthogonal [tors. C(9)-C(10)-C(10A)-C(9A) 53.6°] as is also observed between the aryl groups and pyridyl-imine units [tors. C(6)-N(2)-C(7)-C(8) 110.2°].
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Table 10 Selected bond lengths (Å) and angles (°) for L33

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value (Å/°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)</td>
<td>1.3350(15)</td>
</tr>
<tr>
<td>N(2)-C(7)</td>
<td>1.4219(15)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.3406(15)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.4712(15)</td>
</tr>
<tr>
<td>N(2)-C(6)</td>
<td>1.2638(15)</td>
</tr>
<tr>
<td>C(10)-C(10A)</td>
<td>1.483(2)</td>
</tr>
<tr>
<td>C(6)-N(2)-C(7)</td>
<td>118.42(10)</td>
</tr>
<tr>
<td>N(2)-C(6)-C(5)</td>
<td>121.93(11)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)</td>
<td>115.03(10)</td>
</tr>
</tbody>
</table>

The transformation employed to generate all atoms by symmetry is (1-x, y, 0.5-z).

On comparison of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine (see section 4.2) with L33 with, some differences within the diaryl moiety are revealed with the central carbon-carbon bond being slightly longer [1.490(3) Å vs. 1.483(2) (L33)] and the inclination of the aryl rings away from planarity significantly less [tors. 19.6° vs. 53.6° (L33)]. In the related structure of N,N'-bis(salicylidene)-4,4'-biphenylenediamine, the inclination of the aryl rings away from planarity is less (tors. 0.255°) while the linking carbon-carbon bond is longer than for L33 [at 1.499(6) Å].

L33-L35 show peaks corresponding to their molecular ions in their ES mass spectra while their IR spectra support the formation of the imine units with clearly identifiable absorption $\nu(C=N)_{\text{amine}}$ bands between 1640 and 1648 cm$^{-1}$. In the $^1$H NMR spectrum of L33, a singlet at δ 8.35 for CH=N proton is observed while the CH=N carbon is seen at δ 164.0 in the $^{13}$C NMR spectrum. For L35 and L35, the MeC=N protons are observed as singlets at δ 2.18 (L35) and δ 2.19 (L35) while MeC=N carbons are located at δ 167.9 (L35) and δ 166.1 (L35) in their $^{13}$C NMR spectra. The chemical shifts observed for both the aldimine protons and the methyl protons of the ketimine units are comparable with that measured for L22-L24 and L25-L26, respectively.

4.8.2 Synthesis of complexes 17a and 17b

The reaction of two equivalents of nickel(II)dichloride with L33-L35 in n-butanol at 120 °C overnight gave orange [(Lx)Ni$_2$Cl$_4$] [Lx = L33 (17a), L35 (17b)] in moderate yield (Scheme 12). Both 17a and 17b have been characterised by FAB-MS, IR spectroscopy and by magnetic measurements (see Table 11).
Complexes 17a and 17b show characteristic mass and isotope distributions with fragmentation peaks consistent with the loss of one or two chloride ions. Metal coordination was confirmed by the presence of C=N \text{imine} stretching frequencies in the infrared spectra at around 1595 cm\(^{-1}\) and shifted by ca. 45 cm\(^{-1}\) to lower wavenumber when compared with the free ligands. The magnetic moments (Evans balance at ambient temperature) with their magnitudes at 3.8 and 4.3 \(\mu_b\) are consistent with the presence of two high spin (\(S = 1\)) non-interacting nickel centres (using \(\mu^2 = \Sigma \mu_i^2\), where \(\mu_i\) is the magnetic moment of the individual metal centres). These values are consistent with that measured for the dinickel complexes of classes H and I (see 3.3).

Attempted crystallisation of 17a-17b from a variety of solvents did not give crystals suitable for single crystal X-ray diffraction. However, Sun and co-workers have recently reported a related dicobalt species, \([(4-(2-C_6H_4N)PhCN)-3,5-Me_2C_6H_5)_2]Co_2Cl_4(DMF)_2\), using DMF as the crystallising solvent.\(^{23}\) In \([(2-C_6H_4N)CPhN(3,5-Me_2C_6H_5)_2]Co_2Cl_4(DMF)_2\), the distance between the two cobalt atoms supported on the same ligand was 12.614 Å and can be considered as a good estimation for complexes 17a-17b. It is noteworthy that this is longer than measured for complexes of class E [Ni...Ni distances range from 8.786 (7b') to 8.934 (7d')], and class J.
4.9 Conclusions
The aim of this chapter was to prepare a series of remote encapsulated late TM bimetallic precatalysts/catalysts for the polymerisation of olefins. Five classes of complexes (I-M) were targeted, four in which the catalytic components are displaying different binding domains [viz. pyridine imine (Class I), α-diimine (Class J), bipyridine imine (Class K), phenanthroline-imine (Class L)] connected by a methylene unit and one where the two imino-pyridine based components are directly attached (Class M). A similar synthetic methodology to that employed in the previous chapter furnished twelve novel binucleating ligands (L22-L35) and thirteen new bimetallic complexes (13-17: Chart 2). Most of the ligands and complexes were successfully prepared and characterised using various techniques. For each of the complexes of classes I-L, a methylene unit was positioned on the 4-position of the N-aryl ring between the two catalytic components. In contrast, in complexes of class M, the catalytic components were directly connected to each other at their para position of the aryl groups.

The synthesis of complexes of class J proved to be the most challenging due to the capacity of the α-diimine backbone to rearrange, as observed in Chapters Two and Three. The preparation of the corresponding ligands resulted in a mixture of different products that could not be readily isolated. Indeed, as observed before the use of pyridyl-carbonyl compounds as precursor to well-defined binucleating ligands is superior to imino-carbonyl compounds. This direction was therefore abandoned to focus on the development of encapsulated system with a more resistant ligand backbone.

In addition, complexes 13 could be readily derivatised and crystallographically characterised as 13b' and 13e'. Of particular interest was the influence of the substituent of imine coordinated to the metal (aldimine vs. ketimine) to the structure of the resulting complexes.

The performance of these complexes for the polymerisation of ethylene will be discussed in Chapter Six.
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Chart 2: Lists of the ligands and complexes synthesised in Chapter Four.
4.10 References

8 P. Bamfield and P. M. Quan, Synthesis, 1978, 537.
Chapter Five

Linker Functionalisation in Imino-based Remote Encapsulated Bimetallic Nickel Precatalysts

Synthesis and Characterisation
5.1 Introduction
As documented in Chapter One, the electronic properties of a complex play a pivotal role in determining the performance of an olefin polymerisation catalyst. In remote encapsulated bimetallic systems the linker can, in principle, be used as a means of modifying the electronic properties whilst also controlling the proximity of the catalytic components. In this work, we have expressly targeted sites on the ligand frames for catalyst tethering that were considered unlikely to influence the steric properties at the two polymerisation-active metal centres. In Chapter Four, a facile route to methylene-linked (at the aryl 4-positions) EB systems was realised. In this chapter, we have identified the methylene group as a site for functionalisation with a view to introducing electronically variable substituents (Figure 1). Furthermore, by judicious choice of functional group a method of immobilising EB systems on an organic (or inorganic) support could be accessed. To the knowledge of the author, supported late transition metal EB systems have not yet been disclosed.

![Figure 1](image)

**Figure 1** Functionalised EB catalysts; functionalisable group = electronically active group or site for immobilisation.

Herein, we target three classes of EB catalysts/precatalysts (Chart 1: Classes N-P:). In class N, we focus on preparing benzyl-linked iminopyridyl-dinickel halide complexes and systematically varying the electronic properties of the 4-position of the aromatic moiety on the benzyl group. In class O, we have identified the 4-position of the benzyl-linker for the introduction of a polymerisable side arm (e.g., allylic) while in class P, the 4-position is targeted as a site to allow the introduction of a third catalytic component.
5.2 General synthetic strategy
The general methodology applied to the synthesis of the ligands and complexes in the present chapter was similar to that described in Chapters Three and Four (see sections 3.2 and 4.2). However, the functionalised dianiline reactants to be employed for the condensation reactions are novel in most cases; therefore a section will be included on their synthesis and characterisation. In addition, the use of an allyl-functionalised dinickel complex in a radical initiated styrene-based copolymerisation is described with the intent of making immobilised systems.
5.3 Synthesis of functionalised 4,4'-diaminotriphenylmethines

Diaminotriphenylmethines (DTMs) have received considerable attention due to a number of interesting structural properties both in solution and in the solid-state.1 As a result, they have been employed in a wide range of applications (e.g., dyes,2 high performance polymers,3-5 material science,6 copper corrosion inhibitors).7 Although numerous variations of the backbone have been documented, DTMs that incorporate bulky ortho substituents (i.e., with regard to amine functionality) are limited to 4,4'-diamino-3,3',5,5'-tetraisopropyltriphenylmethine; albeit as a brief mention in a patent.8

In this section, the preparation of six members of the 4,4'-diamino-3,3',5,5'-tetraisopropyl-4''-Y-triphenylmethine family of compounds is described (Scheme 1) with particular emphasis being placed on variation of the Y substituent. The synthetic methodology is similar to that employed in Chapter 4 (see section 4.3) for the synthesis of 4,4'-diaminodiphenylmethanes. Typically, an aqueous mixture of 2,6-diisopropylaniline was reacted at elevated temperature with a range of 4-substituted benzaldehydes in the presence of concentrated hydrochloric acid to afford [(4-NH₂-3,5-diPr₂C₆H₂)₂(4-Y-C₆H₄)CH] (Y = H, OH, Br, i-Pr, CH₂CH=CH₂, NO₂) in moderate to low yield (Scheme 1). All the 4-substituted benzaldehydes were commercially available apart from 4-allyl benzaldehyde which could be readily prepared from the two step reaction of an allyl Grignard with 1,4-dibromobenzene followed by a formylation (see experimental section). All the new 4,4'-diamino-3,3',5,5'-tetraisopropyl-4''-Y-triphenylmethines have been characterised by ElectroSpray mass spectrometry (ESMS), ¹H NMR, ¹³C NMR and IR spectroscopy and elemental analysis. In addition, 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine has been the subject of a single crystal X-ray diffraction study (see experimental section).

\[
\text{Scheme 1 Reagents and conditions: (i) 2 eq. 2,6-diPr₂C₆H₃NH₂, H₂O, conc. H⁺, heat.}
\]

Red crystals of [(4-NH₂-3,5-i-Pr₂C₆H₂)₂(4-OH-C₆H₄)CH] suitable for the X-ray diffraction study were grown by prolonged standing of a hexane solution containing the compound. The molecular structure of [(4-NH₂-3,5-i-Pr₂C₆H₂)₂(4-OH-C₆H₄)CH] is depicted in Figure 2, selected bond distances and angles are listed in Table 1. The molecular structure consists of two 4-amino-3,5-diisopropylphenyl units and one phenol.
unit linked at the 1-position on each aryl group by a methine group [C(1)]. The geometry at C(1) can be best described as distorted tetrahedral [C(2)-C(1)-C(8) 112.8(3)°, C(2)-C(1)-C(20) 111.9(3)°, C(8)-C(1)-C(20) 114.3(3)°]. Inspection of the packing picture reveals that adjacent molecules undergo hydrogen bonding interactions between the hydroxyl hydrogen and one amino nitrogen from another molecule [N...H(1) 1.953 Å and N...O(1) 3.070 Å]. To the knowledge of the author, 4,4'-diamino-3,3',5,5'-tetraisopropytriphenylmethines have not previously been the subject of X-ray diffraction studies.\(^8\) McArdle \textit{et al.} reported the structure of the related methine-linked triaryl species 4,4'-dihydroxy-4'''-bromotriphenylmethine\(^9\) and found that the geometry at the central carbon was similar to that observed in [(4-NH\(_2\)-3,5-\(i\)-Pr\(_2\)C\(_6\)H\(_2\))\(_2\)(4-OH-C\(_6\)H\(_4\))CH].

![Molecular structure of (4-H\(_2\)N-3,5-\(i\)-Pr\(_2\)C\(_6\)H\(_2\))\(_2\)(4-OH-C\(_6\)H\(_4\))CH](image)

\textit{Figure 2} Molecular structure of [(4-H\(_2\)N-3,5-\(i\)-Pr\(_2\)C\(_6\)H\(_2\))\(_2\)(4-OH-C\(_6\)H\(_4\))CH], all the hydrogen atoms, apart from H1A, H1B, H1C, H2A and H2B, have been omitted for clarity.
Table 1 Selected bond distances (Å) and angles (°) for 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxytriphenylmethine

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-C(5)</td>
<td>1.363(4)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.529(5)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(8)</td>
<td>112.8(3)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(20)</td>
<td>111.9(3)</td>
</tr>
<tr>
<td>C(1)-C(8)</td>
<td>1.538(5)</td>
</tr>
<tr>
<td>C(1)-C(20)</td>
<td>1.519(5)</td>
</tr>
<tr>
<td>C(8)-C(1)-C(20)</td>
<td>114.3(3)</td>
</tr>
</tbody>
</table>

In the Electrospray mass spectra for [(4-NH₂-2,6-i-Pr₂C₆H₂)₂(4-Y-C₆H₄)CH] (Y = H, OH, Br, i-Pr, CH₂CH=CH₂, NO₂), peaks corresponding to the molecular ion were observed in each case. The formation of the methine bridge was confirmed in the ¹H and ¹³C NMR spectra with singlets observed between δ 5.19 – 5.39 and between δ 55.6 and 57.0, respectively. The influence of the substituted aromatic group on the electronic properties of the molecule can be appreciated by closer inspection of the ¹H NMR chemical shifts for the central methine group (Table 2). For example, the most downfield chemical shift occurs for Y = H whilst the most upfield signal occurs for Y = OH. However, while these extreme differences could be interpreted in terms of the electron donating capability of Y, the data in between these limits are less clear (Table 3).

Table 2 Selected spectroscopic data for [(4-H₂N-3,5-i-Pr₂C₆H₂)₂(4-Y-C₆H₄)CH] (Y = H, OH, Br, i-Pr, CH₂CH=CH₂, NO₂)

<table>
<thead>
<tr>
<th>Y</th>
<th>¹H NMR</th>
<th>¹³C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y = H</td>
<td>5.39</td>
<td>57.0</td>
</tr>
<tr>
<td>Y = OH</td>
<td>5.19</td>
<td>55.6</td>
</tr>
<tr>
<td>Y = Br</td>
<td>5.20</td>
<td>56.0</td>
</tr>
<tr>
<td>Y = i-Pr</td>
<td>5.29</td>
<td>56.3</td>
</tr>
<tr>
<td>Y = CH₂CH=CH₂</td>
<td>5.21</td>
<td>-</td>
</tr>
<tr>
<td>Y = NO₂</td>
<td>5.32</td>
<td>57.0</td>
</tr>
</tbody>
</table>

Interestingly, during our attempted optimisation of the preparation of [(4-NH₂-3,5-i-Pr₂C₆H₂)₂(4-Y-C₆H₄)CH] (Y = H, OH, Br, i-Pr, CH₂CH=CH₂, NO₂), we found that the addition of alcoholic nucleophiles could effect the outcome of the reaction. For example, it was found that addition of methanol to the reaction between 2,6-diisopropylaniline and 4-nitrobenzaldehyde afforded [(4-NH₂-3,5-i-Pr₂C₆H₂)(4-NO₂-C₆H₄)(MeO)CH] in good yield (Scheme 2). On work-up, a yellow powder was obtained and characterised by ES mass spectrometry and ¹H NMR, ¹³C NMR and IR spectroscopy.
Scheme 2 Reagents and conditions: (i) 2 eq. 2,6-i-Pr₂C₆H₃NH₂, H₂O, MeOH, conc. H⁺, reflux.

Furthermore, recrystallisation of [(4-NH₂-3,5-i-Pr₂C₆H₂)(4-NO₂-C₆H₄)(MeO)CH] from hexane gave yellow-green crystals suitable for a single X-ray diffraction study. The molecular structure of [(4-NH₂-3,5-i-Pr₂C₆H₂)(4-NO₂-C₆H₄)(MeO)CH] is depicted in Figure 3 and selected bond angles and distances are listed in Table 3.

Figure 3 Molecular structure of [(4-NH₂-3,5-i-Pr₂C₆H₂)(4-NO₂-C₆H₄)(MeO)CH]. All the hydrogen atoms, apart from H1A, H2A and H2B, have been omitted for clarity.

In agreement with the spectroscopic and spectrometric data, the molecular structure of [(4-NH₂-3,5-i-Pr₂C₆H₂)(4-NO₂-C₆H₄)(MeO)CH] consists of a methine unit bound by a 3,5-diisopropyl-4-aminophenyl group, a 4-nitrophenyl group and a methoxy group with the geometry at the central carbon approximating to tetrahedral [O(3)-C(1)-C(2) 110.3(5), O(3)-C(1)-C(9) 111.8(5), C(2)-C(1)-C(9) 109.9(5)°].

Table 3 Selected bond distances (Å) and angles (°) for 1-methoxy-1-(4-nitrophenyl)-1-(3,5-diisopropyl-4-amino-phenyl)methine.

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-C(2) 1.508(9)</td>
<td>O(3)-C(1) 1.405(8)</td>
</tr>
<tr>
<td>C(1)-C(9) 1.537(9)</td>
<td>O(3)-C(1)-C(2) 110.3(5)</td>
</tr>
<tr>
<td>O(3)-C(1)-C(9) 111.8(5)</td>
<td>C(2)-C(1)-C(9) 109.9(5)</td>
</tr>
</tbody>
</table>

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5.4 Synthesis of [4,4'-bis(2-iminopyridine)-4'''-Y-triphenylmethine] \( \text{Ni}_2\text{Cl}_4 \) (Class N)

In this section, the method employed for the synthesis of complexes of class N (Figure 4) will be described by firstly outlining the procedure for the ligand synthesis and secondly discussing the subsequent complexation reactions. To our knowledge, there are no previous reports of bimetallic complexes containing a functionalised diaminotriphenylmethine unit incorporated into an imino-based ligand manifold. Closely related examples are the dinickel complexes of class I, which possess a bis(4-(2-iminopyridine)phenyl)methane ligand framework (see section 4.3).

![Figure 4 Target complexes (Class N); R = H, Me; Y = H, OH, Br, i-Pr, CH\(_2\)CH=CH\(_2\), NO\(_2\).](image)

5.4.1 Synthesis of ligands L36-L44

Reaction of two equivalents of 2-pyridine carboxaldehyde with 4,4'-amino-3,3',5,5'-tetraisopropyltriphenylmethine, 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxytriphenylmethine, 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-bromotriphenylmethine, 4,4'-amino-3,3',4'',5,5'-pentaisopropyltriphenylmethine, 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-allyltriphenylmethine or 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-nitrotriphenylmethine in ethanol at 50 °C furnished \([(\text{2-C}_5\text{H}_4\text{N})\text{HCN}(3,5-i'-\text{Pr}_2\text{C}_6\text{H}_2)]_2(4-\text{Y-C}_6\text{H}_4)\text{CH}] \ [Y = \text{H (L36)}, \text{OH (L37)}, \text{Br (L38)}, \text{i-Pr (L39)}, \text{CH}_2\text{CH}=\text{CH}_2 (\text{L40}), \text{NO}_2 (\text{L41})]\) in good yield (Scheme 3). Similarly, the reaction of 2-acetyl-pyridine with 4,4'-amino-3,3',5,5'-tetraisopropyltriphenylmethine, 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxytriphenylmethine or 4,4'-amino-3,3',4'',5,5'-pentaisopropyltriphenylmethine in ethanol at reflux, in the presence of a catalytic amount of acid formic, gave \([(\text{2-C}_5\text{H}_4\text{N})\text{CMeN}(3,5-i'-\text{Pr}_2\text{C}_6\text{H}_2)]_2(4-\text{Y-C}_6\text{H}_4)\text{CH}] \ [Y = \text{H (L42)}, \text{OH (L43)}, \text{i-Pr (L44)}]\) in good yield. Compounds L36-L44 have been characterised by \(^1\text{H NMR, } ^{13}\text{C NMR and IR spectroscopy and ES Mass Spectrometry. In addition, L36, L38 and L40 have been the subject of single crystal X-ray diffraction studies (see experimental section). In the case of L39, the low solubility of the sample in CDCl\(_3\) precluded full identification of the expected number of signals in the } ^{13}\text{C NMR spectrum.}

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Yellow crystals of \textbf{L36} and \textbf{L40} along with red crystals of \textbf{L38} suitable for the X-ray diffraction studies were grown from hexane solutions containing the corresponding complex. The molecular structures of \textbf{L36}, \textbf{L38} and \textbf{L40} are depicted in Figure 5, 6 and 7, respectively; selected bond distances and angles are listed in Table 4. Notably the structure of \textbf{L40} is located on a mirror plane while \textbf{L36} and \textbf{L38} are not symmetry-generated. Nevertheless, the structures of \textbf{L36}, \textbf{L38} and \textbf{L40} are similar and will be discussed together. In each case the core structures are based on two iminopyridine 2,6-substituted aryl units linked by a 4-substituted benzyl group at C(19). The nature of the 4-substituted substituent on the benzyl group varies with Y = H for \textbf{L36}, Y = Br for \textbf{L38} and Y = CH$_2$CH=CH$_2$ for \textbf{L40}. As expected, the angles at the sp$^3$-hybridised C(19) atoms do not deviate significantly from a tetrahedral geometry. In the case of \textbf{L38}, the carbon-bromide bond length, at 1.860(4) Å, is slightly lower than that reported by McArdle and co-workers for the structure of 4,4'-dihydroxy-4''-bromo-triphenylmethine [C-Br 1.904(2) Å].$^9$ As has been observed for other iminopyridine-containing ligands described in this work (e.g., \textbf{L15}, \textbf{L22} and \textbf{L33}), the pyridine and imino nitrogen atoms adopt a transoid configuration [tors. N(1)-C(5)-C(6)-N(2) ca. 177.4° (\textbf{L36}), ca. 178.0° (\textbf{L38}) and 174.5° (\textbf{L40})].
Figure 5 Molecular structure of L36. All the hydrogen atoms, apart from H6, H19 and H38, have been omitted by clarity.

Figure 6 Molecular structure of L38. All the hydrogen atoms, apart from H6, H19 and H38, have been omitted by clarity.
### Table 4 Selected bond distances (Å) and angles (°) for L36, L38 and L40

<table>
<thead>
<tr>
<th></th>
<th>L36</th>
<th>L38</th>
<th>L40a</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-C(1)</td>
<td>1.3392(18)</td>
<td>1.309(6)</td>
<td>1.341(5)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.3377(17)</td>
<td>1.317(6)</td>
<td>1.337(5)</td>
</tr>
<tr>
<td>N(2)-C(6)</td>
<td>1.2579(16)</td>
<td>1.243(5)</td>
<td>1.256(5)</td>
</tr>
<tr>
<td>N(2)-C(7)</td>
<td>1.4262(15)</td>
<td>1.419(5)</td>
<td>1.428(5)</td>
</tr>
<tr>
<td>N(3)-C(29)</td>
<td>1.4326(16)</td>
<td>1.416(5)</td>
<td>-</td>
</tr>
<tr>
<td>N(3)-C(38)</td>
<td>1.2589(17)</td>
<td>1.238(5)</td>
<td>-</td>
</tr>
<tr>
<td>N(4)-C(39)</td>
<td>1.3341(18)</td>
<td>1.322(6)</td>
<td>-</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.4729(17)</td>
<td>1.457(6)</td>
<td>1.487(6)</td>
</tr>
<tr>
<td>C(38)-C(39)</td>
<td>1.472(2)</td>
<td>1.475(6)</td>
<td>-</td>
</tr>
<tr>
<td>C(10)-C(19)</td>
<td>1.5289(16)</td>
<td>1.517(5)</td>
<td>1.537(6)</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.5238(17)</td>
<td>1.493(5)</td>
<td>1.527(8)</td>
</tr>
<tr>
<td>C(19)-C(26)</td>
<td>1.5304(17)</td>
<td>1.525(5)</td>
<td>-</td>
</tr>
<tr>
<td>Br(1)-C(23)</td>
<td>-</td>
<td>1.860(4)</td>
<td>-</td>
</tr>
<tr>
<td>C(1)-N(1)-C(5)</td>
<td>116.55(13)</td>
<td>117.1(5)</td>
<td>115.9(4)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)</td>
<td>114.71(12)</td>
<td>115.5(4)</td>
<td>114.6(5)</td>
</tr>
<tr>
<td>C(6)-N(2)-C(7)</td>
<td>118.65(11)</td>
<td>117.0(4)</td>
<td>118.8(4)</td>
</tr>
<tr>
<td>C(38)-N(3)-C(29)</td>
<td>118.17(12)</td>
<td>118.5(4)</td>
<td>-</td>
</tr>
<tr>
<td>N(3)-C(38)-C(39)</td>
<td>122.75(13)</td>
<td>122.3(4)</td>
<td>-</td>
</tr>
<tr>
<td>N(4)-C(39)-C(38)</td>
<td>114.65(14)</td>
<td>114.8(4)</td>
<td>-</td>
</tr>
<tr>
<td>C(20)-C(19)-C(10)</td>
<td>114.54(10)</td>
<td>111.9(3)</td>
<td>114.7(4)</td>
</tr>
<tr>
<td>C(20)-C(19)-C(26)</td>
<td>111.17(10)</td>
<td>113.3(3)</td>
<td>-</td>
</tr>
<tr>
<td>C(10)-C(19)-C(26)</td>
<td>111.08(10)</td>
<td>112.2(3)</td>
<td>-</td>
</tr>
<tr>
<td>C(10)-C(19)-C(10A)</td>
<td>-</td>
<td>-</td>
<td>109.8(5)</td>
</tr>
</tbody>
</table>

*The symmetric atoms were generated by using the transformation (x, 1.5-y, z)*
In the electrospray mass spectra of L36-L44, peaks corresponding to their respective molecular ions are observed in each case. The IR spectra reveal absorption bands ranging from 1640 to 1650 cm\(^{-1}\), which are consistent with the presence of an imine functionality. In the case of L36-L41, the formation of the aldimine group was confirmed by singlets for the CH=N protons observed at ca. \(\delta 8.26\) in their \(^1\)H NMR spectra while the CH=N carbons were seen at ca. \(\delta 163.0\) in their \(^1\)C NMR spectra. On the other hand, the ketimine-containing compounds L42-L44 were identified by the presence of singlets for the CMe=N protons at ca. \(\delta 2.15\) in their \(^1\)H NMR spectra while the CMe=N carbon atoms were seen at ca. \(\delta 167.8\) and in their \(^1\)C NMR spectra. For both the aldimine- and ketimine-containing ligands, these chemical shifts are consistent with what has been measured for L22-L26 (see section 4.3).

As observed for the diaminetriphenyliumethines synthesised in section 5.2, the chemical shift of the central CH proton in L36-L44 is affected by the 4-position substitution on the benzyl aryl group (Table 5). As was discussed for the
diaminetriphenylmethines, the electron donating capability of the substituent on the 4-
position of the benzyl groups benzyl 4-substituent appears to be determining factor with
the most electron withdrawing substituent (NO₂) resulting in the most downfield
chemical shift (δ 5.52). On the other hand little informative information can be gleaned
from inspection of the corresponding ¹³C NMR data.

### Table 5 Selected spectroscopic data for L₃₆-L₄₄

<table>
<thead>
<tr>
<th>Y</th>
<th>Methine carbon</th>
<th>Imine functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH</td>
<td>CH</td>
</tr>
<tr>
<td></td>
<td>¹H NMR⁴</td>
<td>¹²C NMR</td>
</tr>
<tr>
<td></td>
<td>CH=N</td>
<td>¹H NMR</td>
</tr>
<tr>
<td>L₃₆</td>
<td>H</td>
<td>δ 5.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ 8.26</td>
</tr>
<tr>
<td>L₃₇</td>
<td>OH</td>
<td>δ 5.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ 8.26</td>
</tr>
<tr>
<td>L₃₈</td>
<td>Br</td>
<td>δ 5.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ 8.25</td>
</tr>
<tr>
<td>L₃₉</td>
<td>i-Pr</td>
<td>δ 5.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ 8.26</td>
</tr>
<tr>
<td>L₄₀</td>
<td>CH₂CH=CH₂</td>
<td>δ 5.32</td>
</tr>
<tr>
<td>L₄₁</td>
<td>NO₂</td>
<td>δ 5.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ 8.26</td>
</tr>
</tbody>
</table>

⁴CDCl₃

5.4.2 Synthesis of complexes 1₈a-1₈i

Interaction of two equivalents of NiCl₂ with L₃₆-L₄₄ in n-butanol at elevated
temperature overnight gave [(Lₓ)Ni₂Cl₄] [Lₓ = L₃₆ (1₈a), L₃₇ (1₈b), L₃₈ (1₈c), L₃₉
(1₈d), L₄₀ (1₈e), L₄₁ (1₈f), L₄₂ (1₈g), L₄₃ (1₈h), L₄₄ (1₈i)] in good yield (Scheme
4). Complexes 1₈a-1₈i have been characterised by FAB-MS, IR spectroscopy and by
magnetic susceptibility measurements (Table 6).

![Scheme 4 Reagents and conditions: (i) 2 eq. NiX₂ [MX₂ = NiCl₂], n-BuOH, 120 °C.](image)

The FAB mass spectrometric data exhibit characteristic mass and isotope
distributions for 1₈a-1₈i with fragmentation peaks consistent with the loss of one, two
or three chloride ions from the corresponding molecular ion. The presence of two non-
interacting high spin Ni(II) centres (using μ² = Σμᵢ², where μᵢ is the magnetic moment of

the individual metal centres) was supported by the magnitude of the magnetic moments (measured on an Evans balance at ambient temperature) that range from 3.6 \( \mu_B \) to 4.2 \( \mu_B \). These values are consistent with the values obtained for dinickel EB systems of class E, 7a-7d (see section 3.2) and of class I, 13a-13b (see section 4.3). The IR spectra for all complexes reflect the coordination of the imine to the metal by exhibiting the absorption bands corresponding to \( \nu(C=N) \) bands in the 1591 cm\(^{-1}\) to 1598 cm\(^{-1}\) region.

<table>
<thead>
<tr>
<th>Colour</th>
<th>FAB mass spectra</th>
<th>IR ( \nu(C=N) ) ( ^a )</th>
<th>Magnetic moment( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a Green</td>
<td>844 [M-Cl](^+), 809 [M-2Cl](^+), 773 [M-3Cl](^+)</td>
<td>1597</td>
<td>4.2</td>
</tr>
<tr>
<td>18b Red</td>
<td>859 [M-Cl](^+), 824 [M-2Cl](^+)</td>
<td>1595</td>
<td>4.1</td>
</tr>
<tr>
<td>18c Dark blue</td>
<td>922 [M-Cl](^+), 887 [M-2Cl](^+), 851 [M-3Cl](^+)</td>
<td>1597</td>
<td>4.2</td>
</tr>
<tr>
<td>18d Green blue</td>
<td>887 [M-Cl](^+), 850 [M-2Cl](^+), 815 [M-3Cl](^+)</td>
<td>1596</td>
<td>4.2</td>
</tr>
<tr>
<td>18e Green blue</td>
<td>883 [M-Cl](^+), 848 [M-2Cl](^+), 813 [M-3Cl](^+)</td>
<td>1591</td>
<td>3.6</td>
</tr>
<tr>
<td>18f Green</td>
<td>889 [M-Cl](^+), 853 [M-2Cl](^+)</td>
<td>1595</td>
<td>3.8</td>
</tr>
<tr>
<td>18g Green</td>
<td>871 [M-Cl](^+), 836 [M-2Cl](^+), 801 [M-3Cl](^+)</td>
<td>1597</td>
<td>3.9</td>
</tr>
<tr>
<td>18h Dark red</td>
<td>859 [M-Cl](^+), 824 [M-2Cl](^+), 816 [M-3Cl](^+)</td>
<td>1595</td>
<td>4.0</td>
</tr>
<tr>
<td>18i Blue</td>
<td>913 [M-Cl](^+), 878 [M-2Cl](^+), 841 [M-3Cl](^+)</td>
<td>1598</td>
<td>4.1</td>
</tr>
</tbody>
</table>

* recorded in the solid-state (cm\(^{-1}\)); \(^b\) recorded on an Evans balance at ambient temperature (\( \mu_B \)
5.5 Immobilised EB systems (Class O)
The plastic industry manufactures polyolefins by using supported catalysts due to practical advantages (e.g., recyclability, catalyst stability). Traditional supports for late transition metal-based catalysts (i.e., Ni, Fe), have usually employed mainly silica or alumina. In spite of their numerous applications, these inorganic supports can react with the catalyst and lead to its deactivation. Organic materials can potentially provide a more compatible environment for ethylene polymerisation catalysts and have seen a recent surge of interest. Furthermore, organic materials can be easily functionalised to satisfy the specific requirements. It is recognised by the author that this area has been researched extensively in the last decade, but is beyond the scope of this work and will not be developed here.

In the previous section, the 4-position on the benzyl group on the EB system was recognised as a convenient site for electronic variation without affecting the steric properties at the metal centres. Equally, it could be argued that the 4-position could be employed as a site for anchoring the precatalyst/catalyst to a support (inorganic or organic). In this section, we target the synthesis of polystyrene-supported EB systems (Figure 8: Class O) by using the allylic functionality present in 18e as a comonomer for the polymerisation of styrene.

A similar approach has been reported by Jin et al. for supporting bis(imino)pyridine-iron catalysts (Figure 9) in which the 4-positions on the aryl positions have been employed as the site or sites for immobilisation. Their application for ethylene polymerisation revealed high activities but leading to broad molecular weight distributions. More recently, this same group applied this method to immobilise α-diiimine-nickel precatalysts on a polystyrene support. The supported catalysts, under identical polymerisation conditions, showed high activity, comparable and, in some cases superior, to that observed for the non-supported catalysts.
Chapter Five

5.5.1 Immobilisation strategy

The copolymerisation of 18e with styrene in toluene at 80 °C in the presence of AIBN (2.5 eq) yielded after 12 hours (PS-L40)Ni2Cl4 (19) as a dark brown powder (Scheme 5). The IR spectrum for 19 revealed bands at 1601 cm⁻¹ indicative of the polystyrene while no bands representative of the allyl functionality present in the monomer [ν(C=C)₉ 1633 cm⁻¹ in 18e] could be observed. No further characterisation or purification of 19 was carried out and was used in this state for alkene polymerisation screening (see Chapter Six)

\[ 18e \text{[(L40)Ni₂Cl₄]} \quad 19 \text{[(PS-L40)Ni₂Cl₄]} \]

Scheme 5 Reagents and conditions: (i) xs. CH₂=CH(C₆H₅), AIBN (2.5 eq.), C₇H₈, 80 °C.
5.6 Linker derivatisation towards trimetallic systems (Class P)

In sections 5.4 and 5.5, the 4-position on the benzyl aryl group was modified for inducing electronic variations on the ligand manifold and as a site for tethering the EB system to a support, respectively. In this section, our efforts at utilising the 4-position as a means of introducing a third catalytic component (class P) is discussed.

As explained previously in section 5.2, the reaction of various benzaldehydes with 2,6-diisopropylaniline allowed access to a series of compounds with a diaminotriphenylmethine frame. This reaction appeared to offer more synthetic opportunities, notably by furnishing new precursors for ligand synthesis. The following section will discuss of our attempts to target and synthesise suitable compounds to eventually generate a new type of remote trimetallic precatalyst (Figure 10: Class P).

![Figure 10 Target trimetallic encapsulated precatalysts (Class P).]

The procedure employed for the synthesis of unsymmetrical diaminotriphenylmethine, (i.e., each aniline possess different ortho-substituents to the amine) could potentially allow access to encapsulated trimetallic systems with inequivalent catalytic components. A pathway was designed to afford 4,4',4''-triamino-3,5-diisopropyl-3',5'-dimethylphenylmethane by reducing 4,4'-diamino-3,5-tetraisopropyl-4''-nitrotriphenylmethine (Scheme 6).

![Scheme 6 Reagents and conditions: (i) 5 eq. SnCl₂, H⁺(11M), EtOH; (ii) 3 eq. (2-C₅H₄N)CHO, EtOH]

Treatment of 4,4'-diamino-3,5-tetraisopropyl-4''-nitrotriphenylmethine by tin(II) dichloride in a mixture of ethanol and hydrochloric acid afforded 4,4',4''-triamino-3,5-
diisopropyl-3',5'-dimethylphenylmethane in modest yield. However, the reaction of the triamine with three equivalents of 2-pyridine carboxaldehyde gave a mixture composed by a small amount of the target product and byproducts generated by uncompleted condensation reactions. All our attempts to optimise the reaction failed to improve the yield and thus this direction was abandoned.
5.7 Conclusions

In summary, we have established a general methodology to synthesise a series of functionalised dianimotriphenylmethines [(4-H_2N-3,5-Pr_2C_6H_2)_2(4-Y-C_6H_4)CH] (Y = H, OH, Br, i-Pr, CH_2CH=CH_2, NO_2). These compounds have been employed to generate imino-containing binucleating ligands [((2-C_2H_4N)HCN(3,5-Pr_2C_6H_2))_2(4-Y-C_6H_4)CH] [Y = H (L36), OH (L37), Br (L38), i-Pr (L39), CH_2CH=CH_2 (L40), NO_2 (L41)] and [((2-C_2H_4N)MeCN(3,5-i-Pr_2C_6H_2))_2(4-Y-C_6H_4)CH] [Y = H (L42), OH (L43), i-Pr (L44)]. The ligands, L36-L44, have been employed as bis(bidentate) supports for two nickel dihalide units affording bimetallic complexes (Lx)Ni_2Cl_4 [Lx = L36 (18a), L37 (18b), L38 (18c), L39 (18d), L40 (18e), L41 (18f), L42 (18g), L43 (18h), L44 (18i)] in good yields. In addition, the allyl-containing complex 18e has been supported on polystyrene to give (PS-L40)Ni_2Cl_4 (19). All the new complexes have been characterised by a variety of techniques including FAB mass spectrometry, IR spectroscopy and magnetic susceptibility measurements (Chart 2). In addition, our attempts to prepare trimetallic encapsulated precatalysts were discussed.

The performance of these new remote functionalised bimetallic complexes as precatalysts for ethylene polymerisation will be discussed in Chapter Six.
Chapter Five

5.8 References

Chapter Six

Catalytic Evaluation

EB versus Monometalic Systems as Ethylene Polymerisation Catalysts
6.1 Introduction
This chapter will be concerned with the evaluation for the polymerisation of ethylene of the complexes synthesised in Chapters Two to Five. As explained in section 1.4, one of the key objectives of this thesis was to investigate the effect of having two polymerisation-active late transition metals on the same binucleating ligand framework [i.e., encapsulated bimetallic (EB) systems] with a view to probing possible cooperative interactions. To make valid comparisons, we have also prepared a series of related monometallic precatalysts, many of which have no track record in alkene polymerisation (see Chapter Two). Furthermore, we have identified that in these monometallic systems the 4-position on the imino-aryl group can be used both to induce electronic variation and to link the precatalysts for the construction of the EB system. In addition, it was hoped that this strategy would shed some light on the role of electronic properties in EB systems.

The four generic types of system developed in this work are shown in Figure 1 [viz, monometallic (Classes A-D), fused encapsulated bimetallic (Classes E-H), remote encapsulated (Classes I-M) and functionalised remote encapsulated (Classes N-O)]. For purposes of clarity, the catalytic evaluation conducted in this chapter will be broken down into sections based on the type of ligand binding domain which in turn reflects the metal centre to be employed [viz., imino(bipyridine)-iron, iminopyridine-nickel and iminophenanthroline-iron]. It was considered that in this way the performance of a particular catalytic component could be more significantly correlated with the number of metal centres and the proximity of the metal centres.

Firstly, the standard conditions employed for the catalytic evaluation will be defined (section 6.2). Secondly, the performance of the precatalysts (sections 6.3-6.5) will be investigated before presenting our conclusions about the use of encapsulated bimetallic
precatalysts compared to their most closely related monometallic analogues (section 6.6).

6.1.1 General ethylene polymerisation procedure
Various parameters are highly influential on the performance of a metal-mediated polymerisation and have to be defined prior to the screening and maintained constant to allow continuity between the runs (e.g., run time, temperature, ethylene pressure, solvent, co-catalyst). Unless otherwise stated, the temperature, the duration of the run and the ethylene pressure were fixed for all runs at 20 °C, one hour and one bar, respectively. As all the complexes synthesised in the previous chapter consist of ligand-supported metal halide units, methylaluminoxane (MAO) was employed as the co-catalyst due to its ability to facilitate both the alkylation and the abstraction steps required for the activation of the precatalysts (see section 1.2). In all cases we have employed a M:Al(MAO) ratio of 1:400. Toluene was used as solvent as it is a good media for the reagents, products and catalysts, while being inert under the catalytic conditions employed, easy to handle and inexpensive.

The general screening procedure involves treating the precatalyst (e.g., 0.01 mmol) in toluene (40 ml) with an excess of MAO (400 molar eq. per metal centre) in a Schlenk vessel prior to the introduction of the ethylene gas (Scheme 1). The screening procedure was validated by employing a variety of well-known monometallic polymerisation catalysts [e.g., (z-PrPDI)FeCl₂:MAO] and comparing the activities of our runs against the previously reported values. It is worthy of note that when a run was carried out using only MAO and exempt of a precatalyst, no polymerisation activity was observed.

![Scheme 1 Typical olefinic products produced from a metal-mediated polymerisation of ethylene.](image)

Typically, a run generates either a blend of oligomers (C4-C40) and polymers (>C40), or a single pure fraction of either oligomeric or polymeric material. The polymeric and oligomeric fractions could be conveniently isolated by filtration and/or extraction of the organic phase, respectively. The solid polymer would then be washed
with methanol and dried under reduced pressure at 40 °C overnight while the organic solvent soluble fraction dried to give the oligomers as waxy materials.

In general, the oligomeric/polymeric material produced can adopt one of the four types of unsaturation as shown in Scheme 1 (viz., \( \alpha \)-olefin, internal olefin, trisubstituted and vinylidene). In addition, branched variations of the above are also possible. It is noteworthy that it can be difficult to study the properties of the polymeric fractions by more routine techniques (e.g., GC, NMR spectroscopy) due, in the main, to the low solubility of solid PE in most organic solvents at ambient temperature. Our attention has been focused principally on the organic solvent-soluble oligomers, although some data (e.g., DSC, GPC) have been collected for the solid polymeric materials. GPC gives information about the molecular weight and molecular weight distribution of the polymer while DSC can give an indication of the crystallinity and of the type of polymer.

GC analyses were performed on the oligomeric fractions produced and allowed information to be determined about the distribution of the oligomeric fraction. The distribution of the oligomers is indicative of a mechanism where chain transfer is competitive with chain propagation. In most cases, a Schulz-Flory\(^1\text{-}^3\) distribution of oligomers prevails (see appendices) and can be described by the parameters \( \alpha \) and \( \beta \) (i.e., \( \alpha \) represents the probability of chain propagation while \( \beta \) is the ratio between the rate of chain transfer and the rate of chain propagation). Further complementary information on the oligomeric portion can be determined from both \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopies which can shed light on the linearity and the type of unsaturation.

### 6.1.2 Glossary of Metal-mediated Olefin polymerisation

**Activity**: measure the productivity of the catalyst for the production of polymer and is expressed in g mmol\(^{-1}\) of catalyst.bar\(^{-1}\).h\(^{-1}\). The rating of activity for polymerisation of ethylene is classified as followed very low (<1), low (1-10), moderate (10-100), high (100-1000) and very high (1000-10000). Regardless the catalyst involved, its performance for the polymerization of olefin is a function of the catalyst activity, lifetime, initiation, and decay, are intimately tied to ligand structure, cocatalyst, temperature, olefin concentration, and other factors, as are the polymer molecular weights, molecular weight distributions, and degrees of branching.

**Lifetime**: gives vital information and is related to the amount of time during the catalyst is considered to be still active
Turnover Number (TO) and Turnover frequencies (TOF): is determined by the rate of reactant molecules converted by the moles of catalyst used and the time needed.

Number average molecular weight ($M_n$): is the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample.

Weight average molecular weight, ($M_w$): is the ratio of the average mass per formula unit of a substance to 1/12 of the mass of an atom of nuclide $^{12}$C.

Polydispersity index (PDI): is the ratio of the weight average molecular weight to the number average molecular weight and reveal the shape of the molecular weight distribution.

Polymer microstructure: the polymer can be linear to highly branched (i.e., number, length of branches and additional ramification) and as result possess very different properties.
6.2 Evaluation of iminobipyridine-containing iron precatalysts

This section reports the results of the screening for the polymerisation of ethylene of iron precatalysts supported on ligands incorporating at least one imino(bipyridine) unit (Chart 1, Classes B, G and L). Specifically, the performance of precatalysts 3a, 3b, 9a, 9b, 14a and 14c will be discussed in terms of the activity and also on the basis of the microstructures of the oligomers/polymers produced. Finally, our interpretation and conclusions will be presented with special regard being paid to any differences observed between the use of monometallic and the corresponding encapsulated bimetallic iron precatalysts/catalysts whilst also noting any proximity effects within related encapsulated systems.

![Chart 1](image)

6.2.1 Background

Among the numerous ligand derivatisations that have been carried out on the original bis(imino)pyridine ligand backbone (see section 1.2.3), only two reports mentioned the use of imino(bipyridine)-supported iron catalysts.\(^4\)\(^5\) Gibson and co-workers disclosed the preparation and the screening for the polymerisation of ethylene of \([N-(1-(2,2'-bipyridin)-6-ylethylidene)-2,6-diisopropylbenzenamine]FeCl_2\) (Chart 1: 3b). On treatment with excess MAO, 3b was highly active for the oligomerisation of ethylene and afforded short chain \(\alpha\)-olefins (mainly C6 and C8).\(^5\) The aldimine analogue (3a) has been mentioned in a patent\(^4\) and, to our knowledge, there are no other reports about the ethylene polymerisation capacity of this system. Needless to say, no reports have been disclosed about the use of encapsulated imino(bipyridine)-containing iron precatalysts.
On the other hand, the use of bis(imino)pyridine motif to form encapsulated systems has received some attention by a few groups. Small reported a moderately active system in which two iron centres are supported on the same ligand containing two bis(arylimino)pyridine pockets connected by an methylene bridge (Figure 3: XXIV).6 Liu and co-workers7, 8 claimed to have prepared cyclic trimetallic complexes (XXXVIII). The comparison between XXXVIII with the corresponding bis(imino)pyridine mono-iron system under similar conditions for ethylene polymerisation (i.e., pressure, temperature and cocatalyst) reveals that the encapsulated system displays higher activity and longer catalytic lifetimes. High molecular weight polyethylene with broader MWD’s are produced and the microstructure of the polyethylene is consistent with highly linear α-olefins.

6.2.2 Screening of 3a, 3b, 9a, 9b, 14a and 14c
Using the procedure defined in section 6.2, the complexes were screened for the polymerisation of ethylene; the results are compiled in Table 1. All oligomers produced by runs 1-6 have been the subject of 1H and 13C NMR spectroscopy and GC analysis. The α and β values determined from GC are contained in Table 1, while the results of the 1H NMR analysis are listed in Table 2.

All the precatalysts screened were active for alkene oligomerisation and/or polymerisation with activities ranging from 40 (run 6: remote EB system 14c) to as high as 800 g/mmol·h·bar1 (run 3: fused EB system 9a), with the remaining runs showing an average activity of 100 g/mmol·h·bar1. The performance of monometallic 3b was consistent with the high activity for the oligomerisation to give mainly 1-octene (ca.
600 g/mmol⁻¹ h⁻¹ bar⁻¹ at 5 bar ethylene pressure) as reported by Gibson and colleagues.⁵ Significantly, the proportion of polymer varies considerably from 0% (runs 1-2; monometallic systems) to 63% (run 4; EB systems) (Graphic 1). On inspection of the activities displayed for the monometallic (runs 1-2) and the fused and remote encapsulated systems (runs 3-6), it is observed that their magnitudes do not correlate with the number of polymerisation-active metal centres present. For example, run 3 (bimetallic-9a) displays an activity almost eight times that of run 1 (monometallic-3a) while the activity in run 4 (bimetallic-9b) is comparable with that in run 2 (monometallic-3b). With regard to the encapsulated systems it can be seen that the fused systems (9a, 9b) are more active than the remote systems (14a, 14c), while polymeric product is a feature of all the runs employing EB systems. It is noteworthy that a similar observation concerning the molecular weight variation has been reported by Liu and co-workers using encapsulated trimetallic XXXVI (Figure 3).⁷,⁸

### Table 1 Results obtained from screening precatalysts 3a, 3b, 9a, 9b, 14a and 14c (runs 1-6) for ethylene polymerisation

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Oligomer</th>
<th>Polymer</th>
<th>Activity</th>
<th>Polymer%</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>1.050</td>
<td>0</td>
<td>105</td>
<td>0</td>
<td>0.52</td>
<td>0.93</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>1.400</td>
<td>0</td>
<td>140</td>
<td>0</td>
<td>0.52</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>9a*</td>
<td>3.435</td>
<td>0.562</td>
<td>800</td>
<td>14</td>
<td>0.96</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>9b*</td>
<td>0.210</td>
<td>0.358</td>
<td>114</td>
<td>63</td>
<td>0.77</td>
<td>0.30</td>
</tr>
<tr>
<td>5</td>
<td>14a</td>
<td>0.476</td>
<td>0.401</td>
<td>88</td>
<td>46</td>
<td>0.74</td>
<td>0.34</td>
</tr>
<tr>
<td>6</td>
<td>14c</td>
<td>0.291</td>
<td>0.112</td>
<td>40</td>
<td>28</td>
<td>0.56</td>
<td>0.79</td>
</tr>
</tbody>
</table>

*General Conditions*: Toluene (40 ml), 25 °C, reaction time 1 hr, 400 eq. MAO per metal centre, ethylene pressure 1 bar (100 kPa), reaction quenched with dilute HCl; b measured in g; °g/mmol⁻¹ h⁻¹ bar⁻¹ (based on the sum of the mass of oligomer + mass of polymer); d[mass of polymer/mass of oligomer + mass of polymer] x 100; e probability of chain propagation; f rate of chain transfer/rate of chain propagation; *reaction time 0.5 hr.

The a and β values determined for the oligomeric products for each run (1-6) are, in general, consistent with the proportion of polymer observed (Graphic 2). That is, as the a value (probability of chain propagation) increases the amount of higher molecular weight polymer increases. For example, run 4 results in a a value of 0.77 and 63% of polymer while in run 1 0% polymer corresponds to an a value of 0.52. It is uncertain why in run 3 the large a value does not correlate with the percentage of polymer.
$^1$H and $^{13}$C NMR spectroscopy analysis were performed on the oligomeric products for runs 1-6 to determine information about the microstructure and, in particular, the type of chain ends present. Selected results are contained in Table 2 and represented in Graphics 3 and 4.
Table 2 Interpretation of the $^1$H NMR spectroscopic data for runs 1-6

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Methyl chain ends</th>
<th>Olefinic groups</th>
<th>Terminal</th>
<th>Internal</th>
<th>Trisub.</th>
<th>Vinyl.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Unsat.</td>
<td>Add.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3a</td>
<td>90.38</td>
<td>78.26</td>
<td>12.12</td>
<td>75.74</td>
<td>1.22</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>95.05</td>
<td>78.25</td>
<td>16.8</td>
<td>72.88</td>
<td>2.69</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>9a</td>
<td>56.03</td>
<td>48.55</td>
<td>7.48</td>
<td>44.23</td>
<td>2.16</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>9b</td>
<td>69.81</td>
<td>68.29</td>
<td>1.53</td>
<td>55.74</td>
<td>6.27</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>14a</td>
<td>70.99</td>
<td>63.15</td>
<td>7.84</td>
<td>59.89</td>
<td>1.61</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>14c</td>
<td>73.52</td>
<td>63.26</td>
<td>10.26</td>
<td>57.16</td>
<td>2.8</td>
<td>0</td>
</tr>
</tbody>
</table>

* recorded in CDCl$_3$ at ambient temperature; * per 1000 carbon atoms; * additional chain ends = total – unsaturated chain ends

For all runs, the main oligomeric product consists of linear α-olefins (91-99%) along with small amounts of internal olefins (2-9%) (Graphic 3). Some evidence for trace quantities of vinylidene groups can also be determined although the poor signal to baseline ratio makes the precise value difficult to quantify. Inspection of the ratio of saturated to unsaturated chain ends in all runs reveals an approximate 1:1 ratio indicative of β-H chain transfer processes being operative. In addition, the $^{13}$C NMR spectra for all the oligomeric fractions was consistent with the presence of linear oligomers. In the GC mass spectra, further support for the presence of mainly one olefin unsaturation type was revealed by the presence of single molecular ion peaks separated by 28 Daltons and in the range C6 to C30. The DSC analysis performed on the polyethylene from 9a and 9b revealed that the melting temperature ($T_m$), the temperature of crystallisation ($T_c$) and the crystallinity are consistent with linear low molecular weight polyethylene. GPC analysis were performed on samples from 14a and 14c and confirmed that the polyethylene was low molecular weight polymer with broad MWD (Table 3).

Table 3 GPC data for polymers obtained from runs 5 and 6

<table>
<thead>
<tr>
<th>Run</th>
<th>Precatalyst</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Pdi</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>14a</td>
<td>3348</td>
<td>15406</td>
<td>4.60</td>
</tr>
<tr>
<td>6</td>
<td>14c</td>
<td>1834</td>
<td>30080</td>
<td>16.40</td>
</tr>
</tbody>
</table>

* GPC traces were recorded using PL gel 2 × mixed bed – C, 30 cm, 5 micron columns, 1,2,4-trichlorobenzene eluent and a flow rate of 1.0 ml/min at 160 °C using a refractive index detector.
Encapsulated di-iron systems based on imino(bipyridine) binding domains (9a, 9b, 14a, 14c) have been shown to afford higher molecular weight PE when compared with their most closely related monometallic counterparts (3a, 3b). It is noteworthy that the microstructure of polyethylene is linear with mainly terminal olefins present in all cases (Scheme 2).

Scheme 2 Predominant olefinic type generated using 3a, 3b, 9a, 9b, 14a or 14c as precatalyst; (i) Fe precat./xs. MAO.

The type of polyethylene produced by 9a, 9b, 14a, 14c, is characteristic of iron catalysts reported to date.\textsuperscript{5,9,10} For instance, the propagation step is believed to follow a Corsee-Alman mechanism (see section 1.1.4). The termination pathway is believed to follow a chain transfer to metal step, which can follow three different mechanisms (Scheme 3). Notably, both the \( \beta \)-H transfer to metal and the \( \beta \)-H transfer to monomer result in terminal olefins while the chain transfer to aluminum produce only saturated polyethylene.\textsuperscript{5,9,10}
Three factors (i.e., steric, electronic or catalysts interaction, see Chapter One) can explain the variation of catalytic performance of the EB systems compared to their monometallic counterparts. 3a, 3b, 14a and 14c are all supported on ligands with comparable steric properties imparted by the o-aryl isopropyl substituents on the polymerisation-active metals, thus suggesting that steric is not the origin of the variation. Indeed, reduced steric protection (9a, 9b) still leads to products based on increased polymeric content.

For runs 1-6, all oligomers obtained display similar linear microstructures without any evidence of branches. As documented in section 1.3, cooperation between several metal centres has been mainly observed when one metal incorporates short chain oligomers produced by the other metal centre resulting in increased branching (see section 1.3). However, iron-based systems do not have a track record for the incorporation of \( \alpha \)-olefins into a polyethylene chain. Nevertheless, the broad molecular weight distribution in these EB systems cannot rule out some type of interaction between the polymerisation-active metal centres leading to a blend of oligomer and polymer.

As indicated in Chapter One (section 1.2.5), electronic properties can be preponderant in dictating the performance of a late transition metal polymerisation catalyst. It, therefore, seems reasonable to suppose that the precatalytic components and the linker can modify the electronic properties of the overall system. For instance in this work, the 4-position of the imino-aryl group has been consistently employed for the tether of the two catalytic component systems in all the encapsulated systems developed. This particular configuration for the two catalysts was chosen to keep the
steric properties constant while allowing some communication between the metal centres.

Furthermore, it is unclear how the MAO activator will facilitate its alkylation/abstraction role in an EB system. For example, it could simultaneously alkylate/abstract at both sites or it could take place in a stepwise fashion in any permutation of the metal centre and alkylation/abstraction steps.
6.3 Evaluation of iminopyridine-containing nickel precatalysts

In this section, the results of the screening for the polymerisation of ethylene employing nickel precatalysts supported by ligands incorporating at least one iminopyridine unit are reported (Chart 2, Classes D, E, I, M, N and O). As in the previous catalytic performance discussion, the focus will be on the activity and the microstructure of the oligomers/polymer produced, in this case, by employing precatalysts 6a-6f, 7a-7d, 13a-13e, 17a, 18a-18f and 19. This discussion will be supplemented by our interpretation and conclusions with special regard being paid to any differences observed between the use of monometallic and the corresponding encapsulated bimetallic nickel precatalyst/catalyst whilst also noting any proximity effects within related encapsulated systems (fused vs. remote). In addition, the effect of ‘long-distance’ electronic properties on a remote encapsulated bimetallic ligand manifold will be probed, as will the immobilisation of one of these systems.

- **Class D**
  - 6a: R = H; R' = Me; R'' = H
  - 6b: R = H; R' = Me; R'' = Me
  - 6c: R = H; R' = i-Pr; R'' = H
  - 6d: R = Me; R' = Me; R'' = Me
  - 6e: R = Me; R' = i-Pr; R'' = Me

- **Class E**
  - 7a: X = Br; R = R' = H
  - 7b: X = Br; R = R' = Me
  - 7c: X = Br; R = H; R' = Me
  - 7d: X = Cl; R = R' = H

- **Class M**
  - 17a

- **Class N**
  - 18a: Y = H
  - 18b: Y = OH
  - 18c: Y = Br
  - 18d: Y = i-Pr
  - 18e: Y = CH₂CH=CH₂
  - 18f: Y = NO₂

- **Class O**
  - 19

**Chart 2** Precatalysts 6a-6f, 7a-7d, 13a-13e, 17a, 18a-18f and 19 screened for ethylene polymerisation.
6.3.1 Background

Iminopyridine ligands as supports for group 10 polymerisation-active metal centres (mainly nickel and palladium) were initially reported by Laine et al.\textsuperscript{11-14} These systems have also been the subject of a number of patents.\textsuperscript{15, 16} More recently, this family of catalysts has been reviewed by Alt and co-workers.\textsuperscript{17} All the catalysts tend to exhibit high activities that range from 140 to 1400 g/mmol\textsuperscript{-1} h\textsuperscript{-1} bar\textsuperscript{-1}. Like their \(\alpha\)-diimine group 10 counterparts, these systems produce highly isomerised and branched olefins, although generally with much lower molecular weights.\textsuperscript{16, 18}

The construction of a binucleating ligand manifold containing two iminopyridine binding domains to form EB system has seen a recent surge of interest (see section 1.3.2). Indeed during the writing of this thesis, Sun and Chen reported the screening of complexes of the type XXVIII for the polymerisation of ethylene (Figure 5).\textsuperscript{19} Under their conditions (i.e., 2000 eq. MAO, 4-5 bar of C\(_2\), at 20 °C), XXVIII/MAO displayed high activities and afforded mainly low MW polymer blended with a small amount of oligomer. The analysis of the PE revealed highly branched microstructures with internal olefins being the predominant olefin unsaturation type.

\[ \text{XXXVIII} \]

| R = H; R\(^1\) = R\(^2\) = Me (13a) |
|---|---|
| R = H; R\(^1\) = R\(^2\) = Et (13b) |
| R = H; R\(^1\) = \(\cdots\)Pr; R\(^2\) = Me |
| R = Ph; R\(^1\) = R\(^2\) = Me |
| R = Ph; R\(^1\) = R\(^2\) = Et |
| R = Ph; R\(^1\) = \(\cdots\)Pr; R\(^2\) = Me |

| \[ \text{Figure 5} \text{ Examples of recently reported remote EB precatalysts.} \textsuperscript{19} \] |

6.3.2 Screening of 6a-6f, 7a-7d, 13a-13e, 17a, 18a-18f and 19

Using the procedure outlined in section 6.2, the complexes 6a-6f, 7a-7d, 13a-13e, 17a, 18a-18f and 19 have been screened for the polymerisation of ethylene (Chart 2); the results are compiled in Table 3. All oligomers produced by runs 7-29 have been the subject of \(^1\)H and \(^13\)C NMR spectroscopic analysis in addition to GC. The \(\alpha\) and \(\beta\) values obtained from GC calculations are contained in Table 3, whereas the results of the \(^1\)H NMR analysis are compiled in Table 4. In order to discuss the large number of results, we have divided the following sections on the basis of: general features; monometallic catalysts; EB (fused and remote) versus monometallic catalysts; unsymmetrical EB catalysts; remote EB versus fused and immobilised EB catalysts.
### Table 3 Results obtained from screening precatalysts 6a-6f, 7a-7d, 13a-13e, 17a, 18a-18f and 19 (runs 7-29) for ethylene polymerisation

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Oligomer&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Polymer&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Activity&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Polymer%&lt;sup&gt;d&lt;/sup&gt;</th>
<th>α&lt;sup&gt;e&lt;/sup&gt;</th>
<th>β&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6a</td>
<td>2.134</td>
<td>0.475</td>
<td>522</td>
<td>18</td>
<td>0.85</td>
<td>0.18</td>
</tr>
<tr>
<td>8</td>
<td>6b</td>
<td>1.153</td>
<td>0.901</td>
<td>205</td>
<td>44</td>
<td>0.80</td>
<td>0.26</td>
</tr>
<tr>
<td>9</td>
<td>6c</td>
<td>1.384</td>
<td>0.814</td>
<td>220</td>
<td>37</td>
<td>0.85</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>6d</td>
<td>2.012</td>
<td>0</td>
<td>201</td>
<td>0</td>
<td>0.82</td>
<td>0.22</td>
</tr>
<tr>
<td>11</td>
<td>6e</td>
<td>2.472</td>
<td>0.188</td>
<td>260</td>
<td>7</td>
<td>0.79</td>
<td>0.27</td>
</tr>
<tr>
<td>12</td>
<td>6f</td>
<td>2.189</td>
<td>0.819</td>
<td>301</td>
<td>27</td>
<td>0.74</td>
<td>0.36</td>
</tr>
<tr>
<td>13</td>
<td>7a</td>
<td>0.320</td>
<td>0.770</td>
<td>218</td>
<td>70</td>
<td>0.88</td>
<td>0.14</td>
</tr>
<tr>
<td>14</td>
<td>7b</td>
<td>0.060</td>
<td>1.100</td>
<td>231</td>
<td>94</td>
<td>0.94</td>
<td>0.06</td>
</tr>
<tr>
<td>15</td>
<td>7c</td>
<td>0.440</td>
<td>0.69</td>
<td>245</td>
<td>61</td>
<td>0.85</td>
<td>0.18</td>
</tr>
<tr>
<td>16</td>
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<td>0.731</td>
<td>1.248</td>
<td>198</td>
<td>63</td>
<td>0.83</td>
<td>0.20</td>
</tr>
<tr>
<td>17</td>
<td>13a</td>
<td>1.711</td>
<td>1.187</td>
<td>289</td>
<td>41</td>
<td>0.81</td>
<td>0.23</td>
</tr>
<tr>
<td>18</td>
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<td>0.620</td>
<td>1.400</td>
<td>202</td>
<td>69</td>
<td>0.88</td>
<td>0.14</td>
</tr>
<tr>
<td>19</td>
<td>13c</td>
<td>0.070</td>
<td>1.000</td>
<td>214</td>
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<td>0.89</td>
<td>0.12</td>
</tr>
<tr>
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<td>13d</td>
<td>1.189</td>
<td>0.690</td>
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<td>37</td>
<td>0.81</td>
<td>0.23</td>
</tr>
<tr>
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<td>73</td>
<td>0.83</td>
<td>0.20</td>
</tr>
<tr>
<td>22</td>
<td>17a</td>
<td>-</td>
<td>0.489</td>
<td>51</td>
<td>99</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>18a</td>
<td>0.075</td>
<td>-</td>
<td>15</td>
<td>0</td>
<td>0.85</td>
<td>0.18</td>
</tr>
<tr>
<td>24</td>
<td>18b</td>
<td>0.435</td>
<td>0.211</td>
<td>129</td>
<td>49</td>
<td>0.99</td>
<td>0.01</td>
</tr>
<tr>
<td>25</td>
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<td>0.183</td>
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<td>0.01</td>
</tr>
<tr>
<td>26</td>
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<td>0.279</td>
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<td>0.83</td>
<td>0.20</td>
</tr>
<tr>
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<td>0.955</td>
<td>0</td>
<td>198</td>
<td>0</td>
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<td>-</td>
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<tr>
<td>28</td>
<td>18f</td>
<td>0.630</td>
<td>0.459</td>
<td>218</td>
<td>71</td>
<td>0.88</td>
<td>0.14</td>
</tr>
<tr>
<td>29</td>
<td>19</td>
<td>0.496</td>
<td>-</td>
<td>50</td>
<td>30</td>
<td>0.88</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<sup>a</sup>General Conditions: Toluene (40 ml), 25 °C, reaction time 1 hr, 400 eq. MAO per metal centre, ethylene pressure 1 bar (100 kPa), reaction quenched with dilute HCl; <sup>b</sup>measured in g; <sup>c</sup>g/mmol h bar⁻¹ (based on the sum of the mass of oligomer + mass of polymer); <sup>d</sup>[mass of polymer/mass of oligomer + mass of polymer] x 100; <sup>e</sup>probability of chain propagation; <sup>f</sup>rate of chain transfer/rate of chain propagation.

### 6.4.2.1 General features

All the monometallic and bimetallic nickel systems (runs 7-29) are active for ethylene oligomerisation and/or polymerisation with the activities ranging from 15 g/mmol⁻¹ h⁻¹ bar⁻¹ (run 23) to 522 g/mmol⁻¹ h⁻¹ bar⁻¹ (run 7), with most of the remaining runs averaging to 208 g/mmol⁻¹ h⁻¹ bar⁻¹. All the systems produce blends of internal and
terminal olefins (Scheme 3). In addition, a significant amount of branching has been found regardless of the precatalyst employed (see later for discussion).

![Scheme 3 Principal olefinic types afforded using precatalysts 6a-6f, 7a-7d, 18a-18f or 19; (i) Ni precat./xs. MAO](image)

6.4.2.2 Monometalic catalysts

The monometalic catalysts screened, \((6a-6f: \text{runs 7-12})\) displayed similar catalytic performance. In comparison with the activities reported by Laine and Alt for monometalic \(6b, 6c, 6e\) and \(6f\), \(14, 17\) our systems displayed lower activities; an observation that can be attributed to the milder conditions employed in our runs, (notably lower ethylene pressures). However, internal olefins were the main product with a significant amount of additional methyl groups that could be attributed to the presence of branches; this is consistent with the track record of this type of system.\(^{15-18}\)

6.4.2.3 EB (fused and remote) versus monometalic catalysts

As a general observation and in agreement with that observed in section 6.3, the overall activity of EB systems (runs 13-29) does not result in double activity when compared with the corresponding monometalic system (runs 7-12). Notably, the Ni:Al (MAO) ratio was maintained constant. For example, the activity for the EB system \(13b\) is 202 g/mmol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) (run 18), while the most closely related monometalic system \(6c\) displays an activity of 220 g/mmol\(^{-1}\) h\(^{-1}\) bar\(^{-1}\) (run 9). It is worthy of note that the activities reported by Sun and co-workers for \(13a\) and \(13b\) are higher,\(^{19}\) probably due to the increased amounts of MAO and higher monomer pressures employed in their runs.

For a given ortho aryl substituent (Me or i-Pr), the polymer proportion generally increases when comparing encapsulated precatalysts with monometalic counterparts (Graphics 4 and 5). For example, the use of fused EB systems \(7a-7d\) (\(o\)-substituent = Me) affords ca. 72% polymer which compares with 0-44% when using the most closely related monometalic systems \((6a, 6b, 6d, 6f)\) (Graphic 4). The remote EB systems \(13a\) and \(13d\) (\(o\)-substituent = Me) also have a tendency to give a greater proportion of polymer although this is less significant than those observed for fused \(7a-7d\). Similar
Chapter Six

Trends can also be appreciated when comparing remote EB o-i-Pr-substituted precatalysts (13b, 13e) with their monometallic counterparts (6c, 6e) (Graphic 5).

\[
\begin{array}{c}
6a \quad R = H; \quad R_1 = M e; \quad R_2 = H \\
6b \quad R = H; \quad R_1 = R_2 = M e \\
6d \quad R = R_1 = R_2 = M e \\
6f \\
7a \quad X = B n; \quad R = R' = H \\
7b \quad X = B r; \quad R = H; \quad R' = M e \\
7c \quad X = B r; \quad R = M e; \quad R' = H \\
7d \quad X = C l; \quad R = R' = H \\
13a \quad R = H; \quad R_1 = R_2 = M e \\
13c \quad R = H; \quad R_1 = M e; \quad R_2 = \nu-Pr \\
13d \quad R = M e; \quad R_1 = R_2 = M e
\end{array}
\]

Graphic 4 Polymer percentage as a function of the o-Me-containing precatalysts 6a, 6b, 6d, 6f (monometallic), 7a-7d (fused EB) 13a, 13c and 13d (remote EB) employed (runs 7, 8, 10, 12, 13-16, 17, 19 and 20).

The results of the screening of 18a-18f are particularly interesting as both the polymer proportions and the activity vary considerably when using different para-benzyl substituents (Y). For example, the introduction of a para-Y substituent in place of para-H tends to increase the activity, which is most notable for electron withdrawing substituents \([Y = B r (18c), Y = N O_2 (18f)]\). The influence of the electron donating capability of Y on the percentage of polymer is, however, not so clear.

Significant variations in the polymer proportion can also be observed when using o-methyl substituted monometallic precatalysts 6a, 6b, 6d and 6f (runs 7, 8, 10, 12).
Specifically, the introduction of different imino-carbon or imino para- or meta-aryl substituents is shown to be highly influential.

All these observations suggest that the modification of the electronic properties of the complexes by the introduction of appropriate substituents can influence significantly the overall performance of the system.

![Chemical structures](image)

**Graphic 5** Polymer percentage as function of the o-i-Pr-containing precatalysts 6c, 6e (monometallic), 13b, 13e and 18a-18f (remote EB) employed for runs 9, 11, 18, 21 and 23-28.

GPC data has been collected for several of the polymeric fractions furnished from selected runs (runs 9, 11, 18, 21) and confirms that the molecular weight of the polymer produced by encapsulated systems is higher than that produced by monometallic precatalysts (Table 4).

With regard to differences in the content of the oligomeric fractions afforded using either the monometallic or the EB nickel-based initiators, no firm conclusions can be made. In each case the $^1$H and $^{13}$C NMR spectroscopic data for the oligomeric fractions are consistent with blends of different types of olefin; selected results are contained in Table 5 while some features of the oligomeric microstructures are depicted in Graphics.
6 and 7. For all runs apart from 13d, terminal and internal unsaturation account for the major type of olefin, at an average of 18% and 78%, respectively. Nevertheless, some runs produced small amounts of trisubstituted (runs 7, 13, 18) or vinylidenes (runs 13, 18, 26).

Table 4 GPC data for polymers obtained from runs 9, 11, 18 and 21

<table>
<thead>
<tr>
<th>Run</th>
<th>Precatalyst</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>Pdi</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>6c</td>
<td>488</td>
<td>1120</td>
<td>2.30</td>
</tr>
<tr>
<td>11</td>
<td>6e</td>
<td>862</td>
<td>1756</td>
<td>2.03</td>
</tr>
<tr>
<td>18</td>
<td>13a</td>
<td>1097</td>
<td>5571</td>
<td>5.07</td>
</tr>
<tr>
<td>21</td>
<td>13d</td>
<td>1551</td>
<td>2787</td>
<td>1.79</td>
</tr>
</tbody>
</table>

\( ^a \) GPC traces were recorded using PL gel 2 \( \times \) mixed bed - C, 30 cm, 5 micron columns, 1,2,4-trichlorobenzene as eluent and a flow rate of 1.0 ml/min at 160 °C using a refractive index detector.

For all runs (7-29), a significant amount of the methyl signals that are present in the \(^1\)H NMR spectra for the oligomeric materials cannot be correlated with the total number of unsaturations possible. This proportion of additional methyls account for 27-82% of the total (Graphic 7). It is likely that these additional methyl signals can be attributed to branches on the polymer. This is also consistent with the \(^{13}\)C NMR spectra, which contain a distribution of signals typical of branched polyethylene.\(^\text{20, 21}\) Similarly, the DSC performed on the polyethylene samples obtained using 7a-7c, 13b, 13e revealed low values for the \( T_c \) and of the \( T_m \) that are consistent with low molecular weight polyethylene with a significant amount of branching. It is worthy of note that nickel-based systems have a track record for producing branched polyethylene (see section 1.2).
### Table 5 Interpretation of the $^1$H NMR spectroscopic data determined for runs 7-29*

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Methyl chain ends</th>
<th>Olefinic groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6a</td>
<td>130.96</td>
<td>79.95</td>
</tr>
<tr>
<td>8</td>
<td>6b</td>
<td>121.52</td>
<td>49.35</td>
</tr>
<tr>
<td>9</td>
<td>6c</td>
<td>64.62</td>
<td>39.7</td>
</tr>
<tr>
<td>10</td>
<td>6d</td>
<td>101.50</td>
<td>61.41</td>
</tr>
<tr>
<td>11</td>
<td>6e</td>
<td>103.97</td>
<td>19.39</td>
</tr>
<tr>
<td>12</td>
<td>6f</td>
<td>130.93</td>
<td>28.36</td>
</tr>
<tr>
<td>13</td>
<td>7a</td>
<td>102.68</td>
<td>60.21</td>
</tr>
<tr>
<td>14</td>
<td>7b</td>
<td>123.07</td>
<td>66.67</td>
</tr>
<tr>
<td>15</td>
<td>7c</td>
<td>104.84</td>
<td>68.97</td>
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<tr>
<td>16</td>
<td>7d</td>
<td>100.77</td>
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<td>13a</td>
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</tr>
<tr>
<td>19</td>
<td>13c</td>
<td>96.65</td>
<td>63.45</td>
</tr>
<tr>
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<td>13d</td>
<td>111.5</td>
<td>65.61</td>
</tr>
<tr>
<td>21</td>
<td>13e</td>
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</tr>
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<td>90.35</td>
<td>32.81</td>
</tr>
<tr>
<td>24</td>
<td>18b</td>
<td>129.52</td>
<td>29.83</td>
</tr>
<tr>
<td>25</td>
<td>18c</td>
<td>100.49</td>
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</tr>
<tr>
<td>26</td>
<td>18d</td>
<td>120.36</td>
<td>72.77</td>
</tr>
<tr>
<td>27</td>
<td>18e</td>
<td>104.08</td>
<td>56.41</td>
</tr>
<tr>
<td>28</td>
<td>18f</td>
<td>99.34</td>
<td>45.42</td>
</tr>
<tr>
<td>29</td>
<td>19</td>
<td>105.95</td>
<td>49.06</td>
</tr>
</tbody>
</table>

* recorded in CDCl₃ at ambient temperature; † per 1000 carbon atoms; ‡ additional chain ends = total – unsaturated chain ends.
Chapter Six

The GCMS analysis of the oligomers obtained from runs 7-29 show a complex distribution of peaks as several isomers can be detected at molecular weights separated by 28 amu’s in the range C10 to C40; the precise envelope of peaks depending on the precatalyst employed. As a consequence, the determination of the $\alpha$ values has proved problematic and tend to give an average value around 0.8.
Graphic 7 Relative percentage of oligomeric unsaturation as a function of the precatalyst employed.
6.4.2.4 Unsymmetrical EB catalysts

On inspection of the data determined using an EB system based on an unsymmetrical ligand (7c) and comparing it with that obtained for its symmetrical counterparts (7a, 7b), similar features are apparent. All runs (runs 13-16) display activities of a comparable magnitude and result mainly in polymer (see Table 3). Furthermore, the microstructure of the resulting polymer contains mainly internal unsaturations that range from 80-87%, while the ratio of additional methyl groups falls between 35% (7c)-46% (7b).

When comparing the data for unsymmetrical 13c with that of its symmetrical counterparts (methyl: 13a, isopropyl: 13b), the first feature that is evident is that all three catalysts display comparable activities. On the other hand, the oligomer:polymer ratio shows some differences. For instance, using 13c more polymer (94%) is produced than when employing 13a (41%) and 13b (69%) (see Table 3). Furthermore, the microstructure of the resulting polymer is significantly different with 13c producing mainly terminal olefins (ca. 60%), while 13a and 13b produce mainly internal unsaturations. The explanation as to the microstructural variations is unclear.

6.4.2.5 Remote EB versus fused and immobilised EB catalysts

In terms of productivity, the fused EB catalysts (7a-7d) show similar activities to those displayed for the methylene-linked remote systems (13a-13e) falling in the range 153 - 289 g/mmol h⁻¹ bar⁻¹; although markedly higher than that observed using 17a (in which the catalytic components are linked by a single bond). On the other hand, the variation in activity exhibited by the benzyl-linked remote systems, 18a-18f, is broader (15-317 g/mmol h⁻¹ bar⁻¹) with the polystyrene-immobilised system 19 falling at the lower end of this range (50 g/mmol h⁻¹ bar⁻¹).

On comparison of the oligomeric/polymeric materials obtained using fused 7a-7d with remote EB systems 13a and 13d (all containing o-Me groups) shows that the remote systems produce a lower polymer percentage. Interestingly 17a, despite being an example of a remote EB system, produces only polymer. This latter result may suggest that the nature of the linker can play an important role on the performance of a remote EB system.

A catalytic system based on polystyrene-supported 19 exhibits a reduced activity when compared to its allylic-containing precursor 18e. Nevertheless, the use of both 18e and immobilised 19 afford oligomeric/polymeric material displaying similar MWs.
6.4.3 Interpretation

The use of both nickel-based monometallic and EB precatalysts resulted in a blend of internal and terminal olefins (Scheme 4). In addition, a significant amount of branching has been found regardless of the precatalyst employed.

\[
\text{internal olefin (75-86\%)} \quad + \quad \text{\(\alpha\)-olefin (13-25\%)}
\]

Scheme 4 Principal olefinic types generated using \textit{6a-f, 7a-d, 18a-18f or 19} as precatalysts \(i\) Ni precat. /xs. MAO.

The production of branched polyethylene is typical of group 10 catalysts. An isomerisation pathway in the catalytic cycle is responsible for generating blends of linear polyethylene mixed with significant amounts of isomerised and branched olefins.\textsuperscript{10,22-25} This phenomena, also termed "chain walking" (sometimes called "chain running"), is based on a series of \(\beta\)-hydrogen elimination/re-insertion reactions via \(\beta\)-agostic cationic alkyl intermediates (Scheme 5). The degree of branching and the length of the chain depends not only on the nature of the metal centre, but also on the polymerisation conditions employed \(\textit{i.e.},\) pressure, temperature.\textsuperscript{10,22}

\[
\text{methyl branch in polymer}
\]

Significantly, the runs employing EB precatalysts result in higher molecular weight olefinic materials when compared with monometallic precatalysts with similar steric properties; an observation that has also been noted for the imino(bipyridine)-containing iron systems (see section 6.3). This increase in molecular weight could be a consequence of oligomer incorporation but is likely to be due to a modification of the electronic properties. Notably, the use of precatalysts in which the backbone possesses an electronically active group \(\textit{see Y group variation in 18a-18f}\) leads to a modification of the proportion of polymer in the blend; an observation that has also been noted when
comparing monometallic and EB systems. The branching content observed when using an Ni-based EB system is not significantly increased when compared with its monometallic counterparts. Thus, it is likely that for this type of EB system a mechanism whereby incorporation of the oligomers generated at one nickel centre at the other is not operational.
6.5 Evaluation of imino-phenanthroline-containing iron precatalysts

In this section, the results of the screening for the polymerisation of ethylene of iron precatalysts supported by ligands containing at least one imino-phenanthroline unit, are reported (Chart 3, Classes A, H and L). In particular, the discussion will be concerned with the evaluation of precatalysts 1a-1e, 10, 15a and 15b (Chart 3) and will focus on both their activities and on the microstructures of the oligomers/polymers afforded. Our interpretation and conclusions will be presented with special regard being paid to any differences observed between the use of EB systems and the corresponding monometallic system, whilst also probing the effect of electronic variation in the monometallic systems and any proximity effects within related EB systems.

Chart 3 Precatalysts 1a-1e, 10, 15a and 15b screened for ethylene polymerisation.

6.5.2 Background

Despite the rigidity of the phenanthroline unit (and likely thermal stability; see section 2.3), the use of phenanthroline-containing late transition metal catalysts for the polymerisation of alkenes has received scarcely any attention. Wang and co-workers have described the synthesis and catalytic screening of a range of bis(imino)phenanthroline-supported late-transition metal-based complexes (where M = Fe, Co and Ni) (Figure 6). The nickel systems are the most productive with only moderate to low activities achieved under 20 bar ethylene pressure. The cobalt analogues were less active whereas the iron analogues displayed no activity at all. The nickel systems result in the characteristic blend of branched and isomerised olefins typical of imino-based nickel catalysts, while the cobalt catalysts gave mostly linear oligomers (C4-C10).
It is likely that the low activity of these bis(imino)phenanthroline systems is due to the capacity of the pendant imino arm to coordinate to the metal centre and deactivate the active catalyst. Therefore, as an additional source of interest, and to probe the above hypothesis, we have targeted mono-imine containing phenanthroline-supported catalysts (both monometallic and EB) and, in particular, with iron as the metal centre.

6.5.3 Screening of 1a-1e, 10, 15a and 15b

Using the same procedure outlined in 6.2, 1a-1e, 10, 15a and 15b were screened for the polymerisation of ethylene (Chart 3); the activities, the amount of oligomer and polymer, and the \( \alpha \) and \( \beta \) values obtained from GC are compiled in Table 6. All oligomers produced by runs 30-37 have been the subject of \(^1\)H and \(^{13}\)C NMR spectroscopy; the results of the \(^1\)H NMR spectroscopic analysis are compiled in Table 7. In order to discuss the results, we have divided this section on the basis of: general features; monometallic catalysts – electronic variation; EB (fused and remote) versus monometallic catalysts.

6.5.3.1 General features

All the iron systems screened (runs 30-37) are active for ethylene oligomerisation/polymerisation with activities ranging from 15 g/mmol\(^{1}\) h\(^{-1}\) bar\(^{-1}\) (run 32) to as high as 487 g/mmol\(^{1}\) h\(^{-1}\) bar\(^{-1}\) (run 31) with the remaining runs averaging to 100 g/mmol\(^{1}\) h\(^{-1}\) bar\(^{-1}\) (Table 6). The microstructure of the oligomers was found to be linear with (>91% \( \alpha \)-olefins: Scheme 6) in all cases. As already explained in section 6.3.3, this behaviour is typical of iron catalysts reported to date.\(^5,9,10\) A more complete discussion of the microstructural properties of the oligomers/polymer will be discussed below.

\[
\text{Scheme 6 Principal olefinic type generated using 1a-1e, 10, 15a or 15b as precatalyst; (i) Fe precat./xs. MAO}
\]

\( \alpha \)-olefin (91-98%)
Table 6 Results obtained from screening precatalysts 1a-1e, 10, 15a and 15b for ethylene polymerisation (runs 30-37)

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Oligomer $^b$</th>
<th>Polymer $^b$</th>
<th>Activity $^c$</th>
<th>Polymer$^d$ %</th>
<th>$\alpha^e$</th>
<th>$\beta^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1a</td>
<td>0.266</td>
<td>0.281</td>
<td>58</td>
<td>48</td>
<td>0.91</td>
<td>0.10</td>
</tr>
<tr>
<td>31</td>
<td>1b</td>
<td>4.365</td>
<td>0.507</td>
<td>487</td>
<td>10</td>
<td>0.77</td>
<td>0.30</td>
</tr>
<tr>
<td>32</td>
<td>1c</td>
<td>0.128</td>
<td>0.021</td>
<td>15</td>
<td>14</td>
<td>0.69</td>
<td>0.44</td>
</tr>
<tr>
<td>33</td>
<td>1d</td>
<td>0.850</td>
<td>0.268</td>
<td>112</td>
<td>24</td>
<td>0.72</td>
<td>0.40</td>
</tr>
<tr>
<td>34</td>
<td>1e</td>
<td>0.161</td>
<td>0.206</td>
<td>36</td>
<td>56</td>
<td>0.92</td>
<td>0.08</td>
</tr>
<tr>
<td>35</td>
<td>10</td>
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<td>1.790</td>
<td>453</td>
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</tr>
<tr>
<td>36</td>
<td>15a</td>
<td>0.308</td>
<td>0.570</td>
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<td>65</td>
<td>0.84</td>
<td>0.20</td>
</tr>
<tr>
<td>37</td>
<td>15b</td>
<td>1.184</td>
<td>0.020</td>
<td>120</td>
<td>17</td>
<td>0.70</td>
<td>0.43</td>
</tr>
</tbody>
</table>

$^a$ General Conditions: Toluene (40 ml), 25 °C, reaction time 1 h, 400 eq. MAO per metal centre, ethylene pressure 1 bar (100 kPa), reaction quenched with dilute HCl; $^b$ measured in g; $^c$ g/mmol·h·bar; $^d$ (based on the sum of the mass of oligomer + mass of polymer); $^e$ [mass of polymer/mass of oligomer + mass of polymer] x 100; $^f$ probability of chain propagation; $^g$ rate of chain transfer/rate of chain propagation.

6.5.3.2 Monometallic catalysts – electronic variation

The activities of the monometallic systems (1a-1e) range from 15 to 487 g/mmol·h·bar$^{-1}$ (runs 30-34) with the most active system (1b) possessing a mesityl group as the N-aryl substituent. Replacement of the $p$-Me group in 1b with an H atom to give 1a results in a reduction of the activity; an observation that has also been noted for bis(arylimino)pyridine-iron systems. The nature of the substituent at the 4-position of the aryl group in the 2,6-$i$-Pr-containing complexes 1c-1e is also found to influence the magnitude of the activity with the Br-containing system 1d displaying the highest value. In comparison with the corresponding bis(arylimino)pyridine-iron systems (in terms of the aryl group substitution pattern), the activities of 1 are lower but notably higher than those for the sterically comparable imino(bipyridine)-iron systems (3) reported in this work (see section 6.3).

Unlike the mono-iron imino(bipyridine) systems (3a, 3b), precatalysts 1a-1e all yield both oligomeric and polymeric fractions. For example 1c, the iminophenanthroline analogue of 3a, results in 14% polymer while 3a gives short chain 1-hexene and 1-octene as the main products. The polymeric content within 1 is also affected by the nature of the 4-position of the N-aryl group with the cyano-derivative (1e) leading to 56% polymer content while the 4-methyl species (1b) affords 10%. The $\alpha$ values [range: 0.92-0.69 (runs 30-34)] of the oligomeric portions can, in general, be correlated with the proportion of polymers within the blend with the runs displaying the higher $\alpha$-values also producing the largest proportion of polymer (Graphic 9).
The IR data for all polymeric portions produced using the monometallic systems revealed $\nu$(C=C) bands ca. 1640 cm$^{-1}$ along with two narrow signals centred around 2880 cm$^{-1}$ [$\nu$(C-H)]. No GPC data were recorded for these samples.

Overall, it would seem apparent that the general performance of 1 is more similar to that observed for members of the bis(arylimino)pyridine-iron family of catalysts (that perform as oligomerisation catalysts) than the structurally related imino(bipyridine)-iron systems (3). Notably, in these former examples the steric bulk of the ortho-aryl positions has to be reduced in order to access an oligomerisation catalyst while in 1 bulky ortho groups are present in all cases.

6.5.3.3 EB (fused and remote) versus monometallic catalysts

The activities of the EB systems (10, 15a, 15b) range from 88 to 453 g/mmol$^{-1}$ h$^{-1}$ bar$^{-1}$ (runs 35-37) with the most active system (10) being an example of a fused system. In contrast to the imino(bipyridine)-iron (section 6.3) and the iminopyridine-nickel (section 6.4) systems, the proportion of polymer does not appear to be clearly related to the number of polymerisation-active metal centres in the precatalyst. For example, the o-Me EB systems 10 and 15a afford 40 and 65% polymer while the most closely related monometallic systems 1a and 1b give 48 and 10%, respectively.
With regard to differences in the content of the oligomeric fractions afforded using either the monometallic (1a-1e) or the EB iron-based initiators (10, 15a, 15b), no firm conclusions can be made. In each case the $^1$H and $^{13}$C NMR spectroscopic data for the oligomeric fractions are consistent with mainly $\alpha$-olefins; selected results are contained in Table 7 while the relative percentage of olefinic types present in the oligomers are depicted in Graphic 10.
The total number of observed methyl-ends (from $^1$H NMR) can be quantified (Table 7) and compared with the number of expected methyl-ends (with regard to the degree of unsaturation). In all cases, some methyl-ends (Table 7: column add.) cannot be attributed to the degree of unsaturation and are calculated on the basis of the two previous columns (see appendices). For all runs, the number of additional methyl-ends remains approximately constant for all runs ca. 25 methyl per 1000 carbon atoms. The linearity of the oligomers produced precluded that these additional methyl signals derive from branches. One possible explanation for this increase in saturated ends could be due to an alternative chain transfer mechanism, namely transfer to aluminium (see section 6.3.1). This phenomena is known for bis(imino)pyridine-iron systems and is likely to be operational here.

<table>
<thead>
<tr>
<th>Run</th>
<th>Precat.</th>
<th>Methyl chain ends&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Olefinic groups&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Unsat.</td>
</tr>
<tr>
<td>30</td>
<td>1a</td>
<td>66.27</td>
<td>43.19</td>
</tr>
<tr>
<td>31</td>
<td>1b</td>
<td>84.44</td>
<td>55.90</td>
</tr>
<tr>
<td>32</td>
<td>1c</td>
<td>82.12</td>
<td>57.86</td>
</tr>
<tr>
<td>33</td>
<td>1d</td>
<td>82.29</td>
<td>55.36</td>
</tr>
<tr>
<td>34</td>
<td>1e</td>
<td>66.27</td>
<td>43.19</td>
</tr>
<tr>
<td>35</td>
<td>10</td>
<td>73.16</td>
<td>47.53</td>
</tr>
<tr>
<td>36</td>
<td>15a</td>
<td>57.39</td>
<td>34.75</td>
</tr>
<tr>
<td>37</td>
<td>15b</td>
<td>59.80</td>
<td>33.98</td>
</tr>
</tbody>
</table>

<sup>a</sup>recorded in CDCl$_3$ at ambient temperature; <sup>b</sup>per 1000 carbon atoms; <sup>c</sup>additional chain ends = total – unsaturated chain ends.
The GPC data for the polymeric materials obtained using bimetallic 10, 15a and 15b (runs 35-37) are consistent with higher molecular weight materials (Table 5) and indeed IR studies of the polymers reveal broad $\nu$(C=C) absorption bands at ca. 1640 cm$^{-1}$ along with two narrow signals centred around 2880 cm$^{-1}$ [$\nu$(C-H)].

**Table 5** GPC data for polymers obtained from runs 35-37

<table>
<thead>
<tr>
<th>Run</th>
<th>Precatalyst</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Pdi</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>10</td>
<td>957</td>
<td>1833</td>
<td>1.92</td>
</tr>
<tr>
<td>36</td>
<td>15a</td>
<td>1286</td>
<td>2769</td>
<td>2.15</td>
</tr>
<tr>
<td>37</td>
<td>15b</td>
<td>282</td>
<td>691</td>
<td>2.45</td>
</tr>
</tbody>
</table>

*GPC traces were recorded using PL gel 2 × mixed bed – C, 30 cm, 5 micron columns, 1,2,4-trichlorobenzene as eluent and a flow rate of 1.0 ml/min at 160 °C using a refractive index detector.*

### 6.5.4 Interpretation

It clear from the above that the mono-imino-phenanthroline unit can act as a compatible support for highly active iron catalysts for the oligomerisation/polymerisation of ethylene. All the analysis performed on the oligomers yielded by runs 30-37 indicate that monometallic and EB precatalysts (1a-1e, 10, 15a and 15b) display high selectivity for the production of linear terminal olefins with an activity spanning from moderate to high (Scheme 7). This selectivity for linear terminal olefins is consistent with iron-based systems reported to date (see section 6.3.3).
The nature of the substituent located at the 4-position in the monometallic series of precatalysts (1a-1e) has been found to have a profound effect on the performance of the catalyst. Given the remote location of the 4-position from the active site of the catalyst, it would seem that this effect is electronic in origin. In terms of activity it is not clear whether electron donating or electron withdrawing groups are preferable as both lead to an increase in activity when compared with the 4-H substituted species (1a, 1c). With regard to the percentage of polymer generated, it would seem that precatalysts containing electron withdrawing substituents (1d, 1e) lead to increased polymer content. The origin of this observation is uncertain but could be due to an increased electrophilicity of the metal centre leading a reduced barrier to propagation.

Incorporation of imino-phenanthroline-iron units into EB systems (10, 15a, 15b) does not appear from this data to impact significantly on the performance when compared with monometallics 1. The observation is in contrast to those seen for imino(bipyridine)-iron (section 6.3) and iminopyridine-nickel (section 6.4) systems in which the polymer content increases in the EB systems. The explanation for this difference in behaviour remains uncertain. As with the EB systems containing imino(bipyridine)-iron units the fused iron systems tend to be more active than the remote systems.
6.6 General conclusions

Both EB nickel and iron precatalysts, along with their most closely related monometallic counterparts, have been the subject of a broad screen (37 runs) for ethylene polymerisation using standard Schlenk screening protocols (i.e., 1 bar ethylene, room temperature, toluene as solvent, one hour run time). Many of the new systems exhibit high activities for the polymerisation of ethylene with the most active being 800 g/mmol h⁻¹ bar⁻¹ shown for the fused EB iron system 9a (run 3).

The use of EB precatalysts containing either iminopyridine-nickel or imino(bipyridine)-iron catalytic sites lead to higher molecular weight materials when compared with their corresponding monometallic analogues; no clear variation is, however, observed for the iminophenanthroline-iron systems. The reason for this increase in molecular weight remains unclear but is likely to be electronic in origin. Indeed, we have shown the nature of the 4-position on the N-aryl group can play a significant role on the performance of mononuclear imino-phenanthroline-iron catalysts (1), and given this has been selected as a site for construction of the EB system a similar role seems probable. Furthermore, the effect of long range variation in electronic properties on benzyl-bridged EB nickel systems (18a-18f) has been demonstrated. In unsymmetrical EB nickel precatalysts an increase in polymer content has also been observed when compared against the corresponding symmetrical systems (cf., 13c, 13a, 13b). However, the cooperation between the catalytic sites in terms of microstructural variation of the oligomer/polymer generated seems unlikely given the similarity of the spectroscopic data for the oligomers collected for both EB systems and monometallic systems. This is most clearly demonstrated by the strictly linear α-olefins that are generated by all iron catalysts regardless of being EB or monometallic.

Part of the design strategy developed in this thesis was to target EB systems that could systematically be changed in terms of the inter-catalytic site distance. This has been realised to some degree with the synthesis of three families of dinuclear nickel precatalysts. (viz., Class D, E, I, M). While the activity of these systems and polymer:oligomer ratio vary, the microstructural differences are unclear.
6.7 References

Chapter Seven

Experimental
Chapter Seven

7.1 General
All operations, unless otherwise stated, were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk and cannular techniques or in a nitrogen purged glove box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use or were employed directly from a Solvent Purification System (Innovative Technology, Inc). The electrospray (ES) mass spectra were recorded using a micromass Quattro LC mass spectrometer with dichloromethane or methanol as the matrix [Masslynx software. open-access autosampler injection]. FAB mass spectra (including High resolution) were recorded on a Kratos Concept spectrometer (xenon gas, 7 kV) with NBA as matrix. The infrared spectra were recorded in the solid state with Universal ATR sampling accessories on a Perkin Elmer Spectrum One FTIR instrument. NMR spectra were recorded on a Bruker ARX 250/300 MHz spectrometer ($^1$H) and 62.9/75 MHz ($^{13}$C); chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in Hertz (Hz). The high temperature GPC analysis were performed on a PL-220 instrument equipped with two mixed bed – C Columns (Polymer Laboratory) and a refractive index detector. Analyses were undertaken using 1,2,4-trichlorobenzene as solvent at 160 °C and the $M_w$s were calculated using a universal calibration curve based on polystyrene standards using Easycal PS-2 (Polymer Laboratory). Magnetic susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature. The magnetic moments were calculated following standard methods and corrections for underlying diamagnetism were applied to the data. Data for X-ray determination were collected on a Bruker APEX 2000 CCD diffractometer (see section 7.5). Melting points (Mp) were measured on a Gallenkamp melting point apparatus (model MFB-595) in open capillary tubes and were uncorrected. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The reagents [1,10]-phenanthroline monohydrate, hydrogen peroxide (30%), glacial acetic acid, hydrochloric acid, sodium hydroxide, potassium cyanide, benzoyl chloride, sodium borohydride, selenium dioxide, 1,4-dioxane, N,N’-dimethylformamide, N,N’-dimethylacetamide, 1,2-ethandiol, para-toluene sulfonic acid, n-butyllithium (1.6M in hexane), tributyltin chloride, 2-bromopyridine, 2,3-butanedione, 2-pyridinecarboxaldehyde, 2-acetylpyridine, 2,3,5,6-tetramethyl-benzene-1,4-diamine, cetyltrimethylammoniumbromide (CTAB), benzaldehyde, para-hydroxybenzaldehyde, para-isopropylbenzaldehyde para-bromobenzaldehyde, palladium on carbon paste.
formaldehyde (37/40 wt.% solution in water) were purchased from Aldrich Chemical Co. and used without further purification. Nickel dichloride, nickel dibromide, 1,2-dimethoxyethane, iron dichloride, cobalt dichloride were purchased from Aldrich Chemical Co and were stored and employed under a dry, oxygen-free nitrogen atmosphere. All anilines were obtained from Aldrich and distilled prior to use. The preparation of [1,10]-phenanthroline-2-yl-methanol, 4-bromo-2,6-dimethylaniline, 4-bromo-2,6-diisopropylaniline, 4-cyano-2,6-diisopropylaniline, 2,2'-bipyridine-6-acetyl, 2,2'-bipyridine-6-formyl, 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine, and tetrakistriphenylphosphinepalladium followed previously reported procedures. All other chemicals were obtained commercially and used without further purification.
7.2 Synthesis of Reagents

7.2.1 Preparation of [1,10]-phenanthroline-2-carboxaldehyde
A red suspension of [1,10]-phenanthroline-2-yl-methanol (2.500 g, 0.012 mol) and selenium dioxide (6.000 g, 0.179 mol, 15 eq.) in dioxane (150 ml) was refluxed at 110 °C for 2 hrs. Hot filtration through minimum amount of celite followed by the washing of the residue with dichloromethane (150 ml) afford a red liquid. The solvent was removed under reduced pressure, [1,10]-phenanthroline-2-carboxaldehyde was obtained as a red solid. (1.75 g, 71 % yield).

Compound [(C<sub>12</sub>H<sub>7</sub>)CHO]: ES mass spectrum, m/z 209; IR (cm<sup>-1</sup>), 1707 (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 7.66 (dd, 3<sup>J</sup>H-H 4.6, 7.9, 1H, Phen-H), 7.80 (m, 2H, Phen-H), 8.22 (dd, 2H, 3<sup>J</sup>H-H 7.0, 4<sup>J</sup>H-H 1.8, Phen-H), 8.31 (d, 1H, 3<sup>J</sup>H-H 8.5, Py-H), 9.21 (dd, 1H, 3<sup>J</sup>H-H 4.6, 4<sup>J</sup>H-H 1.8, 1H, Phen-H); 10.55 (s, 1H, HC=O); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 119.1 (s, Ar), 120.5 (s, Ar), 122.2 (s, Ar), 125.5 (s, Ar), 125.6 (s, Ar) 126.7 (s, Ar) 127.7 (s, Ar), 127.8 (s, Ar), 128.2 (s, Ar), 128.6 (s, Ar), 135.2 (s, Ar), 135.7 (s, Ar), 144.8 (s, Ar), 149.5 (s, Ar), 200.9 (s, C=N); Mp: 150-153 °C.

7.2.2 Preparation of 3-(2,6-diisopropyl-phenylimino)-butan-2-one
To a solution of 2,3-butanedione (5.0 ml, 5.70 mmol) in toluene (10 ml) was added 2,6-diisopropylaniline (10.100 g, 5.70 mmol, 1 eq.) and the solution stirred at ambient temperature for two days. The aqueous water layer was removed and a further equivalent of 2,3-butanedione (5.0 ml, 5.70 mmol, 1 eq.) added to the orange solution. The reaction was stirred for a further day and dried over MgSO<sub>4</sub>. Following filtration, all volatiles were removed under reduced pressure to afford 3-(2,6-diisopropyl-phenylimino)-butan-2-one as an orange liquid (12.141 g, 87%).

Compound [(2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NC(Me)C(Me)O]: ES mass spectrum, m/z 245 [M+H]<sup>+</sup>; IR (cm<sup>-1</sup>), 1703 (C=O) 1651 (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 1.06 (d, 12H, 3<sup>J</sup>H-H 6.7, CH(CH<sub>3</sub>)<sub>2</sub>), 1.74 (s, 3H, C(CH<sub>3</sub>)N), 2.50 (s, 3H, C(CH<sub>3</sub>)O), 2.50 (sept, 2H, 3<sup>J</sup>H-H 6.7, CH(CH<sub>3</sub>)<sub>2</sub>), 7.0-7.1 (m, 3H, Ar-H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K): δ 15.4 (s, CH<sub>3</sub>), 23.1 (s, CH<sub>3</sub>), 23.5 (s, CH<sub>3</sub>), 28.8 (s, CH), 123.5 (s, Ar), 124.8 (s, Ar), 135.0 (s, Ar), 145.4 (s, Ar), 167.0 (s, (CH<sub>3</sub>)CN), 200.6 (s, (CH<sub>3</sub>)CO).
7.2.3 Preparation of 3,3',5,5'-tetraisopropyI-4,4'-diaminodiphenylmethane

Based on a preparation reported for a related series of compounds,\textsuperscript{10} 3,3',5,5'-tetraisopropyI-4,4'-diaminodiphenylmethane was prepared as follows. To a solution of 2,6-diisopropylaniline (5.000 g, 0.028 mol) and formaldehyde (1.377 g, 0.018 mol, 0.65 eq.) was added concentrated hydrochloric acid (5 ml). The biphasic solution was stirred vigorously at 110 °C overnight. The dark reddish solution was allowed to cool to ambient temperature and diluted with dichloromethane (10 ml). The minimum amount of concentrated hydrochloric acid was added (ca. 2 ml) and the solution stirred at room temperature for 2 hrs before being filtered. The white salt collected was washed thoroughly with dichloromethane and air-dried. The salt was suspended in diethyl ether (70 ml) and stirred with an aqueous solution of saturated sodium hydroxide until complete dissolution of the solid. The aqueous phase was extracted with diethyl ether (2 x 70 ml), the combined organic phases dried over magnesium sulphate and concentrated under reduced pressure to give 3,3',5,5'-tetraisopropyI-4,4'-diaminodiphenylmethane as a purple oil. Recrystallisation from hexane afforded the product as a white solid (2.100 g, 41%).

Compound [(4-H_N_2,6-i-Pr_2C_6H_2)_2CH_2]: ES mass spectrum, m/z 366 [M+H]^+; IR (cm\textsuperscript{-1}), 3361 (N-H); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 293 °K): δ 1.14 (d, 24H, \textsuperscript{3}J\textsubscript{H-H} 7.8, CH(CH\textsubscript{3})), 2.82 (sept, 4H, \textsuperscript{3}J\textsubscript{H-H} 7.8, CH(CH\textsubscript{3})), 3.46 (br, 4H, NH\textsubscript{2}), 3.76 (s, 2H, CH\textsubscript{2}), 6.77 (s, 4H, Ar-H), \textsuperscript{13}C \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 293 K): δ 21.5 (s, CH\textsubscript{3}), 26.9 (s, CH), 40.2 (s, CH\textsubscript{2}), 122.2 (s, Ar), 130.5 (s, Ar), 131.5 (s, Ar), 136.9 (s, Ar); Anal. Calcd for (C\textsubscript{25}H\textsubscript{38}N\textsubscript{2}): C, 81.97; H, 10.38; N, 7.65. Found: C, 82.18; H, 10.09; N, 7.79%.

7.2.4 Preparation of 4,4'-diamino-3,5-R\textsubscript{1}-3'-R\textsubscript{2}-5'-R\textsubscript{3}diphenylmethane

(i) \textit{R}\textsubscript{1} = isopropyl, \textit{R}\textsubscript{2} = \textit{R}\textsubscript{3} = methyl: To a solution of 2,6-dimethylaniline (2.500 g, 0.021 mol), 2,6-diisopropylaniline (3.650 g, 0.021 mol, 1 eq.) and formaldehyde (1.49 g, 0.014 mol, 0.65 eq.) was added concentrated hydrochloric acid (5 ml). The biphasic solution was stirred vigorously at 110 °C overnight. The resulting dark blue solution was allowed to cool to ambient temperature and diluted with dichloromethane (ca. 10 ml). The minimum amount of concentrated hydrochloric acid (ca. 2 ml) was added and the solution stirred at ambient temperature for 2 hrs before being filtered. The white salt collected was washed thoroughly with dichloromethane and air-dried. The remaining salt was suspended in diethyl ether (70 ml) and stirred with an aqueous solution of
saturated sodium hydroxide until complete dissolution of the solid. The aqueous phase was extracted with diethyl ether (2 x 70 ml), the combined organic phases dried over magnesium sulphate and concentrated under reduced pressure to give a clear oil. Recrystallisation of the residue from the minimum amount of hot hexane afforded white crystalline 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyldiphenylmethane which could be further purified by sublimation (45-50 °C, 0.1 mmHg) (0.340 g, 5%).

Compound [(4-H2N-2,6-i-Pr2C6H2)(4-H2N-2,6-Me2C6H2)CH2]: ES mass spectrum, m/z 311 [M+H]+; IR (cm⁻¹), 3410 (N-H); ¹H NMR (CDCl₃, 293 K): δ 1.17 (d, 12H, 3 J_H-H 7.8, CH(CH₃)), 2.07 (s, 6H, CH₃), 2.84 (sept, 2H, 3 J_H-H 7.5, CH(CH₃)), 3.47 (br, 4H, NH₂), 3.69 (s, 2H, CH₂), 6.70 (s, 2H, Ar-H), 6.79 (s, 2H, Ar-H); ¹³C {¹H} NMR (CDCl₃, 293 K) δ 18.1 (s, CH₃), 22.9 (s, CH₃), 28.4 (s, CH), 41.3 (s, CH₂), 122.3 (s, Ar), 123.8 (s, Ar), 129.0 (s, Ar), 132.1 (s, Ar), 133.0 (s, Ar), 138.4 (s, Ar), 140.7 (s, Ar).

Anal. Calcd for (C₂₁H₃₀N₂): C: 81.22 H: 9.75 N: 9.02. Found C: 81.38 H: 10.00 N: 9.01%. mp = 88 °C. In addition, a single crystal X-ray diffraction study of 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyldiphenylmethane confirmed the structural type, details can be found in Table 2.

(ii) R¹ = isopropyl, R² = methyl; R³ = hydrogen: Employing the method outlined in 7.2.4(i) with 2-methylaniline (2.502 g, 0.023 mol), 2,6-diisopropylaniline (4.140 g, 0.023 mol, 1 eq.), formaldehyde (1.696 g, 0.023 mol, 1 eq.) and concentrated hydrochloric acid (5 ml) at a temperature of 130 °C for 8 hrs, gave the crude product as a brown residue. Attempted recrystallisation of the residue from hot hexane gave 4,4'-diamino-3,5-diisopropyl-3',5'-methyldiphenylmethane as an impure pale brown oil (0.480 g, 7%).

Compound [(4-H2N-2,6-i-Pr2C6H2)(4-H2N-2-MeC₆H₃)CH2]: ES mass spectrum, m/z 297 [M+H]+; ¹H NMR (CDCl₃, 293 K): δ 1.19 (d, 12H, 3 J_H-H 7.5, CH(CH₃)), 2.05 (s, 3H, CH₃), 2.84 (sept, 2H, 3 J_H-H 7.5, CH(CH₃)), 3.54 (br, 4H, NH₂), 3.71 (s, 2H, CH₂), 6.49-6.54 (d, 1H, Ar-H), 6.71-6.82 (m, 4H, Ar-H); ¹³C {¹H} NMR (CDCl₃, 293 K), δ 18.1 (s, CH₃), 23.0 (s, CH₃), 28.4 (s, CH), 41.3 (s, CH₂), 115.5 (s, Ar), 122.8 (s, Ar), 127.6 (s, Ar), 129.4 (s, Ar), 131.2 (s, Ar), 138.5 (s, Ar), 142.8 (s, Ar).
Chapter Seven

7.2.5 Preparation of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine

The procedure employed was based on a method used to make 3,3',5,5'-tetramethylbiphenyl-4,4'-diamine. A mixture containing 4-bromo-2,6-diisopropylaniline (12.800 g, 50 mmol), CTAB (2.000 g, 5.5 mmol, 0.11 eq.), 5% palladium on charcoal (0.800 g, 50% paste), sodium hydroxide (21.1 ml, 8.0M, 0.169 mol) and sodium formate (3.400 g, 50 mmol, 1 eq.) was mixed in water (30 ml) and heated to reflux for 4 hrs. A further quantity of sodium formate (3.400 g, 50 mmol, 1 eq.) was then added to the boiling solution and the reaction mixture stirred vigorously under reflux for a further 20 hrs. The reaction mixture was cooled to room temperature, the solid filtered off and the residue washed with copious amounts of chloroform. The organic phase was separated from the aqueous layer and dried over magnesium sulphate. The organic phase was rapidly filtered through silica and the silica washed several times with chloroform. The filtrate was concentrated, distilled under reduced pressure at 150 °C (0.1 mmHg) to remove the remaining 2,6-diisopropylaniline to give 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine as a dark reddish solid (0.520 g, 5%). Recrystallisation of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine from hexane afforded dark red crystals suitable for X-ray determination.

Compound [(4-H2N-2,6-\textit{i}-Pr2C6H2)2]: ES mass spectrum, m/z 353 [M+H]+; IR (cm⁻¹), 3401, 3368 (N-H); \textsuperscript{1}H NMR (CDCl₃, 293 K): δ 1.25 (d, 24 H, \textit{J}_HH 7.2, CH(CH₃)₂), 2.92 (sept, 4H, \textit{J}_H-H 7.2, CH(CH₃)₂), 3.70 (br, 4H, NH₂), 7.11 (s, 4H, Ar-H); \textsuperscript{13}C {\textsuperscript{1}H} NMR (CDCl₃, 293 K): δ 21.5 (s, CH₃), 27.1 (s, CH), 120.7 (s, Ar), 131.6 (s, Ar), 132.1 (s, Ar), 137.8 (s, Ar); Anal. Calcd for (C₂₅H₃₈N₂) C: 81.74 H: 10.31 N: 7.94. Found C: 82.07 H: 10.24 N: 7.80%. In addition, a single crystal X-ray diffraction study of 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine has confirmed the structural type; details can be found in Table 2.

7.2.6 Preparation of \textit{p}-allylbenzaldehyde

A two step procedure was employed for the synthesis of \textit{p}-allylbenzaldehyde from 1,4-dibromobenzene.

\textit{i} 1-bromo-4-propyl-2-enylbenzene: To a suspension of magnesium turnings (5.700 g, 0.23 mol) in dry diethyl ether (130 ml) was added 1,4-dibromobenzene (50.000 g, 0.23 mol, 1 eq.) in two portions. The solution was stirred for one hour at 20 °C under an
atmosphere of nitrogen. The Grignard reagent was cannular filtered into a solution of allyl bromide (28.000 g, 0.23 mol, 1 eq.) in dry diethyl ether (15 ml). The green suspension was stirred overnight before being hydrolysed with a solution of saturated aqueous ammonium chloride. The slurry was then filtered and the solids were washed with diethyl ether (2 x 15 ml). The organic phases were combined, dried over magnesium sulphate and concentrated under reduced pressure to give a green-brown solid. The resulting compound was purified by distillation (bp = 45 °C at 1 bar) and to give 1-bromo-4-propyl-2-enylbenzene as a transparent liquid (20.752 g, 46%). Compound 1-Br-4-(CH₂CHCH₂)C₆H₄: ES mass spectrum, \(m/z\) 197 [M+H]⁺.

(ii) p-allylbenzaldehyde: 1-bromo-4-propyl-2-enylbenzene (5.000 g, 0.026 mol) was added to a suspension of magnesium turnings (1.860 g, 0.076 mol, 3 eq.) in dry THF (55 ml) in two portions. The solution was stirred for one hour at 20 °C under an atmosphere of nitrogen. The Grignard reagent prepared above was cannular filtered into a flask containing a solution of dimethylformamide (5.587 g, 0.076 mol, 3 eq.) in dry tetrahydrofuran (40 ml). The yellow suspension was stirred overnight before being hydrolysed with a solution of saturated aqueous ammonium chloride. The slurry was then filtered and the solids were washed with THF (2 x 15ml). The organic phases were combined, dried over magnesium sulphate and concentrated under reduced pressure to give a green-brown solid. The above oil was distilled (bp = 62 °C at 1 bar) to give p-allylbenzaldehyde as a yellow liquid (2.293 g, 21%)

Compound (4-CH₂CHCH₂C₆H₄)CHO: ES mass spectrum, \(m/z\) 146 [M+H]⁺; \(^1\)H NMR (CDCl₃, 293 K): δ 3.26 (d, 2H, \(^3\)J_H-H 6.7, CH₂CH), 4.95 (td, 2H, \(^3\)J_H-H 1.5, \(^4\)J_H-H 0.6, CH₂CH), 5.78 (m, 1H, CH₂CH), 7.15 (d, 2H, \(^3\)J_H-H 7.9, Ar-H), 7.62 (d, 2H , \(^3\)J_H-H 8.1, Ar-H), 9.8 (s, HC=O) ; \(^13\)C \({\{^1\}H}\) NMR (CDCl₃, 293 K), δ 39.9 (s, CH₂), 115.4 (s, CH₂), 129.6 (s, Ar), 129.8 (s, Ar), 130.0 (s, Ar), 130.80 (s, Ar), 135.1 (s, CH), 191.4(s, CH)

7.2.7 Preparation of 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-Y-triphenylmethine

(i) \(Y = \text{hydrogen}\): To a solution of 2,6-diisopropaniline (5.000 g, 0.028 mol) and benzaldehyde (1.946 g, 0.018 mol, 0.65 eq.) was added concentrated hydrochloric acid (5 ml). The biphasic solution was stirred vigorously at 140 °C overnight. The resulting
dark green solution was allowed to cool to ambient temperature and diluted with dichloromethane (ca. 10 ml). The minimum amount of concentrated hydrochloric acid was added and the solution stirred at ambient temperature for 2 hrs before being filtered. The yellow salt collected was washed thoroughly with dichloromethane and air-dried. The salt was suspended in diethyl ether (70 ml) and stirred with an aqueous solution of saturated sodium hydroxide until the complete dissolution of the solid. The aqueous phase was extracted with diethyl ether (2 x 70 ml), the combined organic phases dried over magnesium sulphate and concentrated under reduced pressure to give 4,4'-diamino-3,3',5,5'-tetraisopropyl-triphenylmethine as a pale blue solid (1.520 g, 24%).

Compound [(4-H$_2$N-2,6-i-Pr$_2$C$_6$H$_2$x(4-H$_2$)HC]: ES mass spectrum, $m/z$ 443 [M+H]$^+$; 
IR (cm$^{-1}$) 3474, 3442, 3371 (N-H); $^1$H NMR (CDCl$_3$, 293 K): 1.24 (d, 24H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)), 2.96 (sept, 4H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)), 3.67 (br, 4H, NH$_2$), 5.39 (s, 1H, CHPh), 6.86 (s, 4H, Ar-H), 7.19-7.31 (m, 5H, Ar-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): 23.0 (s, CH$_3$), 28.4 (s, CH), 57.0 (s, CH), 124.4 (s, Ar), 125.9 (s, Ar), 128.3 (s, Ar), 129.7 (s, Ar), 132.7 (s, Ar), 135.0 (s, Ar), 138.3 (s, Ar), 146.7 (s, Ar); Found C: 83.56 H: 10.26 N: 6.24 Expected C: 83.33 H: 10.40 N: 6.27%.

(ii) $Y = 	ext{hydroxy}$: Employing the method outlined in 7.2.5(i) with 2,6-diisopropylaniline (5.000 g, 0.028 mol), para-hydroxybenzaldehyde (2.240 g, 0.018 mmol, 0.65 eq.) and concentrated hydrochloric acid (1 ml) at a temperature of 130 °C for 12 hrs, gave 4,4'-diamino-3,3',5,5'-tetraisopropyl-4'-hydroxy-triphenylmethine as a red solid (1.110 g, 17%).

Compound [(4-H$_2$N-2,6-i-Pr$_2$C$_6$H$_2$x(4-OH-C$_6$H$_4$)HC]: ES mass spectrum, $m/z$ 459 [M+H]$^+$; IR (cm$^{-1}$) 3417, 3327 (N-H, O-H); $^1$H NMR (CDCl$_3$, 293 K): 1.10 (d, 24H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)$_2$), 2.82 (sept, 4H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)$_2$), 3.56 (br, 4H, NH$_2$), 5.19 (s, 1H, CH), 6.69 (s, 4H, Ar-H), 6.92 (d, 2H, $^3$J$_{H-H}$ 8.2, Ar-H), 7.27 (d, 2H, $^3$J$_{H-H}$ 8.2, Ar-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): 22.5 (s, CH$_3$), 22.6 (s, CH$_3$), 28.0 (s, CH), 55.6 (s, CH$_3$), 114.4 (s, Ar), 124.0 (s, Ar), 130.2 (s, Ar), 132.7 (s, Ar), 135.4 (s, Ar), 137.3 (s, Ar), 138.1 (s, Ar), 153.6 (s, Ar); mp = 205 °C. In addition, a single crystal X-ray diffraction study of 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine has confirmed the structural type, details can be found in Table 2.
(iii) \( Y = \text{bromo} \): Employing the method outlined in 7.2.5(i) with 2,6-diisopropylaniline (5.000 g, 0.28 mol), \textit{para}-bromobenzaldehyde (3.413 g, 18.3 mmol, 0.65 eq.) and concentrated hydrochloric acid (1 ml) at a temperature of 120 °C for 12 hrs gave 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-bromo-triphenylmethine as a pale blue solid (1.320 g, 45%).

Compound \([(4\text{-H}_2\text{N}-2,6-\text{t-Pr}_2\text{C}_6\text{H}_2)_2(4-\text{Br-C}_6\text{H}_4)\text{HC}]): \text{ES mass spectrum, } m/z \ 523 [M+H]^{+}; \text{IR (cm}^{-1}) \ 3321 (\text{N-H}); ^1\text{H NMR (CDCl}_3, \ 293 \text{ K}): \delta \ 1.10 (d, 24H, ^3J_{\text{H-H}} \ 6.7, \text{CH(CH}_3)_2), 2.82 (sept, 4H, ^3J_{\text{H-H}} \ 6.7, \text{CH(CH}_3)_2), 3.56 (br, 4H, \text{NH}_2), 5.20 (s, 1H, CPH), 6.68 (s, 4H, Ar-H), 6.92 (d, 2H, ^3J_{\text{H-H}} \ 8.3, \text{Ar-H}), 7.27 (d, 2H, ^3J_{\text{H-H}} \ 8.3, \text{Ar-H}); ^{13}\text{C \{^1\text{H}} \text{ NMR (CDCl}_3, \ 293 \text{ K}): 22.5 (s, } \text{CH}_3), 22.5 (s, } \text{CH}_3), 28.0 (s, } \text{CH}, 56.0 (s, } \text{CH}_3), 119.3 (s, } \text{Ar}), 123.8 (s, } \text{Ar}), 130.9 (s, } \text{Ar}), 131.1 (s, } \text{Ar}), 132.3 (s, } \text{Ar}), 133.8 (s, } \text{Ar}), 138.1 (s, } \text{Ar}), 145.5 (s, } \text{Ar})

(iv) \( Y = \text{isopropyl} \): Employing the method outlined in 7.2.5(i) with 2,6-diisopropylaniline (2.00 g, 11.3 mmol), \textit{para}-isopropylbenzaldehyde (1.087 g, 7.34 mmol, 0.65 eq.) and concentrated hydrochloric acid (1 ml) at 120 °C for 12 hrs, gave 4,4'-amino-3,3',4'',5,5'-pentaisopropyl-triphenylmethine as a white solid after recrystallisation from hot hexane (1.640 g, 46%).

Compound \([(4\text{-H}_2\text{N}-2,6-\text{t-Pr}_2\text{C}_6\text{H}_2)_2(4-((\text{CH}_3)_2\text{CH})-\text{C}_6\text{H}_4)\text{HC}]): \text{ES mass spectrum, } m/z \ 485 [M+H]^{+}; \text{IR (cm}^{-1}) \ 3400 (\text{N-H}); ^1\text{H NMR (CDCl}_3, \ 293 \text{ K}): \delta \ 1.19 (d, 24H, ^3J_{\text{H-H}} \ 6.9, \text{CH(CH}_3)_2), 1.23 (d, 6H, ^3J_{\text{H-H}} \ 6.9, \text{CH(CH}_3)_2), 2.91 (sept, 5H, ^3J_{\text{H-H}} \ 6.9, \text{CH(CH}_3)_2), 5.29 (s, 1H, CPH), 6.82 (s, 4H, Ar-H), 7.03-7.10 (m, 4H, Ar-H); ^{13}\text{C \{^1\text{H}} \text{ NMR (CDCl}_3, \ 293 \text{ K): 22.4 (s, } \text{CH}_3), 22.5 (s, } \text{CH}_3), 24.1 (s, } \text{CH}_3), 28.0 (s, } \text{CH(CH}_3)_2), 33.6 (s, } \text{CH(CH}_3)_2), 56.3 (s, } \text{CPh}), 124.0 (s, } \text{Ar}), 126.0 (s, } \text{Ar}), 129.1 (s, } \text{Ar}), 132.2 (s, } \text{Ar}), 134.8 (s, } \text{Ar}), 137.9 (s, } \text{Ar}), 143.6 (s, } \text{Ar}), 145.9 (s, } \text{Ar}); \text{Anal. Calcd for } (\text{C}_{32}\text{H}_{52}\text{N}_2): C, 84.24; H, 9.98; N, 5.8. \text{Found C, 84.36, H, 10.12; N, 5.83%}.

(v) \( Y = 4-\text{allyl} \): Employing the method outlined in 7.2.5(i) with 2,6-diisopropylaniline (1.700 g, 9.61 mmol), \textit{p}-allylbenzaldehyde (1.100 g, 6.24 mmol, 0.65 eq.) and concentrated hydrochloric acid (1 ml) at 120 °C for 12 hrs gave 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-allyl-triphenylmethine as a white solid after recrystallisation from hot hexane (0.311 g, 13%).
Compound [(4-H2N-2,6-i-Pr2C6H2)2(4-(CH2CH=CH2)-C6H4)HC]: ES mass spectrum, m/z 483 [M+H]+; IR (cm⁻¹) 3398 (N-H); ¹H (CDCl₃, 293 K): δ 1.10 (d, 24H, J₃H-H 6.9, CH(CH₃)₂), 2.82 (sept, 5H, J₃H-H 6.9, CH(CH₃)₂), 3.27 (ddd, 5H, J₃H-H 6.4, J₄H-H 1.2, 1.5, CH₂), 3.49 (br, 2H, NH₂), 4.9-5.0 (m, 2H, CHCH₂), 5.21 (s, 1H, CHPH), 4.90-5.00 (m, 2H, CHCH₂), 5.82-5.96 (m, 2H, CHCH₂), 6.72 (s, 4H, Ar-H), 6.96 (s, 4H, Ar-H).

(vi) **Y = nitro**:

Employing the method outlined in 7.2.5(i) with 2,6-diisopropylaniline (5.000 g, 28.3 mmol), para-nitrobenzaldehyde (2.773 g, 18.4 mmol, 0.65 eq.) and concentrated hydrochloric acid (5 ml) gave 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-nitro-triphenylmethine as a yellow solid (1.010 g, 15%).

Compound [(4-H2N-2,6-i-Pr2C6H2)2(4-NO₂-C6H4)HC]: ES mass spectrum, m/z 488 [M+H]+; IR (cm⁻¹) 3394, 3478 (N-H) 1515, 1345 (NO₂); ¹H (CDCl₃, 293 K): δ 1.09 (d, 24H, J₃H-H 6.7, CH(CH₃)), 2.81(s, 4H, J₃H-H 6.7, CH(CH₃)), 3.56 (br, 4H, NH₂), 5.32 (s, 1H, CHPH), 6.67 (s, 4H, Ar-H), 7.21 (dt, 2H, J₃H-H 8.8, J₄H-H 1.9, Ar-H), 8.00 (dt, 2H, J₃H-H 8.8, J₄H-H 1.9, Ar-H); ¹³C {¹H} NMR (CDCl₃, 293 K): 23.0 (s, CH₃), 28.4 (s, CH), 57.0 (s, CH), 124.4 (s, Ar), 125.9 (s, Ar), 128.3 (s, Ar), 129.7 (s, Ar), 132.7 (s, Ar), 135.0 (s, Ar), 138.3 (s, Ar), 146.7 (s, Ar).

### 7.2.8 Preparation of 1-methoxy-1-(4-nitrophenyl)-1-(3,5-diisopropyl,4-amino-phenyl)methane

To a solution of 2,6-diisopropylaniline (2.000 g, 11.3 mmol) and para-nitrobenzaldehyde (1.706 g, 11.3 mmol, 1 eq.) was added concentrated hydrochloric acid (2 ml) and methanol (2 ml). The biphasic solution was stirred at 120 °C overnight. The resulting yellow green solution was allowed to cool to ambient temperature and diluted with dichloromethane. The minimum amount of concentrated hydrochloric acid (ca. 2 ml) was added and the solution stirred at ambient temperature for 2 hrs before being filtered. The yellowish salt collected was washed thoroughly with dichloromethane and air-dried. The salt was suspended in diethyl ether (70 ml) and stirred with an aqueous solution of saturated sodium hydroxide until the complete dissolution of the solid. The aqueous phase was extracted with diethyl ether (2 x 70 ml), the combined organic phases dried over magnesium sulphate and concentrated under
reduced pressure to give 1-methoxy, 1-(4-nitrophenyl), 1-(3,5-diisopropyl, 4-aminophenyl)methane as a yellow solid (0.480 g, 12%).

Compound \([\text{4-H}_2\text{N-2,6-i-Pr}_2\text{C}_6\text{H}_2]_2(4-\text{NO}_2\text{C}_6\text{H}_4)\)(OMe)HC]: ES mass spectrum, \(m/z\) 344 [M+H]^+; IR (cm\(^{-1}\)) 3489 (N-H) 1517, 1347 (NO\(_2\)); \(^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 1.09 (d, 6H, \(3\)J\(_{H-H}\) 6.7, CH(CH\(_3\))), 1.11 (d, 6H, \(3\)J\(_{H-H}\) 6.7, CH(CH\(_3\))), 2.81 (s, 4H, \(3\)J\(_{H-H}\) 6.7, CH(CH\(_3\))), 3.29 (s, 1H, CHPh), 3.56 (br, 2H, NH\(_2\)), 6.82 (s, 2H, Ar-H), 7.44 (d, 2H, \(3\)J\(_{H-H}\) 8.8 Ar-H), 8.11 (d, 2H, \(3\)J\(_{H-H}\) 8.8, Ar-H); \(^{13}\)C \({\text{^1}}\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 22.3 (s, CH\(_3\)), 22.4 (s, CH\(_3\)), 56.9 (s, CH), 121.9 (s, Ar), 123.5 (s, Ar), 127.3 (s, Ar), 129.9 (s, Ar), 132.6 (s, Ar), 140.3 (s, Ar), 150.6 (s, Ar). In addition, a single crystal X-ray diffraction study of 1-methoxy, 1-(4-nitrophenyl), 1-(3,5-diisopropyl, 4-aminophenyl)methane confirmed the structural type; details can be found in Table 2.

7.2.9 Preparation of 4,4',4''-triamino-3,3',5,5'-tetraisopropyl triphenylmethine

To a solution of 4,4'-amino-3,3',5,5'-tetraisopropyl-4',4''-nitrotriphenylmethine (0.500 g, 1.026 mmol) dissolved in a mixture of ethanol (7 ml) and concentrated hydrochloric acid (7 ml) was added tin chloride (0.970 g, 5.13 mmol, 5 eq.). The slurry was stirred at 80 °C overnight to give an orange solution after which time chloroform (15 ml) was introduced. After neutralisation with a saturated solution of sodium hydroxide, the organic layer was separated and the aqueous layer extracted with chloroform (2 x 15 ml). The combined organic layers are washed twice with water, dried over magnesium sulphate, filtered and concentrated under reduced pressure to afford 4,4',4''-triamino-3,3',5,5'-tetraisopropyl triphenylmethine as a purple oil (0.250 g, 47%).

Compound \([(4-\text{H}_2\text{N-3,5-i-Pr}_2\text{C}_6\text{H}_2)_2(4-\text{H}_2\text{N-C}_6\text{H}_4)\text{HC}]: \text{ES mass spectrum, } m/z 459 [M+H]^+; \text{IR (cm}^{-1}\text{) 3321 (N-H); } ^1\text{H NMR (CDCl}_3, 293 K): \delta 1.09 (d, 24H, } 3\text{J}_{H-H} 6.7, \text{CH(CH}_3))\), 2.82 (s, 4H, \(3\)J\(_{H-H}\) 6.7, CH(CH\(_3\))), 3.47 (br, 4H, NH\(_2\)), 5.14 (s, 1H, CHPh), 6.49 (dt, 2H, \(3\)J\(_{H-H}\) 8.5 \(4\)J\(_{H-H}\) 2.0, Ar-H), 6.71 (s, 4H, Ar-H), 6.82 (dt, 2H, \(3\)J\(_{H-H}\) 8.5 \(4\)J\(_{H-H}\) 2.0, Ar-H).
7.3 Synthesis of Ligands

7.3.1 Preparation of N-([1,10]-phenanthroline-2-yl)methylene)-2,6-R$_1^1$-4-R$_2^2$-benzenamine (L1-L5)

(i) L1 $R_1^1 = \text{methyl; } R_2^2 = \text{hydrogen}$: To a solution of [1,10]-phenanthroline-2-carboxaldehyde (0.200 g, 0.96 mmol) in ethanol (2 ml) was added 2,6-dimethylaniline (0.122 ml, 1.01 mmol, 1 eq.). The solution was allowed to stir at 50 °C for 0.5 hrs and one drop of acetic acid was added. The red suspension was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the residue dissolved in chloroform (25 ml), dried over magnesium sulphate and filtered. The solvent was removed and the residue dried under reduced pressure to afford N-([1,10]-phenanthroline-2-yl)methylene)-2,6-dimethylbenzenamine (L1) as a red oil (0.222 g, 74%).

Compound L1: ES mass spectrum, $m/z$ 312 [M+H]$^+$; IR (cm$^{-1}$) 1637 (C=N); $^1$H NMR (CDCl$_3$, 293 K): δ 2.12 (s, 6H, Ar-CH$_3$), 6.69 (s, 2H, Ar-CH$_3$), 7.60 (dd, $^3$J$_{H,H}$ 4.6, 7.9, 1H, Phen-H), 7.80 (s, 2H, Phen-H), 8.22 (dd, 1H, $^3$J$_{H,H}$ 7.0, $^4$J$_{H,H}$ 1.8, Phen-H), 8.31 (d, 1H, $^3$J$_{H,H}$ 6.4, Phen-H), 8.31 (d, 1H, $^3$J$_{H,H}$ 8.5, Py-H), 8.78 (s, 1H, HC=N), 9.21 (dd, 1H, $^3$J$_{H,H}$ 4.6, $^4$J$_{H,H}$ 1.8, 1H, Phen-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): δ 17.2 (s, C, Me), 119.1 (s, Ar), 120.5 (s, Ar), 122.2 (s, Ar), 125.5 (s, Ar), 125.6 (s, Ar) 126.7 (s, Ar) 127.7 (s, Ar), 127.8 (s, Ar), 128.2 (s, Ar), 128.6 (s, Ar), 135.2 (s, Ar), 135.7 (s, Ar), 144.8 (s, Ar), 149.5 (s, Ar), 163.1 (s, C=N).

(ii) L2 $R_1^1 = R_2^2 = \text{methyl}$: Employing the method outlined in 7.3.1(i) with [1,10]-phenanthroline-2-carboxaldehyde (1.500 g, 7.21 mmol), 2,4,6-trimethylaniline (1.02 ml, 7.2 mmol, 1 eq.) and ethanol (2 ml), gave N-([1,10]-phenanthroline-2-yl)methylene)-2,4,6-trimethylbenzenamine (L2) as a black oil (1.800 g, 77%).

Compound L2: ES mass spectrum, $m/z$ 326 [M+H]$^+$; IR (cm$^{-1}$) 1631 (C=N); $^1$H NMR (CDCl$_3$, 293 K): δ 2.07 (s, 6H, Ar-CH$_3$), 2.12 (s, 3H, Ar-CH$_3$), 6.69 (s, 2H, Ar-CH$_3$), 7.60 (dd, $^3$J$_{H,H}$ 4.6, 7.9, 1H, Phen-H), 7.80 (s, 2H, Ar-H), 8.22 (dd, 1H, $^3$J$_{H,H}$ 7.0, $^4$J$_{H,H}$ 1.8, Phen-H), 8.31 (d, 1H, $^3$J$_{H,H}$ 6.4, Phen-H), 8.31 (d, 1H, $^3$J$_{H,H}$ 8.5, Phen-H), 8.77 (s, 1H, HC=N), 9.20 (dd, 1H, $^3$J$_{H,H}$ 4.6, $^4$J$_{H,H}$ 1.8, 1H, Phen-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): δ 16.5 (s, Ar-CH$_3$), 17.3 (s, Ar-CH$_3$), 19.3 (s, Ar-CH$_3$), 19.8 (s, Ar-CH$_3$), 119.3 (s, Ar), 120.8 (s, Ar), 122.2 (s, Ar), 125.5 (s, Ar), 125.6 (s, Ar), 126.7 (s, Ar), 127.8 (s,
(iii) **L3** $R^1 = \text{isopropyl}; R^2 = \text{hydrogen}: $ Employing the method outlined in 7.3.1(i) with [1,10]-phenanthroline-2-carboxaldehyde (0.313 g, 1.50 mmol), 2,6-diisopropylaniline (0.300 ml, 1.60 mmol, 1.05 eq.) and ethanol (2 ml), gave $N$-((1,10)-phenanthroline-2-yl)methylene)-2,6-diisopropylbenzenamine (L3) as a yellow powder (0.320 g, 58%).

**Compound L3:** ES mass spectrum, $m/z$ 368 [M+H]$^+$; IR (cm$^{-1}$) 1627 (C=N); $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 1.10 (d, 12H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)$_2$), 2.87 (sept, 2H, $^3$J$_{H-H}$ 6.7, CH(CH$_3$)$_2$), 7.08-7.14 (m, 3H, Ar-CH$_3$), 7.60 (dd, $^3$J$_{H-H}$ 4.4, 8.2, 1H, Phen-H), 7.82 (s, 2H, Ar-H), 8.24 (dd, 1H, $^3$J$_{H-H}$ 8.2, $^4$J$_{H-H}$ 1.8, Phen-H), 8.65 (d, 1H, $^3$J$_{H-H}$ 8.2, Phen-H), 8.76 (s, 1H, HC=N), 9.19 (dd, 1H, $^3$J$_{H-H}$ 4.4, $^4$J$_{H-H}$ 1.5, 1H, Phen-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): $\delta$ 23.3 (s, CH(CH$_3$)$_2$), 28.0 (s, CH(CH$_3$)$_2$), 118.7 (s, Ar), 120.5 (s, Ar), 122.8 (s, Ar), 123.0 (s, Ar), 123.3 (s, Ar), 124.5 (s, Ar), 126.6 (s, Ar), 127.8 (s, Ar), 129.0 (s, Ar), 129.9 (s, Ar), 136.5 (s, Ar), 136.9 (s, Ar), 145.9 (s, Ar), 148.3 (s, Ar), 150.6 (s, Ar), 154.6 (s, Ar), 163.5 (s, C=N). In addition, a single crystal X-ray diffraction study of $N$-((1,10)-phenanthroline-2-ylmethylene)-2,6-diisopropylbenzenamine has confirmed the structural type, details can be found in Table 3.

(iv) **L4** $R^1 = \text{isopropyl}; R^2 = \text{bromo}: $ Employing the method outlined in 7.3.1(i) with [1,10]-phenanthroline-2-carboxaldehyde (0.313 g, 1.50 mmol), 4-bromo-2,6-diisopropylaniline (0.257 g, 1.01 mmol, 1.05 eq.) ethanol (2 ml), gave $N$-((1,10)-phenanthroline-2-yl)methylene)-4-bromo-2,6-diisopropylbenzenamine (L4) as a red powder (0.374 g, 55%).

**Compound L4:** ES mass spectrum, $m/z$ 448 [M+H]$^+$; IR (cm$^{-1}$) 1637 (C=N); $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 1.09 (d, 12H, $^3$J$_{H-H}$ 6.9, CH(CH$_3$)$_2$), 2.93 (sept, 2H, $^3$J$_{H-H}$ 6.9, CH(CH$_3$)$_2$), 7.2 (s, 2H, Ar-H), 7.62 (dd, 1H, $^3$J$_{H-H}$ 4.4, 8.2, Phen-H), 7.79 (s, 2H, Phen-H), 8.24 (dd, 1H, $^3$J$_{H-H}$ 8.2, $^4$J$_{H-H}$ 1.5, Phen-H), 8.32 (d, 1H, $^3$J$_{H-H}$ 8.2, Phen-H), 8.6 (d, 1H, $^3$J$_{H-H}$ 8.5, Phen-H), 8.69 (s, 1H, HC=N), 9.20 (d, 1H, $^3$J$_{H-H}$ 4.4, $^4$J$_{H-H}$ 1.8, Phen-H); $^{13}$C ($^1$H) NMR (CDCl$_3$, 293 K): $\delta$ 21.1 (s, CH(CH$_3$)$_2$) 27.2 (s, CH(CH$_3$)$_2$), 119.4 (s, Ar),
120.4 (s, Ar), 122.1 (s, Ar), 124.7 (s, Ar), 125.2 (s, Ar), 125.4 (s, Ar), 126.9 (s, Ar), 127.4 (s, Ar), 128.0 (s, Ar), 128.8 (s, Ar), 133.6 (s, Ar), 135.5 (s, Ar), 135.9 (s, Ar), 148.5 (s, Ar), 149.6 (s, Ar), 153.2 (s, Ar), 163.2 (s, C, C=N).

(v) L5 \( R^I = \text{isopropyl}; R^2 = \text{cyano} \): Employing the method outlined in 7.3.1(i) with [1,10]-phenanthroline-2-carboxaldehyde (0.200 g, 0.96 mmol), 2,6-diisopropyl-4-cyanoanil (0.203 g, 1.01 mmol, 1.05 eq.) and ethanol (2 ml), gave \( N-([1,10]-\text{phenanthroline-2-yl})\text{methylene}-4\text{-cyano-2,6-diisopropylbenzenamine (L5)} \) as a red powder (0.256 g, 68%).

**Compound L5:** ES mass spectrum, \( m/z \) 393 [M+H]⁺; IR (cm⁻¹) 1639 (C=N); \( ^1\text{H} \) NMR (CDCl₃, 293 K): \( \delta \) 1.12 (d, 12H, \( ^3\text{J}_{\text{H-H}} \) 6.7, CH(CH₃)₂), 2.94 (sept, 2H, \( ^3\text{J}_{\text{H-H}} \) 6.7, CH(CH₃)₂), 7.20 (s, 2H, Ar-H), 7.66 (dd, 1H \( ^3\text{J}_{\text{H-H}} \) 8.2, 4.4, Phen-H), 7.90 (s, 2H, Phen-H), 8.27 (dd, 1H \( ^3\text{J}_{\text{H-H}} \) 7.9, \( ^4\text{J}_{\text{H-H}} \) 1.8, Phen-H), 8.40 (d, 1H, \( ^3\text{J}_{\text{H-H}} \) 8.2, Phen-H), 8.61 (d, 1H, \( ^3\text{J}_{\text{H-H}} \) 8.5, Phen-H), 8.69 (s, 1H, HC=N), 9.2 (d, 1H, \( ^3\text{J}_{\text{H-H}} \) 1.8, Phen-H), \( ^{13}\text{C} \) {\( ^1\text{H} \) NMR (CDCl₃, 293 K): \( \delta \) 21.8 (s, CH(CH₃)₂), 27.8 (s, CH(CH₃)₂), 99.1 (s, CN), 119.3 (s, Ar), 120.0 (s, Ar), 121.9 (s, Ar), 122.5 (s, Ar), 125.3 (s, Ar), 125.4 (s, Ar), 126.4 (s, Ar), 127.3 (s, Ar), 128.8 (s, Ar), 128.4 (s, Ar), 131.1 (s, Ar), 135.5 (s, Ar), 144.8 (s, Ar), 149.9 (s, Ar), 151.3 (s, Ar), 152.7 (s, Ar), 163.0 (s, C=N).

7.3.2 Preparation of \( N-((2,2'-\text{bipyridin-6-yl})\text{methylene}-2,6\text{-diisopropylbenzenamine (L6)} \)

To a suspension of 2,2'-bipyridine-6-carboxaldehyde (0.144 g, 0.78 mmol) in ethanol (2 ml) was added 2,6-diisopropylaniline (0.180 g, 1.02 mmol, 1.3 eq.) and one drop of acetic acid. The brown solution was refluxed for 24 hrs. On cooling to 0 °C the suspension was filtered, washed with cold ethanol and dried under reduced pressure to afforded \( N-((2,2'-\text{bipyridin-6-yl})\text{methylene}-2,6\text{-diisopropylbenzenamine (L6)} \) as a yellow solid (0.171 g, 63%).

**Compound L6:** ES mass spectrum, \( m/z \) 344 [M+H]⁺; HRMS (FAB): Calcld for C₂₃H₂₅N₃ [M+H]⁺, found 344.21266, C₂₃H₂₆N₃ requires 344.21267; IR (cm⁻¹) 1639 (C=N); \( ^1\text{H} \) NMR (CDCl₃, 293 K): \( \delta \) 1.12 (d, 12H, \( ^3\text{J}_{\text{H-H}} \) 6.7, CH(CH₃)), 2.93 (sept, 2H, \( ^3\text{J}_{\text{H-H}} \) 6.7, CH(CH₃)), 6.82 (m, 3H, Ar-CH₃), 7.29 (ddd, 1H, \( ^3\text{J}_{\text{H-H}} \) 5.0, 7.6, \( ^4\text{J}_{\text{H-H}} \) 0.9, Py-H), 7.80 (ddd, 1H, \( ^3\text{J}_{\text{H-H}} \) 7.6, 7.9, \( ^4\text{J}_{\text{H-H}} \) 1.8, Py-H), 7.92 (ddd, 1H, \( ^3\text{J}_{\text{H-H}} \) 7.6, 7.9, \( ^4\text{J}_{\text{H-H}} \) 0.6, Py-H), 8.25 (dd, 1H, \( ^3\text{J}_{\text{H-H}} \) 7.9, \( ^4\text{J}_{\text{H-H}} \) 1.2, Py-H), 8.34 (s, 1H, HC=N), 8.48 (ddd, 1H, \( ^3\text{J}_{\text{H-H}} \) 8.5, Py-H).
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7.9, 7.6, 4\( ^1\text{H-H} \) 0.9, Py-H), 8.65 (ddd, 1H, \( ^3\text{J}_{\text{H-H}} \) 5.0, \( ^4\text{J}_{\text{H-H}} \) 0.9, 1.8, Py-H); \( ^{13}\text{C} \{^1\text{H}\} \)

NMR (CDCl\(_3\), 293 K): \( \delta \) 15.1 (s, CH(CH\(_3\))) 30.9 (s, CH(CH\(_3\))), 120.9 (s, Ar), 121.3 (s, Ar), 122.5 (s, Ar), 123.4 (s, Ar), 123.9 (s, Ar), 136.9 (s, Ar), 137.5 (s, Ar) 137.6 (s, Ar), 136.4 (s, Ar), 147.4 (s, Ar), 149.2 (s, Ar), 149.3 (s, Ar), 155.8 (s, Ar), 156.0 (s, Ar), 164.3 (s, C=N); mp = 128 °C.

7.3.3 Preparation of \( \text{N-(1-(2,2'-bipyridin-6-yl)ethylidene)diisopropylbenzenamine (L7)} \)

To a suspension of 6-acetyl-2,2'-bipyridine (0.180 g, 0.91 mmol) in n-butanol (1 ml) was added 2,6-diisopropylaniline (0.210 g, 1.18 mmol, 1.3 eq.) and one drop of acetic acid. The brown solution was refluxed for 24 hrs. The solvent was removed under reduced pressure at 50 °C overnight to afford \( \text{N-(1-(2,2'-bipyridin-6-yl)ethylidene)-2,4,6-trimethylbenzenamine (L7)} \) as a black oily residue (0.188 g, 58%).

The spectroscopic data for L7 were consistent with the previous data reported by Gibson et al.\(^{12}\)

7.3.4 Preparation of \( \text{N-((2-(2,6-diisopropylphenyl)imino)-1-methyl-propylidene)-2,3,5,6-tetramethyl-benzene-1,4-diamine (L8)} \)

A mixture of 3-(2,6-diisopropyl-phenylimino)-butan-2-one (1.200 g, 4.90 mmol) and 2,3,5,6-tetramethyl-benzene-1,4-diamine (1.000 g, 6.10 mmol, 1.3 eq.) in toluene (4 ml) was stirred with 20 drops of dilute formic acid (2 ml in 10 ml of toluene) acid for 0.5 hrs. The suspension was heated for three days at 50 °C. On cooling, the suspension was filtered and washed with cold toluene. The filtrate was evaporated, dissolved into chloroform (2 ml) and cooled to \(-78\) °C for 0.5 hrs before being filtered. The remaining filtrate was heated at 80 °C under reduced pressure overnight to give \( \text{N-((2-(2,6-diisopropylphenyl)imino)-1-methyl-propylidene)-2,3,5,6-tetramethyl-benzene-1,4-diamine (L8)} \) as a black oily solid (1.253 g, 67%).

Compound L8: ES mass spectrum, \( m/z \) 391[M+H]\(^{+}\); IR (cm\(^{-1}\)) N-H) 3398, 1639 (C=N); \( ^1\text{H} \) NMR (CDCl\(_3\), 293 K): \( \delta \) 1.05-1.10 (d, 12H, \( ^3\text{J}_{\text{H-H}} \) 6.8, CH(CH\(_3\))) 1.94 (s, 6H, Ar-Me), 1.96 (s, 3H, (CH\(_3\))C=N), 2.02 (s, 3H, (CH\(_3\))C=N), 2.09 (s, 6H, Ar-Me), 2.61 (sept, 2H, \( ^3\text{J}_{\text{H-H}} \) 6.8, CH(CH\(_3\))), 3.40 (s, br, 2H, NH\(_2\)), 6.99-7.15 (m, 3H, Ar-H); \( ^{13}\text{C} \{^1\text{H}\} \) NMR (CDCl\(_3\), 293 K): \( \delta \) 12.5 (s, Ar), 13.6 (s, Ar), 14.9 (s, Ar), 15.6 (s, Ar), 21.7
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(s, Ar), 22.0 (s, Ar), 27.4 (s, Ar), 117.8 (s, Ar), 119.4 (s, Ar), 121.9 (s, Ar), 122.6 (s, Ar), 134.1 (s, Ar), 137.4 (s, Ar), 139.7 (s, Ar), 145.3 (s, Ar), 167.4 (s, (CH₃)C=N), 167.7 (s, (CH₃)C=N).

7.3.5  Preparation of N-((pyridin-2-yl)methylene)-2,6-R₁-4-R²-benzenamine (L9-L11)

(i) L9  \( R¹ = \text{methyl}, \ R² = \text{hydrogen} \): A mixture of 2-pyridinecarboxaldehyde (0.14 ml, 1.48 mmol) and 2,6-dimethylaniline (0.180 g, 1.65 mmol, 1 eq.) in ethanol (2 ml) was stirred for 8 hrs at ambient temperature. The brown suspension was cooled, filtered and the residue washed with cold ethanol affording \( N-((\text{pyridin-2-yl})\text{methylene})-2,6\)-dimethylbenzenamine as a yellow solid (0.243 g, 70%).

The spectroscopic data for L9 were consistent with the previous data reported by Alt et al.\(^{13}\)

(ii) L10  \( R¹ = R² = \text{methyl} \): Employing the method outlined in 7.3.5(i) with 2-pyridinecarboxaldehyde (0.141 ml, 1.48 mmol), 2,4,6-trimethylaniline (0.200 g, 1.48 mmol, 1 eq.) and ethanol (2 ml), gave \( N-((\text{pyridin-2-yl})\text{methylene})-2,4,6\)-trimethylbenzenamine (L10) as a yellow solid (0.260 g, 78%).

Compound L10: ES mass spectrum, \( m/z \ 225 \ [M+H]^+ \); IR (cm\(^{-1}\)) 1641 (C=N); \(^1\)H NMR (CDCl₃, 293 K): \( \delta \ 2.07 \) (s, 6H, Ar-CH₃), 2.22 (s, 3H, Ar-CH₃), 6.82 (s, 2H, Ar-CH₃), 7.32 (ddd, \(^3\)J\(_{H-H}\) 4.6, 7.6 \(^4\)J\(_{H-H}\) 1.2, 1H, Py-H), 7.76 (ddddd, 1H, \(^3\)J\(_{H-H}\) 7.6, 7.9 \(^4\)J\(_{H-H}\) 0.8, 0.9, Py-H), 8.20 (ddd, 1H, \(^3\)J\(_{H-H}\) 7.9 \(^4\)J\(_{H-H}\) 0.8, 0.9, Py-H), 8.26 (s, 1H, HC=N), 8.63 (ddd, 1H, \(^3\)J\(_{H-H}\) 4.7 \(^4\)J\(_{H-H}\) 0.8, 0.9, Py-H); \(^13\)C \( \{^1\)H\} NMR (CDCl₃, 293 K): \( \delta \ 18.2 \) (s, Ar-CH₃), 20.8 (s, Ar-CH₃), 121.2 (s, Ar), 125.3 (s, Ar), 126.9 (s, Ar), 128.9 (s, Ar), 133.5 (s, Ar), 136.8 (s, Ar), 147.9 (s, Ar), 149.6 (s, Ar), 154.5 (s, Ar), 163.4 (s, C=N).

(iii) L11  \( R¹ = \text{isopropyl}, \ R² = \text{hydrogen} \): Employing the method outlined in 7.3.5(i) with 2-pyridinecarboxaldehyde (0.141 ml, 1.48 mmol), 2,6-diisopropylaniline (0.261 g, 1.48 mmol, 1 eq.) and ethanol (2 ml), gave \( N-((\text{pyridin-2-yl})\text{methylene})-2,6\)-diisopropylbenzenamine (L11) as a yellow solid (0.293 g, 74%).
The spectroscopic data for L11 were consistent with the previous data reported by Alt et al.\textsuperscript{13}

7.3.6 Preparation of \(N\)-(1-(pyridin-2-yl)ethylidene)-2,6-\(R^1\)-4-\(R^2\)-benzenamine (L12, L13)

(i) **L12** \(R^1 = R^2 = \text{methyl}\): To a mixture of 2-acetylpyridine (0.17 ml, 1.51 mmol) and 2,4,6-trimethylaniline (0.205 g, 1.51 mmol, 1 eq.) in \(n\)-butanol (2 ml) was added 2 drops of acetic acid and was stirred at 130 °C overnight. The dark brownish oil was cooled and dried under reduced pressure for 24 hrs. The brown oil was washed several times with hexane, the hexane was concentrated to afford \(N\)-(1-(pyridin-2-yl)ethylidene)-2,4,6-trimethylbenzenamine (L12) as a brown oil (0.179 g, 50%).

Compound L12: ES mass spectrum, \(m/z\) 239 [M+H]+; IR (cm\(^{-1}\)) 1644 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K) \(\delta\) 1.92 (s, 6H, Ar-CH\(_3\)), 2.10 (s, (CH\(_3\))C=N, 3H), 2.21 (s, 3H, Ar-CH\(_3\)), 6.82 (s, 2H, Ar-CH\(_3\)), 7.32 (ddd, 1H, \(\text{J}_{HH} = 4.6\), 7.6 \(\text{J}_{HH} = 1.2\), Py-H), 7.76 (ddddd, 1H, \(\text{J}_{HH} = 7.6\), 7.9 \(\text{J}_{HH} = 0.8, 0.9\), Py-H), 8.20 (ddd, 1H, \(\text{J}_{HH} = 7.9\), 4.7 \(\text{J}_{HH} = 0.8, 0.9\), Py-H), 8.63 (ddddd, 1H, \(\text{J}_{HH} = 4.7\), 4.7 \(\text{J}_{HH} = 0.8, 0.9\), Py-H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl\(_3\), 293 K): \(\delta\) 16.6 (s, CH\(_3\)C=N), 17.9 (s, Ar-CH\(_3\)), 20.8 (s, Ar-CH\(_3\)), 121.3 (s, Ar), 124.8 (s, Ar), 125.3 (s, Ar), 128.5 (s, Ar), 132.2 (s, Ar), 136.4 (s, Ar), 146.2 (s, Ar), 148.5 (s, Ar), 156.6 (s, Ar), 167.4 (s, C=N).

(ii) **L13** \(R^1 = \text{isopropyl}, R^2 = \text{hydrogen}\): Employing the method outlined in 7.3.6(i) with 2-acetylpyridine (0.17 ml, 1.51 mmol) and 2,6-diisopropylaniline (0.268 g, 1.51 mmol, 1 eq.), \(n\)-butanol (2 ml) and 2 drops of glacial acetic acid, gave \(N\)-(1-(pyridin-2-yl)ethylidene)-2,6-diisopropylbenzenamine (L13) as a brown oil (0.250 g, 58%).

The spectroscopic data for L13 were consistent with the previous data reported by Alt et al.\textsuperscript{13}

7.3.7 Preparation of \(N\)-(1-(pyridin-2-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L14)

To a mixture of 2-acetylpyridine (0.30 ml, 0.27 mmol) and 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.615 g, 0.37 mmol, 1.4 eq.) in toluene (2 ml) was added 2 drops of formic acid. The suspension was heated for three days at 50 °C. The dark reddish suspension was
cooled, filtered and the residue washed with cold toluene. The filtrate was evaporated, dissolved in chloroform (2 ml) and cooled to −78 °C for 0.5 hrs before being filtered. Hexane was added to the filtrate and all volatiles were removed under reduced pressure to give \( \text{N-(1-(pyridin-2-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L14)} \) as a brown solid (0.310 g, 43%).

**Compound L14**: ES mass spectrum, \( m/z \) 268 \([M+H]^+\); IR (cm\(^{-1}\)) 3378 (N-H), 1632 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 1.99 (s, 6H, Ar-CH\(_3\)), 2.11 (s, 3H, (CH\(_3\))C=N), 2.13 (s, 6H, Ar-CH\(_3\)), 3.40 (s, br, 2H, NH\(_2\)), 7.35 (ddd, 1H, \(^3\)J\(_{\text{H-H}}\) 4.6, 7.6 \(^4\)J\(_{\text{H-H}}\) 1.2, Py-H), 7.78 (ddd, 1H, \(^3\)J\(_{\text{H-H}}\) 7.6, 7.9 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H), 8.28 (ddd, 1H, \(^3\)J\(_{\text{H-H}}\) 7.9 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H), 8.69 (ddd, 1H, \(^3\)J\(_{\text{H-H}}\) 4.7 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H); \(^{13}\)C \({}^{1}\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 14.0 (s, Ar-CH\(_3\)), 15.0 (s, Ar-CH\(_3\)), 17.0 (s, (CH\(_3\))C=N), 119.2 (s, Ar), 121.6 (s, Ar), 122.0 (s, Ar), 125.0 (s, Ar), 136.8 (s, Ar), 138.7 (s, Ar), 141.4 (s, Ar), 148.9 (s, Ar), 157.3 (s, Ar), 168.1 (s, C=N); mp = 112 °C.

### 7.3.8 Preparation of \( \text{N,N'-bis((pyridin-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L15)} \)

To a suspension of 2,3,5,6-tetramethyl-benzene-1,4-diamine (1.500 g, 9.15 mmol) in absolute ethanol (100 ml) was added 2-pyridinecarboxaldehyde (1.9 ml, 0.02 mol, 2.2 eq.) dropwise. After stirring overnight at 50 °C, the suspension was filtered, washed with cold ethanol and dried under reduced pressure to give \( \text{N,N'-bis((pyridin-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L15)} \) in good yield as a pale yellow solid (2.812 g, 90%).

**Compound L15**: ES mass spectrum, \( m/z \) 343 \([M+H]^+\); FABMS Calcd for C\(_{24}\)H\(_{22}\)N\(_4\), found 343.19225, requires 343.19227; IR (cm\(^{-1}\)) 1641 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K) 2.01 (s, 12H, Ar-CH\(_3\)), 7.34 (ddd, 2H, \(^3\)J\(_{\text{H-H}}\) 4.6, 7.6 \(^4\)J\(_{\text{H-H}}\) 1.2, Py-H), 7.78 (ddd, 2H, \(^3\)J\(_{\text{H-H}}\) 7.6, 7.9 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H), 8.28 (s, 2H, HC=N), 8.31 (ddd, 2H, \(^3\)J\(_{\text{H-H}}\) 7.9 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H), 8.68 (ddd, 2H, \(^3\)J\(_{\text{H-H}}\) 4.7 \(^4\)J\(_{\text{H-H}}\) 0.8, 0.9, Py-H); \(^{13}\)C \({}^{1}\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 15.0 (s, CH\(_3\)), 121.2 (s, Ar), 123.5 (s, Ar), 125.2 (s, Ar), 136.7 (s, Ar), 147.2 (s, Ar), 149.6 (s, Ar), 154.6 (s, Ar), 163.8 (s, C=N); mp = 228 °C. In addition, a single crystal X-ray diffraction study of L15 has confirmed the structural type, details can be found in Table 3.
7.3.9 Preparation of $N,N'$-bis(1-(pyridin-2-yl)ethylidene)-2,3,5,6-
tetramethylbenzene-1,4-diamine (L16)

To a mixture of 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.500 g, 3.05 mmol) and 2-
acetylpyridine (0.75 ml, 6.71 mmol, 2.2 eq.) in absolute ethanol (50 ml) was added three
drops of formic acid. The solution was heated to 90 °C and stirred overnight. The
suspension was filtered, the residue washed with cold ethanol and dried under reduced
pressure to give $N,N'$-bis(1-(pyridin-2-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-
diamine (L16) in low yield as a yellow solid (0.823 g, 73%).

Compound L16: ES mass spectrum, $m/z$ 371 [M+H]$^+$; FABMS Calcd for C$_{24}$H$_{27}$N$_4$,
found 371.22352, requires 371.22357; IR (cm$^{-1}$) 1631 (C=N); $^1$H NMR (CDCl$_3$, 293 K):
$\delta$ 1.99 (s, 12H, Ar-CH$_3$), 2.19 (s, 6H, (CH$_3$)C=N), 7.35 (ddd, $^3$J$_{H-H}$ 4.6, 7.6 $^4$J$_{H-H}$ 1.2, 2H,
Py-H), 7.83 (ddd, 2H, $^3$J$_{H-H}$ 7.6, 7.9 $^4$J$_{H-H}$ 0.8, 0.9, Py-H), 8.36 (ddd, 2H, $^3$J$_{H-H}$ 7.9 $^4$J$_{H-H}$
0.8, 0.9, Py-H), 8.69 (ddd, 2H, $^3$J$_{H-H}$ 4.7 $^4$J$_{H-H}$ 0.8, 0.9, Py-H); $^{13}$C {$^1$H} NMR (CDCl$_3$,
293 K): $\delta$ 14.8 (s, Ar-CH$_3$), 17.0 (s, CH$_3$), 121.6 (s, Ar), 125.1 (s, Ar), 136.8 (s, Ar),
144.8 (s, Ar), 149.0 (s, Ar), 157.2 (s, Ar), 168.3 (s, C=N); mp = 206 °C.

7.3.10 Preparation of $N$-(1-(pyridin-2-yl)ethylidene)-$N'$-((pyridin-2-
yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L17)

To a solution of 2,3,5,6-tetramethyl-N-(1-(pyridin-2-yl)ethylidene)-benzene-1,4-diamine
(L17) (0.250 g, 0.94 mmol) in absolute ethanol (6 ml) was added
2-pyridinecarboxaldehyde (0.11 ml, 1.00 mmol, 1.1 eq.) in ethanol (4 ml). One drop of
formic acid was added after thirty minutes of stirring at room temperature. The solution
was allowed to stir at room temperature overnight. On cooling to −78 °C, the suspension
was filtered, washed with cold ethanol and dried under reduced pressure to give $N$-(1-
(pyridin-2-yl)ethylidene)-$N'$-((pyridin-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-
diamine (L17) as a pale yellow powder (0.170 g, 51%).

Compound L17: ES mass spectrum, $m/z$ 357 [M+H]$^+$; FABMS found 357.20791,
C$_{23}$H$_{25}$N$_4$ requires 357.20792; IR (cm$^{-1}$) 1632, (C=N); $^1$H NMR (CDCl$_3$, 293 K):
$\delta$ 1.90 (s, 6H, Ar-CH$_3$), 2.03 (s, 6H, Ar-CH$_3$), 2.11 (s, 3H, (CH$_3$)C=N), 7.31 (ddd, 2H, $^3$J$_{H-H}$
4.6, 7.6 $^4$J$_{H-H}$ 1.2, Py-H), 7.74 (ddd, 2H, $^3$J$_{H-H}$ 7.6, 7.9 $^4$J$_{H-H}$ 0.8, 0.9, Py-H), 8.30 (s, 1H,
CH=N), 8.31 (ddd, 2H, $^3$J$_{H-H}$ 7.9 $^4$J$_{H-H}$ 0.8, 0.9, Py-H), 8.64 (ddd, 2H, $^3$J$_{H-H}$ 4.7 $^4$J$_{H-H}$ 0.8,
0.9, Py-H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 293 K): $\delta$ 13.4 (s, Ar-CH$_3$), 14.0 (s, Ar-CH$_3$), 15.7
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(s, (CH₃)C=N), 120.1 (s, Ar), 120.2 (s, Ar), 120.8 (s, Ar), 122.3 (s, Ar), 123.7 (s, Ar),
124.1 (s, Ar), 135.4 (s, Ar), 135.7 (s, Ar), 144.1 (s, Ar), 145.3 (s, Ar), 147.5 (s, Ar),
148.6 (s, Ar), 153.7 (s, Ar), 155.5 (s, Ar), 166.6 (s, C≡N); 168.3 (s, (CH₃)C=N); mp =
198-201 °C.

7.3.11 Preparation of \(N, N'_\)-bis((2-(2,6-diisopropylphenyl)imino)-1-methyl-
propylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L18)

To a mixture of 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.500 g, 3.05 mmol) and 3-
(2,6-diisopropyl-phenylimino)-butan-2-one (1.494 g, 6.10 mmol, 2.0 eq.) in absolute
ethanol (15 ml) was added three drops of concentrated formic acid. The solution was
heated to 50 °C and stirred overnight. The suspension was filtered, the solid was washed
with cold ethanol and dried under reduced pressure to afford \(N, N'_\)-bis((2-(2,6-
diisopropylphenyl)imino)-1-methyl-propylidene)-2,3,5,6-tetramethylbenzene-
1,4-diamine (L18) as a yellow solid (1.321 g, 70%).

**Compound L18:** ES mass spectrum, \(m/z\) 619 [M+H]+; IR (cm⁻¹) (C=N) 1644; \(^1\)H
NMR (CDCl₃, 293 K): \(\delta\) 1.05-1.15 (m, 24H, CH(CH₃)₂), 1.98 (s, 12H, Ar-Me), 2.00 (s,
6H, (CH₃)C=N), 2.07 (s, 6H, (CH₃)C=N), 2.65-272 (m, 4H, CH(CH₃)₂), 6.99-7.15 (m,
6H, Ar-H); \(^{13}\)C \(^{1}\)H NMR (CDCl₃, 293 K): \(\delta\) 14.7 (s, Ar-Me), 16.3 (s, (CH₃)C=N),
17.0 (s, (CH₃)C=N), 23.2 (s, CH(CH₃)₂), 23.5 (s, CH(CH₃)₂), 28.9 (s, CH(CH₃)₂), 121.6
(s, Ar), 123.4 (s, Ar), 124.2 (s, Ar), 135.5 (s, Ar), 144.7 (s, Ar), 169.3 (s, (CH₃)C=N),
169.6 (s, (CH₃)C=N); mp = 193-195 °C.

7.3.12 Preparation of \(N, N'_\)-bis((2,2'-bipyridin-6-yl)methylene)-2,3,5,6-
tetramethylbenzene-1,4-diamine (L19)

To a suspension of 2,2'-bipyridine-6-carboxaldehyde (0.386 g, 2.10 mmol) in diethyl ether
(5 ml) was added 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.171 g, 0.52 mmol, 0.5 eq.)
and one drop of formic acid. The orange solution was heated to reflux for 48 hrs. On
cooling to 0 °C, the suspension was filtered, washed with cold ethanol and dried under
reduced pressure to afford \(N, N'_\)-bis((2,2'-bipyridin-6-yl)methylene)-2,3,5,6-tetramethylbenzene-
1,4-diamine (L19) as a yellow solid (0.172 g, 31%).

**Compound L19:** ES mass spectrum, \(m/z\) 497 [M+H]+; IR (cm⁻¹) 1635 (C≡N); \(^1\)H
NMR (CDCl₃, 293 K), \(\delta\) 2.08 (s, 12H, Ar-CH₃), 7.26 (ddd, 2H, \(^3\)Jₕ₋ₕ 6.1, \(^4\)Jₕ₋ₕ 1.1, 0.9,
Py-H), 7.76 (td, 2H, \(^3\)Jₕ₋ₕ 7.8, \(^4\)Jₕ₋ₕ 1.6, Py-H), 7.90 (t, 2H, \(^3\)Jₕ₋ₕ 7.9, Py-H), 8.29 (dd,
2H, $^3$J$_{H-H}$ 7.8, $^4$J$_{H-H}$ 0.9, Py-H), 8.34 (s, 2H, HC=N), 8.43 (d, 2H, $^3$J$_{H-H}$ 7.8, Py-H), 8.45 (dd, 2H, $^3$J$_{H-H}$ 7.8 $^4$J$_{H-H}$ 0.9, Py-H), 8.64 (d, 2H, $^3$J$_{H-H}$ 3.9, Py-H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 293 K): δ 14.1 (s, Ar-CH$_3$), 119.9 (s, Ar), 120.2 (s, Ar), 121.5 (s, Ar), 122.4 (s, Ar), 122.9 (s, Ar), 136.0 (s, Ar), 136.6 (s, Ar), 146.4 (s, Ar), 148.3 (s, Ar), 153.2 (s, Ar), 154.7 (s, Ar), 163.3 (s, C=N); mp > 230 °C.

7.3.13 Preparation of $N,N'$-bis((1-(2,2'-bipyridin-6-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L20)

To a suspension of 6-acetyl-2,2'-bipyridine (0.386 g, 1.95 mmol) in absolute ethanol (5 ml) was added 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.160 g, 0.97 mmol, 0.5 eq.) and one drop of formic acid. The brown solution was refluxed for 24 hrs. On cooling to 0 °C the suspension was filtered, washed with cold ethanol and dried under reduced pressure to afford $N,N'$-bis(1-(2,2'-bipyridin-6-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L20) as a pale yellow solid (0.098 g, 19%).

Compound L20: ES mass spectrum, $m/z$ 525 [M+H]$^+$; FABMS $m/z$ 525 [M+H]$^+$; IR (cm$^{-1}$) 1645 (C=N); $^1$H NMR (CDCl$_3$, 293 K), δ 1.96 (s, 12H, Ar-CH$_3$), 2.26 (s, 6H, (CH$_3$)C=N), 7.29 (ddd, 2H, $^3$J$_{H-H}$ 5.6 $^4$J$_{H-H}$ 1.2, 0.9, Py-H), 7.81 (ddd, 2H, $^3$J$_{H-H}$ 7.8 $^4$J$_{H-H}$ 1.6, Py-H), 7.90 (dd, 2H, $^3$J$_{H-H}$ 7.8, Py-H), 8.43 (d, 2H, $^3$J$_{H-H}$ 7.4, Py-H), 8.50 (d, 2H, $^3$J$_{H-H}$ 7.8, Py-H), 8.53 (d, 2H, $^3$J$_{H-H}$ 7.8, Py-H), 8.65 (d, 2H, $^3$J$_{H-H}$ 4.8, Py-H); $^{13}$C {$^1$H} NMR (CDCl$_3$, 293 K): δ 14.8 (s, CH$_3$), 16.9 (s, CH$_3$), 121.4 (s, Ar), 121.5 (s, Ar), 122.3 (s, Ar), 124.2 (s, Ar), 137.3 (s, Ar), 137.8 (s, Ar), 145.0 (s, Ar), 149.6 (s, Ar), 155.3 (s, Ar), 156.3 (s, Ar), 165.5 (s, Ar), 167.8 (s, Ar), 168.6 (s, C=N); mp > 230 °C.

7.3.14 Preparation of $N,N'$-bis([1,10]-phenanthroline-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L21)

To a solution of [1,10]-phenanthroline-2-carboxaldehyde (0.270 g, 1.29 mmol) in ethanol (5 ml) was added 2,3,5,6-tetramethyl-benzene-1,4-diamine (0.106 g, 0.65 mmol, 0.5 eq.) The solution was allowed to stir at 60 °C for 0.5 hrs and one drop of glacial acetic acid was added. The red suspension was stirred at 60 °C overnight. The solid was collected by filtration and was washed with cold ethanol and dried ad vacuo to afford $N,N'$-bis([1,10]-phenanthroline-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine (L21) as a yellow powder (0.151 g, 42%).
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Compound (L21) ES mass spectrum, 545 m/z [M+H]⁺; FABMS Calculated for C₂₃H₂₅N₄, found 545.36434, requires 545.36442; IR (cm⁻¹) 1639 (C=N); ¹H NMR (CDCl₃, 293 K) δ 2.08 (s, 12H, ArCH₃), 7.63 (dd, ³JH-H 4.1, 8.0, 2H, Phen-H), 7.84 (s, 4H, Ar-H), 8.26 (dd, 2H, ³JH-H 8.0 ⁴JH-H 1.8, Phen-H), 8.36 (dd, 2H, ³JH-H 8.5 ⁴JH-H 0.9, Phen-H), 8.69 (d, 2H, ³JH-H 8.5, Phen-H), 8.78 (s, 2H, HC=N), 9.19 (dd, 2H, ³JH-H 4.4 ⁴JH-H 1.8, 1H, Phen-H); mp > 230 °C.

7.3.15 Preparation of N,N'-bis((pyridin-2-yl)methylene)-3,5-R¹₂-3'-R²²-5'-R³³-4,4'-diaminodiphenylmethane (L22-L24)

(i) R¹ = R² = R³ = methyl: To a suspension of 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane (0.500 g, 1.97 mmol) in absolute ethanol (2 ml) was added 2-pyridinecarboxaldehyde (0.56 ml, 5.905 mmol, 3 eq.) and one drop of formic acid. The mixture was stirred at 45 °C overnight. On cooling to room temperature the suspension was filtered, washed with cold ethanol and dried under reduced pressure to afford N,N'-bis((pyridin-2-yl)methylene)-3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane (L22) as a yellow solid (0.380 g, 47%).

Compound L22: ES mass spectrum, m/z 433 [M+H]⁺; 1635 (C=N), ¹H NMR (CDCl₃, 293 K), δ 2.12 (s, 12H, CH₃), 3.69 (s, 2H, CH₂), 6.88 (s, 4H, Ar-H), 7.31 (ddd, 2H, ³JH-H 4.6, 7.6 ⁴JH-H 1.2, Py-H), 7.78 (ddddd, 2H, ³JH-H 7.6, 7.9, ⁴JH-H 0.8, 0.9, Py-H), 8.19 (ddd, 2H, ³JH-H 7.9 ⁴JH-H 0.8, 0.9, Py-H), 8.21 (s, 2H, HC=N), 8.63 (ddd, 2H, ³JH-H 4.7 ⁴JH-H 0.8, 0.9, 2H, Py-H); ¹³C ¹H NMR (CDCl₃, 293 K): 18.4 (s, CH₃), 40.9 (s, CH₂), 121.2 (s, Ar), 125.2 (s, Ar), 127.0 (s, Ar), 136.7 (s, Ar), 137.1 (s, Ar), 148.3 (s, Ar), 149.6 (s, Ar), 154.6 (s, Ar), 163.3 (s, C=N). In addition, a single crystal X-ray diffraction study of L22 has confirmed the structural type, details can be found in Table 3.

(ii) R¹ = R² = R³ = isopropyl: Employing the method outlined in 7.3.15(i) with 4,4'-diamino-3,5,3',5'-tetraisopropylidiphenylmethane (1.600 g, 4.37 mmol), 2-pyridinecarboxaldehyde (1.24 ml, 13.11 mmol, 3 eq.), absolute ethanol (10 ml) and two drops of formic acid, gave N,N'-bis((pyridin-2-yl)methylene)-3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane (L23) as a yellow solid (1.680 g, 49%).
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**Compound L23:** ES mass spectrum, \( m/z \) 545 [M+H]+; FABMS found 545.36434, C_{37}H_{43}N_{4} requires 545.36442; IR (cm\(^{-1}\)) 1638 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K), \( \delta \) 1.10 (d, 24H, \( ^3\)J\(_{H-H}\) 6.9, CH(CH\(_3\))\(_2\)), 2.91 (sept, 4H, \( ^3\)J\(_{H-H}\) 6.9, CH(CH\(_3\))\(_2\)), 3.95 (s, 2H, CH\(_3\)), 6.93 (s, 4H, Ar-H), 7.29 (ddd, 2H, \( ^3\)J\(_{H-H}\) 4.6, 7.6 \( ^4\)J\(_{H-H}\) 1.2, Py-H), 7.81 (ddddd, 2H, \( ^3\)J\(_{H-H}\) 7.6, 7.9 \( ^4\)J\(_{H-H}\) 0.8, 0.9, 2H, Py-H), 8.20 (dd, \( ^3\)J\(_{H-H}\) 7.9 \( ^4\)J\(_{H-H}\) 0.8, 0.9, 2H, Py-H), 8.23 (s, 2H, HC=N), 8.66 (dd, 2H, \( ^3\)J\(_{H-H}\) 4.7 \( ^4\)J\(_{H-H}\) 0.8, 0.9, 2H, Py-H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl\(_3\), 293 K): 18.1 (s, CH\(_3\)), 22.4 (s, CH), 39.4 (s, CH\(_2\)), 122.8 (s, Ar), 125.3 (s, Ar), 126.1 (s, Ar), 135.6 (s, Ar), 136.4 (s, Ar), 142.6 (s, Ar), 147.9 (s, Ar), 157.4 (s, Ar), 163.1 (s, C=N); mp = 130 °C.

(iii) \( R^1 = \) isopropyl; \( R^2 = R^3 = \) methyl: Employing the method outlined in 7.3.15(i) with 4,4’-diamino-3,5-diisopropyl-3’,5’-dimethylidiphenylmethane (0.200 g, 0.65 mmol), 2-pyridinecarboxaldehyde (0.183 ml, 1.94 mmol, 3 eq.), absolute ethanol (2 ml) and two drops of formic acid, gave N,N’-bis((pyridin-2-yl)methylene)-3,5-diisopropyl-3’,5’-dimethyl-4,4’-diaminodiphenylmethane (L24) as a yellow solid (0.196 g, 62%).

**Compound L24:** ES mass spectrum, \( m/z \) 487 [M+H]+; 1638 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K), \( \delta \) 1.08 (d, 24H, \( ^3\)J\(_{H-H}\) 6.9, CH(CH\(_3\))\(_2\)), 2.08 (s, 6H, CH\(_3\)), 2.88 (sept, 4H, CH(CH\(_3\))\(_2\)), 3.84 (s, 2H, CH\(_3\)), 6.81 (s, 2H, Ar-H), 6.91 (s, 2H, Ar-H), 7.27 (ddd, 2H, \( ^3\)J\(_{H-H}\) 4.6, 7.6 \( ^4\)J\(_{H-H}\) 1.2, Py-H), 7.75 (ddddd, 2H, \( ^3\)J\(_{H-H}\) 7.6, 7.9 \( ^4\)J\(_{H-H}\) 0.8, 0.9, 2H, Py-H), 8.1-8.3 (m, 4H, Py-H/HC=N), 8.64 (dd, 2H, \( ^3\)J\(_{H-H}\) 4.7 \( ^4\)J\(_{H-H}\) 0.8, 0.9, 2H, Py-H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl\(_3\), 293 K): 18.8 (s, CH\(_3\)), 23.9 (s, CH), 28.4 (s, CH), 43.4 (s, CH\(_2\)), 121.7 (s, Ar), 124.2 (s, Ar), 125.7 (s, Ar), 128.2 (s, Ar), 129.0 (s, Ar), 137.2 (s, Ar), 137.7 (s, Ar), 150.0 (s, Ar), 156.2 (s, Ar), 163.4 (s, C=N), 163.9 (s, C=N).

7.3.16 Preparation of N,N’-bis((pyridin-2-yl)ethylidene)-3,5,3’,5’-R\(^1\)-4,4’-diaminodiphenylmethane (L25-L26)

(i) **L25** \( R^1 = \) methyl: To a suspension of 4,4’-diamino-3,5,3’,5’-tetramethyldiphenylmethane (0.500 g, 1.97 mmol) in absolute ethanol (3 ml) was added 2-acetylpseudine (0.463 ml, 4.13 mmol, 2.1 eq.) along with one drop of formic acid and the solution stirred at reflux for one night. On cooling to room temperature the black solution was dried over magnesium sulphate, filtered and dried under reduced pressure at 45 °C overnight to give N,N’-bis(1-(pyridin-2-yl)ethylidene)-3,5,3’,5’-tetramethyl-4,4’-diaminodiphenylmethane (L25) as a black oil (0.420 g, 47%).
Compound L25: ES mass spectrum m/z 461 [M+H]+; IR (cm⁻¹) 1639 (C=N);¹ H NMR (CDCl₃, 293 K), 1.92 (s, 12H, CH₃), 2.17 (s, 6H, (CH₃)C=N), 2.08 (sept, 4H, CH(CH₃)₂), 3.72 (s, 2H, CH₂), 6.91 (s, 4H, Ar-H), 7.26 (ddd, 2H, 3J_H-H 4.6, 7.6 4J_H-H 1.2, Py-H), 7.74 (dddd, 2H, 3J_H-H 7.6, 7.9 4J_H-H 0.8, 0.9, Py-H), 8.15 (ddd, 2H, 3J_H-H 7.9 4J_H-H 0.8, 0.9, Py-H), 8.64 (ddd, 2H, 3J_H-H 4.7 4J_H-H 0.8, 0.9, Py-H);¹³C {¹H} NMR (CDCl₃, 293 K): 16.7 (s, CH₃), 18.0 (s, CH₃), 40.8 (s, CH₂), 121.3 (s, Ar), 124.8 (s, Ar), 125.3 (s, Ar), 128.5 (s, Ar), 136.2 (s, Ar), 136.4 (s, Ar), 146.6 (s, Ar), 148.5 (s, Ar), 156.5 (s, Ar), 167.3 (s, C=N).

(ii) L26 R¹ = isopropyl: Employing the method outlined in 7.3.16(i) with 4,4'-diamino-3,5,3',5'-tetraisopropylidiphenylmethane (0.500 g, 1.37 mmol), 2-acetylpyridine (0.439 ml, 4.70 mmol, 3.4 eq.), absolute ethanol (3 ml) and two drops of formic acid, gave N,N'-bis(l -(pyridin-2-yl)ethylidene)-3,5,3',5'-tetraisopropyl-4,4'-diaminodiphenylmethane (1.680 g, 49%) as a yellow solid.

Compound L26: ES mass spectrum, m/z 573 [M+H]+; IR (cm⁻¹) 1639 (C=N);¹ H NMR (CDCl₃, 293 K), δ 1.08 (d, 24H, CH(CH₃)₂), 2.17 (s, 6H, (CH₃)C=N), 2.67 (sept, 4H, CH(CH₃)₂), 3.94 (s, 2H, CH₂), 6.91 (s, 4H, Ar-H), 7.26 (ddd, 2H, 3J_H-H 4.6, 7.6 4J_H-H 1.2, Py-H), 7.74 (ddddd, 2H, 2J_H-H 7.6, 7.9 4J_H-H 0.8, 0.9, Py-H), 8.15 (ddd, 2H, 2J_H-H 7.9 4J_H-H 0.8, 0.9, Py-H), 8.64 (ddd, 2H, 2J_H-H 4.7 4J_H-H 0.8, 0.9, Py-H);¹³C {¹H} NMR (CDCl₃, 293 K): δ 17.7 (s, CH₃), 23.4 (s, CH), 23.7 (s, CH), 28.6 (s, CH₃), 41.8 (s, CH₂), 121.7 (s, Ar), 124.1 (s, Ar), 125.1 (s, Ar), 136.1 (s, Ar), 136.7 (s, Ar), 144.6 (s, Ar), 148.9 (s, Ar), 157.0 (s, Ar), 167.6 (s, C=N); Found C: 81.51 H: 8.28 N: 9.82%; mp = 125-130 °C. Expected C: 81.76 H: 8.46 N: 9.78%; mp = 125-130 °C.

7.3.17 Preparation of N,N'-bis((2,2'-bipyridin-6-yl)methylene)-3,5,3',5'-tetraisopropyl-4,4'-diaminodiphenylmethane (L28)

To a suspension of 2,2'-bipyridine-6-carboxaldehyde (0.385 g, 2.09 mmol) in absolute ethanol (5 ml) was added 4,4'-diamino-3,5,3',5'-tetraisopropylidiphenylmethane (0.191 g, 0.53 mmol, 0.25 eq.) and one drop of formic acid. The brown solution was heated to reflux for 24 hrs. On cooling to 0 °C, the suspension was filtered, washed with cold ethanol and dried under reduced pressure to give N,N'-bis((2,2'-bipyridin-6-
yl)methylene)-3,5,3',5'-tetraisopropyl-4,4'-diaminodiphenylmethane (L28) as a brown solid (0.190 g, 52%).

Compound L28: ES mass spectrum, \( m/z \) 699 [M+H]+; IR (cm\(^{-1}\)) 1644 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 1.11 (d, 24H, \( ^3 J_{H-H} 6.6, \) CH(CH\(_3\))\(_2\)), 2.95 (sept, 4H, \( ^3 J_{H-H} 6.1, ^4 J_{H-H} 0.9, 1.2, \) Py-H), 7.21 (ddd, 2H, \( ^3 J_{H-H} 7.8, ^4 J_{H-H} 1.6, 1.8, \) Py-H), 7.86 (t, 2H, \( ^3 J_{H-H} 7.8, \) Py-H), 8.21 (dd, 2H, \( ^3 J_{H-H} 7.8, ^4 J_{H-H} 0.9, \) Py-H), 8.34 (s, 2H, HC=N), 8.41 (d, 2H, \( ^3 J_{H-H} 7.8, \) Py-H), 8.44 (dd, 2H, \( ^3 J_{H-H} 7.4, ^4 J_{H-H} 0.9, \) Py-H), 8.60 (dd, 2H, \( ^3 J_{H-H} 4.5, ^4 J_{H-H} 0.7, \) Py-H); \(^{13}\)C \( \{^1\)H\} NMR (CDCl\(_3\), 293 K): \( \delta \) 23.6 (s, CH\(_3\)), 28.0 (s, CH), 41.6 (s, CH\(_2\)), 121.0 (s, Ar), 121.2 (s, Ar), 121.3 (s, Ar), 122.6 (s, Ar), 122.7 (s, Ar), 123.7 (s, Ar), 123.9 (s, Ar), 137.0 (s, Ar), 137.3 (s, Ar), 137.6 (s, Ar), 146.5 (s, Ar), 149.2 (s, Ar), 154.1 (s, Ar), 154.1 (s, Ar), 163.6 (s, C=N); mp = 124 °C.

7.3.18 Preparation of \( N,N'\)-bis((1-(2,2'-bipyridin-6-yl)ethylidene)-3,5,3',5'-R\(_1\)R\(_2\)-diaminodiphenylmethane (L29, L30)

(i) \( \text{L29} R' = \text{methyl} \): To a suspension of 6-acetyl-2,2'-bipyridine (0.100 g, 0.51 mmol) in \( n\)-butanol (5 ml) was added 4,4'-diamino-3,5,3',5'-tetramethyldiphenylmethane (0.064 g, 0.25 mmol, 0.4 eq.) and one drop of acetic acid. The brown solution was heated to reflux for 48 hrs. On cooling to room temperature, the black solution was dried over magnesium sulphate, filtered and dried under reduced pressure to give \( N,N'\)-bis((1-(2,2'-bipyridin-6-yl)ethylidene)-3,5,3',5'-tetramethyl-4,4'-diaminodiphenylmethane (L29) as a brown solid (0.085 g, 55%).

Compound L29: ES mass spectrum, \( m/z \) 614 [M+H]+; IR (cm\(^{-1}\)) 1644 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 1.97 (s, 12H, CH\(_3\)), 2.25 (s, 6H, CH\(_3\)), 3.81 (s, 2H, CH\(_2\)), 6.88 (s, 4H, Ar-H), 7.28 (ddd, 2H, \( ^3 J_{H-H} 6.1, ^4 J_{H-H} 0.9, 1.2, \) Py-H), 7.80 (dd, 2H, \( ^3 J_{H-H} 7.8, ^4 J_{H-H} 1.6, 1.8, \) Py-H), 7.88 (dd, 2H, \( ^3 J_{H-H} 7.8, 7.8, \) Py-H), 8.35 (dd, 2H, \( ^3 J_{H-H} 7.8, ^4 J_{H-H} 0.9, \) Py-H), 8.44 (dd, 4H, \( ^3 J_{H-H} 7.4 ^4 J_{H-H} 0.9, \) Py-H), 8.46 (dd, 2H, \( ^3 J_{H-H} 7.4 ^4 J_{H-H} 0.9, \) Py-H), 8.65 (dd, 2H, \( ^3 J_{H-H} 4.8 ^4 J_{H-H} 0.7, \) Py-H).

(ii) \( \text{L30} R' = \text{isopropyl} \): Employing the method outlined in 7.3.18(i) with 6-acetyl-2,2'-bipyridine (0.100 g, 0.505 mmol), 4,4'-diamino-3,5,3',5'-tetraisopropylidiphenylmethane (0.092 g, 0.25 mmol, 0.5 eq.), \( n\)-butanol (5 ml) and one
drop of acetic acid, gave \( N,N'\)-bis((1-(2,2'-bipyridin)-6-yl)ethyldiene)-3,5,3',5'-tetraisopropyl-4,4'-diaminodiphenylmethane (L30) as a yellow solid (0.104 g, 57%).

**Compound L30:** ES mass spectrum, \( m/z \) 727 [M+H]+; IR (cm\(^{-1}\)) 1644 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 1.10 (d, 24H, \( ^3\)J\(_{\text{H-H}} \) 6.9, CH(CH\(_3\))\(_2\)), 2.25 (s, 6H, CH\(_3\)), 2.95 (sept, 4H, \( ^3\)J\(_{\text{H-H}} \) 6.9, CH(CH\(_3\))\(_2\)), 3.28 (s, 2H, CH\(_2\)), 6.95 (s, 4H, Ar-H), 7.21 (ddd, 2H, \( ^3\)J\(_{\text{H-H}} \) 6.1, \( ^4\)J\(_{\text{H-H}} \) 0.9, 1.2, Py-H), 7.72 (ddd, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.8, \( ^4\)J\(_{\text{H-H}} \) 1.6, 1.8, Py-H), 7.86 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.8, Py-H), 8.21 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.8, \( ^4\)J\(_{\text{H-H}} \) 0.9, Py-H), 8.34 (s, 2H, HC=N), 8.41 (d, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.8, Py-H), 8.44 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.4, \( ^4\)J\(_{\text{H-H}} \) 0.9, Py-H), 8.65 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 4.5 \( ^4\)J\(_{\text{H-H}} \) 0.7, Py-H); \(^1\)C \(^{13}\)NMR (CDCl\(_3\), 293 K): \( \delta \) 23.0 (s, CH\(_3\)), 23.3 (s, CH\(_3\)), 28.3 (s, CH), 41.4 (s, CH\(_2\)), 121.1 (s, Ar), 121.2 (s, Ar), 121.9 (s, Ar), 127.1 (s, Ar), 135.7 (s, Ar), 136.3 (s, Ar), 136.9 (s, Ar), 137.4 (s, Ar), 141.7 (s, Ar), 149.2 (s, Ar), 154.9 (s, Ar), 155.8 (s, Ar), 156.1 (s, Ar), 158.6 (s, Ar), 167.3 (s, C=N); Anal. Calcd for (C\(_{49}\)H\(_{54}\)N\(_3\)) C: 80.94 H: 7.50 N: 11.56; Found C: 79.38 H: 7.47 N: 11.19%.

7.3.19 Preparation of \( N,N'\)-bis(((1,10)-phenanthrolin-2-yl)methylene)-3,5,3',5'-R\(_1\)4-4,4'-diaminodiphenylmethane (L31, L32)

(i) **L31** \( R' = \text{methyl} \): To a solution of [1,10]-phenanthroline-2-carboxaldehyde (0.200 g, 0.96 mmol) in ethanol (5 ml) was added 4,4'-diamino-3,5,3',5'-tetramethylidiphenylmethane (0.122 g, 0.48 mmol, 0.5 eq.) The solution was allowed to stir at 50 °C for 0.5 hr and one drop of acetic acid was added. The red suspension was stirred at 90 °C overnight. The solid was collected by filtration and was washed with cold ethanol and dried under reduced pressure to afford \( N,N'\)-bis(((1,10)-phenanthroline-2-yl)methylene)-3,5,3',5'-tetramethyl-4,4'-diaminodiphenyl methane (L31) as a dark oil (0.151 g, 37%).

**Compound L31** ES mass spectrum, \( m/z \) 635 [M+H]+; IR (cm\(^{-1}\)) 1643 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \( \delta \) 1.08 (s, 12H, \( ^3\)J\(_{\text{H-H}} \) 6.7, CH\(_3\)), 3.89 (s, 2H, CH\(_2\)), 6.97 (s, 2H, Ar-H), 7.60 (dd, \( ^3\)J\(_{\text{H-H}} \) 4.4, 8.2, 2H, Phen-H), 7.82 (s, 2H, Phen-H), 8.22 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 7.9 \( ^4\)J\(_{\text{H-H}} \) 1.7, Phen-H), 8.32 (d, 2H, \( ^3\)J\(_{\text{H-H}} \) 8.2, Phen-H), 8.22 (d, 2H, \( ^3\)J\(_{\text{H-H}} \) 8.2, Phen-H), 8.78 (s, 2H, HC=N), 9.19 (dd, 2H, \( ^3\)J\(_{\text{H-H}} \) 4.4 \( ^4\)J\(_{\text{H-H}} \) 1.5, 1H, Phen-H).

(ii) **L32** \( R' = \text{isopropyl} \): Employing the method outlined in 7.3.18(i) with [1,10]-phenanthroline-2-carboxaldehyde (0.200 g, 0.96 mmol), 4,4'-diamino-3,5,3',5'-
tetraisopropyldiphenylmethane (0.176 g, 0.48 mmol, 0.5 eq.), n-butanol (5 ml) and one drop of acetic acid, gave \(N, N'-\text{bis}([1,10]\text{-phenanthroline}-2-yl)methylene\)-3,5,3',5'-tetraisopropyl-4,4'-diaminodiphenyl methane (L32) as a yellow solid (0.151 g, 42%).

Compound L32: ES mass spectrum, \(m/z\) 747 \([M+H]^+\); IR (cm\(^{-1}\)) 1627 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 1.08 (d, 24H, \(3_J_{H-H} 6.7, \text{CH}(\text{CH}_3)_2\)), 2.92 (sept, 4H, \(3_J_{H-H} 6.7, \text{CH}(\text{CH}_3)_2\)), 3.89 (s, 2H, CH), 6.97 (s, 4H, Ar-H), 7.60 (dd, \(3_J_{H-H} 4.4, 8.2, \text{2H, Phen-H}\), 7.82 (s, 2H, Phen-H), 8.22 (dd, 2H, \(3_J_{H-H} 7.9, 4_J_{H-H} 1.7, \text{Phen-H}\)), 8.32 (d, 2H, \(3_J_{H-H} 8.2, \text{Phen-H}\)), 8.22 (d, 2H, \(3_J{H-H} 8.2, \text{Phen-H}\)), 8.78 (s, 2H, HC=N), 9.19 (dd, 2H, \(3_J{H-H} 4.4, 4_J{H-H} 1.5, 1\text{H, Phen-H}\)).

7.3.20 Preparation of \(N, N'-\text{bis}((\text{pyridin-2-yl})methylene)-3,5,3',5'-\text{tetramethylbiphenyl-4,4'-diamine} (L33)

To a suspension of 3,5,3',5'-tetramethyl-biphenyl-4,4'-diamine (0.480 g, 2.00 mmol) in absolute ethanol (10 ml) was added 2-pyridinecarboxaldehyde (0.66 ml, 7.00 mmol, 3.5 eq.). The mixture was stirred and heated to reflux overnight. On cooling to room temperature, the suspension was filtered, washed with cold ethanol and dried under reduced pressure to give 3,5,3',5'-tetramethyl-\(N, N'-\text{bis}((\text{pyridin-2-yl})\text{methylene})\)-biphenyl-4,4'-diamine (L33) in good yield as a yellow solid (0.510 g, 62%).

Compound L33: ES mass spectrum, \(m/z\) 419 \([M+H]^+\); IR (cm\(^{-1}\)) 1648 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 2.20 (s, 12H, (Ar-CH\(_3\))), 7.25 (s, 4H, Ar-H), 7.35 (ddd, \(3_J_{H-H} 4.6, 7.6, 4_J{H-H} 1.2, \text{2H, Py-H}\)), 7.78 (ddd, \(3_J{H-H} 7.6, 7.9, 4_J{H-H} 0.8, 0.9, 2\text{H, Py-H}\)), 8.29 (ddd, \(3_J{H-H} 7.9, 4_J{H-H} 0.8, 0.9, 2\text{H, Py-H}\)), 8.35 (s, 2H, HC=N), 8.71 (ddd, \(3_J{H-H} 4.7, 4_J{H-H} 0.8, 0.9, 2\text{H, Py-H}\)); \(^13\)C \(^{1}\)H NMR (CDCl\(_3\), 293 °K): \(\delta\) 18.9 (s, Me), 121.7 (s, Ar), 125.8 (s, Ar), 127.1 (s, Ar), 127.8 (s, Ar), 137.2 (s, Ar), 137.3 (s, Ar), 149.7 (s, Ar), 150.1 (s, Ar), 157.3 (s, Ar), 164.0 (s, C=N), mp = 183 C. Anal. Calcd for (C\(_{28}\)H\(_{26}\)N\(_4\)): C 80.34; H 6.27; N 13.38. Found: C 80.15; H 6.35; N 13.32%; mp = 162 °C. In addition, a single crystal X-ray diffraction study of \(N, N'-\text{bis}((\text{pyridin-2-yl})\text{methylene})\)-3,5,3',5'-tetramethylbiphenyl-4,4'-diamine (L33) has confirmed the structural type, details can be found in Table 4.

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7.3.21 Preparation of \(N,N'-\text{bis}(1\text{-}(\text{pyridin}-2\text{-yl})\text{ethylidene})\)-3,5,3',5'-tetramethylbiphenyl-4,4'-diamine (L34)

To a suspension of 3,5,3',5'-tetramethyl-biphenyl-4,4'-diamine (0.500 g, 2.10 mmol) in absolute ethanol (10 ml) was added 2-acetylpyridine (0.79 ml, 7.10 mmol, 3.4 eq.) and two drops of formic acid. The suspension was heated to reflux overnight. On cooling to room temperature the suspension was filtered, washed with cold ethanol and dried under reduced pressure to give \(N,N'-\text{bis}(1\text{-}(\text{pyridin}-2\text{-yl})\text{ethylidene})\)-3,5,3',5'-tetramethylbiphenyl-4,4'-diamine (L34) as a yellow solid (0.510 g, 41%).

**Compound L34:** ES mass spectrum, \(m/z\) 447 \([M+H]^+\); IR (cm\(^{-1}\)) 1643 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 2.04 (s, 12H, Ar-CH\(_3\)), 2.19 (s, 6H, (CH\(_3\))C=N), 7.26 (s, 4H, Ar-H), 7.37 (ddd, 2H, \(3J_{HH}\) 4.6, 7.6, \(4J_{HH}\) 1.2, Py-H), 7.77 (ddd, 2H, \(3J_{HH}\) 7.6, 7.9, \(4J_{HH}\) 0.8, 0.9, Py-H), 8.34 (ddd, 2H, \(3J_{HH}\) 7.9 \(4J_{HH}\) 0.8, 0.9, Py-H), 8.64 (ddd, 2H, \(3J_{HH}\) 4.7, \(4J_{HH}\) 0.8, 0.9, Py-H); \(^{13}\)C \({}^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 17.2 (s, Ar-CH\(_3\)), 18.5 (s, (CH\(_3\))C=N), 121.8 (s, Ar), 125.3 (s, Ar), 126.2 (s, Ar), 126.8 (s, Ar), 136.4 (s, Ar), 136.9 (s, Ar), 148.0 (s, Ar), 149.0 (s, Ar), 156.9 (s, Ar), 167.9 (s, C=N); Anal. Calcd for (C\(_{30}\)H\(_{30}\)N\(_4\)): C 80.67; H 6.78; N 12.54. Found: C 80.49; H 6.81; N 12.45%; mp = 214 °C

7.3.22 Preparation of \(N,N'-\text{bis}(1\text{-}(\text{pyridin}-2\text{-yl})\text{ethylidene})\)-3,5,3',5'-tetraisopropylbiphenyl-4,4'-diamine (L35)

A mixture of of 3,5,3',5'-tetraisopropyl-biphenyl-4,4'-diamine (0.210 g, 0.60 mmol), 2-acetylpyridine (3.0 ml, 26.85 mmol, 45 eq.) and one drop of formic acid was heated to 150 °C for 3 hrs. The 2-acetylpyridine was distilled off and absolute ethanol introduced to precipitate the product. Following filtration, washing with cold ethanol and drying under reduced pressure, \(N,N'-\text{bis}(1\text{-}(\text{pyridin}-2\text{-yl})\text{ethylidene})\)-3,5,3',5'-tetraisopropylbiphenyl-4,4'-diamine (L35) was isolated as a yellow solid (0.280 g, 85%).

**Compound 3,5,3',5'-tetraisopropyl-N,N,-bis(l-(pyridin-2-yl)ethylidene)-biphenyl-4,4'-diamine (L35):** ES mass spectrum, \(m/z\) 559 \([M+H]^+\); IR (cm\(^{-1}\)) 1639 (C=N); \(^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 1.19 (d, 12H, \(3J_{HH}\) 6.9, CH(CH\(_3\))\(_2\)), 2.18 (s, 6H, MeC=N), 2.72 (sept, 4H, \(3J_{HH}\) 6.9, CH(CH\(_3\))\(_2\)), 7.24 (s, 4H, Ar-H), 7.25 (ddd, 2H, \(3J_{HH}\) 4.6, 7.6 \(4J_{HH}\) 1.2, Py-H), 7.72 (ddd, 2H, \(3J_{HH}\) 7.6, 7.9 \(4J_{HH}\) 0.8, 0.9, Py-H), 8.31 (ddd, 2H, \(3J_{HH}\) 7.9 \(4J_{HH}\) 0.8, 0.9, Py-H), 8.48 (ddd, 2H, \(3J_{HH}\) 4.7 \(4J_{HH}\) 0.8, 0.9, Py-H); \(^{13}\)C \({}^1\)H NMR (CDCl\(_3\), 293 K): \(\delta\) 16.4 (s, CH\(_3\)), 21.9 (s, CH\(_3\)), 22.3 (s, CH\(_3\)), 27.4 (s, CH), 120.3 (s,
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Ar), 120.7 (s, Ar), 123.8 (s, Ar), 135.0 (s, Ar), 135.5 (s, Ar), 144.4 (s, Ar), 147.6 (s, Ar), 155.5 (s, Ar), 166.1 (s, C=N).

7.3.23 Preparation of N,N'-bis((pyridin-2-yl)methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-Y-triphenylmethine (L36-L41)

(i) L36 $Y = \text{hydrogen}$: To a suspension of 4,4'-amino-3,3',5,5'-tetraisopropyl-triphenylmethine (0.200 g, 0.45 mmol) in absolute ethanol (3 ml) was added 2-pyridinecarboxaldehyde (0.17 ml, 1.81 mmol, 3 eq.) and two drops of formic acid. The mixture was stirred at 50 °C overnight. On cooling to room temperature the suspension was filtered, washed with cold ethanol and dried under reduced pressure to afford N,N'-bis((pyridin-2-yl)methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-triphenylmethine (L36) as a pale yellow solid (0.372 g, 82%).

Compound L36: ES mass spectrum, $m/z$ 622 [M+H]+; $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 1.03 (d, $^3$J$_{HH}$ 7.5 24H, CH(CH$_3$)), 2.82 (sept, $^3$J$_{HH}$ 7.5, 4H, CH(CH$_3$)$_2$), 5.23 (s, 1H, CH), 6.86 (s, 4H, Ar-H), 7.1-2 (m, 5H, Ar-H), 7.33 (ddd, $^3$J$_{HH}$ 4.6, 7.6 $^4$J$_{HH}$ 1.2, 2H, Py-H), 7.77 (ddd, $^2$H, $^3$J$_{HH}$ 7.6, 7.9 $^4$J$_{HH}$ 0.8, 0.9, Py-H), 8.19 (ddd, 2H, $^3$J$_{HH}$ 7.9 $^4$J$_{HH}$ 0.8, 0.9, Py-H), 8.26 (s, 2H, HC=N), 8.65 (ddd, 2H, $^3$J$_{HH}$ 4.7 $^4$J$_{HH}$ 0.8, 0.9, Py-H); $^{13}$C $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 23.9 (s, CH$_3$), 28.4 (s, CH), 57.6 (s, CH), 121.7 (s, Ar), 124.8 (s, Ar), 125.7 (s, Ar), 126.3 (s, Ar), 128.5 (s, Ar), 129.9 (s, Ar), 137.2 (s, Ar), 137.4 (s, Ar), 140.1 (s, Ar), 147.0 (s, Ar), 148.2 (s, CH), 150.0 (s, Ar), 156.7 (s, Ar), 162.5 (s, C=N); Anal. Calcd for (C$_{43}$H$_{48}$N$_4$): C, 83.17; H, 7.80; N, 9.02. Found: C, 83.29; H, 7.96; N, 9.03%; mp = 228 °C. In addition, a single crystal X-ray diffraction study of L36 has confirmed the structural type, details can be found in Table 3.

(ii) L37 $Y = \text{hydroxy}$: Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine (0.200g, 0.44 mmol), 2-pyridinecarboxaldehyde (0.19 ml, 1.31 mmol, 3 eq.), absolute ethanol (2 ml), gave N,N'-bis((pyridin-2-yl)methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine (0.288 g, 66%) as a yellow solid.

Compound L37: ES mass spectrum, $m/z$ 637 [M+H]+; IR (cm$^{-1}$) 3352, (OH), 1640 (C=N); $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 1.00 (d, $^3$J$_{HH}$ 6.7, CH(CH$_3$)$_2$), 2.88 (sept, 4H, CH(CH$_3$)$_2$), 5.34 (s, 1H, CH), 6.65 (d, 2H, $^3$J$_{HH}$ 8.8, Ar-H), 6.84 (s, 4H, Ar-H), 6.94 (d,
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2H, J\text{H-H} 8.8, \text{Ar-H}), 7.35 (ddd, 2H, J\text{H-H} 4.6, 7.6 J\text{H-H} 1.2, \text{Py-H}), 7.78 (ddd, 2H, J\text{H-H} 7.6, 7.9 J\text{H-H} 0.8, 0.9, \text{Py-H}), 8.22 (ddd, 2H, J\text{H-H} 7.9 J\text{H-H} 0.8, 0.9, \text{Py-H}), 8.26 (s, 2H, CH=NC), 8.66 (ddd, 2H, J\text{H-H} 4.7 J\text{H-H} 0.8, 0.9, \text{Py-H}); ^{13}\text{C} \{^1\text{H}\} \text{NMR (CDCl}_3, 293 K): \delta 23.8 (s, CH(CH_3)_2), 24.0 (s, CH(CH_3)_2), 28.4 (s, CH(CH_3)_2), 56.0 (s, CH), 115.0 (s, Ar), 121.5 (s, Ar), 124.0 (s, Ar), 124.3 (s, Ar), 125.4 (s, Ar), 127.9 (s, Ar), 130.4 (s, Ar), 132.6 (s, Ar), 136.8 (s, Ar), 137.1 (s, Ar), 140.7 (s, Ar), 146.0 (s, Ar), 149.5 (s, Ar), 154.5 (s, Ar), 163.2 (s, C=NC).

(iii) L38 Y = bromo: Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-bromo-triphenylmethine (0.200 g, 0.71 mmol), 2-pyridinecarboxaldehyde (0.20 ml, 0.21 mmol, 3 eq.), absolute ethanol (2 ml), gave \textit{N,N'-bis((pyridin-2-yl)methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-bromo-triphenylmethine} (0.241 g, 63%) as a yellow solid.

Compound L38: ES mass spectrum, m/z 701 [M+H]^+; IR (cm\(^{-1}\)) 1640 (C=NC); \textit{^1}\text{H} \text{NMR (CDCl}_3, 293 K): \delta 1.01 (d, 12H, J\text{H-H} 6.7, CH(CH_3)_2), 2.88 (sept, J\text{H-H} 6.7, 4H, CH(CH_3)_2), 5.36 (s, 1H, CH), 6.83 (s, 4H, Ar-H), 6.99 (d, 2H, J(HH) 8.2, Ar-H), 7.36 (ddd, 2H, J\text{H-H} 4.6, 7.6 J\text{H-H} 1.2, \text{Py-H}), 7.77 (ddddd, 2H, J\text{H-H} 7.6, 7.9 J\text{H-H} 0.8, 0.9, \text{Py-H}), 8.20 (ddd, 2H, J\text{H-H} 7.9 J\text{H-H} 0.8, 0.9, \text{Py-H}), 8.25 (s, 2H, CH=NC), 8.65 (ddd, 2H, J\text{H-H} 4.7 J\text{H-H} 0.8, 0.9, \text{Py-H}); ^{13}\text{C} \{^1\text{H}\} \text{NMR (CDCl}_3, 293 K): \delta 23.5 (s, CH(CH_3)_2), 23.6 (s, CH(CH_3)_2), 28.0 (s, CH(CH_3)_2), 56.2 (s, CH), 119.8 (s, Ar), 121.3 (s, Ar), 124.2 (s, Ar), 125.3 (s, Ar), 131.1 (s, Ar), 131.2 (s, Ar), 136.8 (s, Ar), 137.2 (s, Ar), 139.5 (s, Ar), 144.4 (s, Ar), 146.5 (s, Ar), 149.7 (s, Ar), 154.4 (s, Ar), 163.1 (s, C=NC); mp = 198 °C In addition, a single crystal X-ray diffraction study of L38 has confirmed the structural type, details can be found in Table 4.

(iv) L39 Y = isopropyl: Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',4''-pentaisopropyl-triphenylmethine (0.300 g, 0.62 mmol), 2-pyridinecarboxaldehyde (0.18 ml, 0.19 mmol, 3 eq.), absolute ethanol (2 ml), gave \textit{N,N'-bis((pyridin-2-yl)methylene)-4,4'-amino-3,3',5,5'-pentaisopropyl-4''-isopropyl-triphenylmethine} (0.316 g, 77%) as a yellow solid.
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Compound L39: ES mass spectrum, \( m/z \) 663 \([M+H]^+\); IR \((\text{cm}^{-1})\) \(\text{C}=\text{N} \) 1647; \( ^1\text{H} \) NMR \((\text{CDCl}_3, 293 \text{ K})\): \( \delta \) 1.01 (d, 24H, \( ^3\text{J}_{\text{H-H}} 6.7, \text{CH}(\text{CH}_3)_2 \)), 1.17 (d, 6H, \( ^3\text{J}_{\text{H-H}} 6.7 \)), \( \text{CH}(\text{CH}_3)_2 \), 2.86 (sept, 5H, \( ^3\text{J}_{\text{H-H}} 6.7, \text{CH}(\text{CH}_3)_2 \)), 5.38 (s, 1H, CH), 6.86 (s, 4H, Ar-H), 7.07 (m, 4H, Ar-H), 7.35 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 1.2, \text{Py-H} \)), 7.77 (ddddd, 2H, \( ^3\text{J}_{\text{H-H}} 7.6, 7.9 \)), 8.19 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 0.8, 0.9, \text{Py-H} \)), 8.26 (s, 2H, HC=\( \text{N} \)), 8.65 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 0.8, 0.9, \text{Py-H} \)) \( ^{13}\text{C} \) \({^1\text{H}} \) NMR \((\text{CDCl}_3, 293 \text{ K})\): \( \delta \) 23.9 (s, \( \text{CH}(\text{CH}_3)_2 \)), 24.0 (s, \( \text{CH}(\text{CH}_3)_2 \)), 28.4 (s, \( \text{CH}(\text{CH}_3)_2 \)), 34.1 (s, \( \text{CH}(\text{CH}_3)_2 \)), 56.4 (s, CH), 121.3 (s, Ar), 125.6 (s, Ar), 129.3 (s, Ar), 137.1 (s, Ar), 137.3 (s, Ar), 137.8 (s, Ar), 142.9 (s, Ar), 146.5 (s, Ar), 146.8 (s, Ar), 150.0 (s, Ar), 154.9 (s, Ar), 163.4 (s, \( \text{C}=\text{N} \)); mp = 108 °C

(v) L40 \( Y = \text{allyl} \): Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-allyl-triphenylmethine \((0.300 \text{ g}, 0.62 \text{ mmol})\), 2-pyridinecarboxaldehyde \((0.18 \text{ ml}, 0.19 \text{ mmol}, 3 \text{ eq.})\), absolute ethanol \((2 \text{ ml})\), gave \( N,N' \)-(\( \text{pyridin-2-yl} \))-methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-allyl-triphenylmethine \((0.106 \text{ g}, 52\%)\) as a yellow solid.

Compound L40: ES mass spectrum, \( m/z \) 661 \([M+H]^+\); IR \((\text{cm}^{-1})\) \(\text{C}=\text{N} \) 1650; \( ^1\text{H} \) NMR \((\text{CDCl}_3, 293 \text{ K})\): \( \delta \) 1.02 (d, 24H, \( ^3\text{J}_{\text{H-H}} 6.7, \text{CH}(\text{CH}_3)_2 \)), 2.88 (sept, 4H, \( ^3\text{J}_{\text{H-H}} 6.7, \text{CH}(\text{CH}_3)_2 \)), 3.27 (ddd, 5H, \( ^3\text{J}_{\text{H-H}} 6.4, \text{CH}_2 \)), 4.90-5.00 (m, 2H, CHCH_2), 5.38 (s, 1H, CH), 5.96 (m, 2H, CHCH_2), 6.72 (s, 4H, Ar-H), 6.98 (s, 4H, Ar-H), 7.34 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 1.2, \text{Py-H} \)), 7.77 (ddddd, 2H, \( ^4\text{J}_{\text{H-H}} 0.6, 1.8, \text{Py-H} \)), 8.19 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 0.6, 1.8, \text{Py-H} \)), 8.26 (s, 2H, HC=\( \text{N} \)), 8.65 (ddd, 2H, \( ^4\text{J}_{\text{H-H}} 0.6, 1.7, \text{Py-H} \)).

(vi) L41 \( Y = \text{nitro} \): Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-nitro-triphenylmethine \((0.200 \text{ g}, 0.41 \text{ mmol})\), 2-pyridinecarboxaldehyde \((0.54 \text{ ml}, 1.23 \text{ mmol}, 3 \text{ eq.})\), absolute ethanol \((2 \text{ ml})\), gave \( N,N' \)-(\( \text{pyridin-2-yl} \))-methylene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-allyl-triphenylmethine \((0.110 \text{ g}, 63\%)\) as a yellow solid.

Compound L42: ES mass spectrum, \( m/z \) 666 \([M+H]^+\); IR \((\text{cm}^{-1})\) 1643; \( ^1\text{H} \) NMR \((\text{CDCl}_3, 293 \text{ K})\): \( \delta \) 1.01 (d, \( ^3\text{J}_{\text{H-H}} 6.7, 24\text{ H CH}(\text{CH}_3)_2 \)), 2.88 (sept, 4H, \( ^3\text{J}_{\text{H-H}} 6.7, \text{Py-H} \)).
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CH(CH$_3$)$_2$, 5.51 (s, 1H, CH), 6.81 (s, 4H, Ar-H), 7.26 (ddd, 2H, $^3$J$_{HH}$ 4.6, $^7$J$_{HH}$ 1.2, Py-H), 7.77 (ddddd, 2H, $^3$J$_{HH}$ 7.6, $^7$J$_{HH}$ 0.8, 0.9, Py-H), 8.18 (dd, 2H, $^3$J$_{HH}$ 7.9 $^4$J$_{HH}$ 0.8, 0.9, Py-H), 8.26 (s, 2H, (CH$_3$)$_2$), 8.65 (ddd, 2H, $^3$J$_{HH}$ 4.7 $^4$J$_{HH}$ 0.8, 0.9, Py-H); $^{13}$C NMR (CDCl$_3$, 293 K): $\delta$ 23.5 (s, CH(CH$_3$)$_2$), 23.6 (s, CH(CH$_3$)$_2$), 28.0 (s, CH(CH$_3$)$_2$), 56.7 (s, CH), 121.4 (s, Ar), 123.4 (s, Ar), 124.2 (s, Ar), 125.4 (s, Ar), 130.2 (s, Ar), 136.8 (s, Ar), 137.5 (s, Ar), 138.4 (s, Ar), 146.4 (s, Ar), 146.9 (s, Ar), 149.7 (s, Ar), 153.2 (s, Ar), 154.3 (s, Ar), 163.2 (s, C=N).

7.3.24 Preparation of $N,N'$-bis(1-(pyridin-2-yl)ethylidene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-Y-triphenylmethine (L42-L44)

(i) L42 $Y = \text{hydrogen}$: To a suspension of $\alpha,\alpha'$-bis(4-amino-3,5-diisopropylphenyl)-toluene (0.200 g, 0.45 mmol) in absolute ethanol (10 ml) was added 2-acetylpyridine (0.18 ml, 1.58 mmol, 3.5 eq.). The mixture was stirred and heated to reflux overnight. On cooling to room temperature, the suspension was filtered, washed with cold ethanol and dried under reduced pressure to give $N,N'$-bis(1-(pyridin-2-yl)ethylidene)-4,4'-amino-3,3',5,5'-tetraisopropyltriphenylmethine (L42) as a dark oil (0.115 g, 41%).

Compound L42: ES mass spectrum, $m/z$ 649 [M+H]$^+$; IR (cm$^{-1}$), 1644 (C=N); $^1$H NMR (CDCl$_3$, 293 K): $\delta$ 0.99 (d, $^3$J$_{HH}$ 6.7, 24H CH(CH$_3$)$_2$), 2.15 (s, 6H, (CH$_3$)$_2$C=N), 2.67 (sept, $^3$J$_{HH}$ 6.7, 4H, CH(CH$_3$)$_2$), 5.35 (s, 1H, CH), 6.53 (d, 2H, $^3$J$_{HH}$ 8.7, Ar-H), 6.79 (d, 2H, $^3$J$_{HH}$ 1.8, Ar-H), 6.87 (d, 2H, $^3$J$_{HH}$ 1.8, Ar-H), 6.91 (d, 2H, $^3$J$_{HH}$ 1.8, Ar-H), 7.1-2 (m, 5H, Ar-H), 7.32 (ddd, 2H, $^3$J$_{HH}$ 5.0, 7.6 $^4$J$_{HH}$ 1.2, Py-H), 7.75 (ddd, 2H, $^3$J$_{HH}$ 7.6, 7.9 $^4$J$_{HH}$ 1.8, Py-H), 8.28 (ddd, 2H, $^3$J$_{HH}$ 7.9 $^4$J$_{HH}$ 0.8, 0.9, Py-H H), 8.60 (ddd, 2H, $^3$J$_{HH}$ 5.0 $^4$J$_{HH}$ 0.8, 1.8, ArH).

(ii) L43 $Y = \text{hydroxy}$: Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine (0.200g, 0.44 mmol), 2-acetylpyrididine (0.171 ml, 1.53 mmol, 3.5 eq.), absolute ethanol (2 ml), gave $N,N'$-bis(1-(pyridin-2-yl)ethylidene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4''-hydroxy-triphenylmethine (L43) (0.176 g, 63%) a yellow solid.

Compound L43: ES mass spectrum, $m/z$ 665 [M+H]$^+$; IR (cm$^{-1}$), 1645 (C=N); $^1$H NMR (CDCl$_3$, 293 K), $\delta$ 0.97 (d, $^3$J$_{HH}$ 6.7, 24H CH(CH$_3$)$_2$), 2.16 (s, 6H, (CH$_3$)$_2$C=N), 2.67 (sept, 4H, $^3$J$_{HH}$ 6.7, CH(CH$_3$)$_2$), 5.35 (s, 1H, CH), 6.53 (d, 2H, $^3$J$_{HH}$ 8.7, Ar-H),

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6.79 (d, 2H, 3J_H-H 1.8, Ar-H), 6.87 (d, 2H, 3J_H-H 1.8, Ar-H), 6.91 (d, 2H, 3J_H-H 8.7, Ar-H), 7.32 (ddd, 2H, 3J_H-H 5.0, 7.6 4J_H-H 1.2, Py-H), 7.75 (ddd, 2H, 3J_H-H 7.6, 7.9 4J_H-H 1.8, Py-H), 8.28 (ddd, 2H, 3J_H-H 7.9 4J_H-H 0.8, 0.9, Py-H-H), 8.60 (ddd, 2H, 3J_H-H 5.0 4J_H-H 0.8, 1.8, Ar-H); 13C {1H} NMR (CDCl3, 293 K): δ 17.6 (s, CH3), 23.0 (s, CH), 23.1 (s, CH), 23.2 (s, CH), 23.3 (s, CH), 28.3 (s, CH3), 55.8 (s, CH2), 114.9 (s, Ar), 122.5 (s, Ar), 124.3 (s, Ar), 124.4 (s, Ar), 124.9 (s, Ar), 130.4 (s, Ar), 135.5 (s, Ar), 135.6 (s, Ar), 136.6 (s, Ar), 137.3 (s, Ar), 140.0 (s, Ar), 143.9 (s, Ar), 148.6 (s, Ar), 154.1 (s, Ar), 156.4 (s, Ar), 167.9 (s, C=N).

(iii) **L44** Y = isopropyl: Employing the method outlined in 7.3.23(i) with 4,4'-amino-3,3',5,5'-tetraisopropyl-4'''-isopropyl-triphenylmethine (0.200 g, 0.41 mmol), 2-acetylpyridine (0.162 ml, 1.45 mmol, 3.5 eq.), absolute ethanol (2 ml), gave **N,N'-bis(1-(pyridin-2-yl)ethylidene)-4,4'-amino-3,3',5,5'-tetraisopropyl-4'''-isopropyl-triphenylmethine (L44)** (0.174 g, 64%) as a yellow solid.

**Compound L44**: ES mass spectrum, m/z 691 [M+H]+; IR (cm⁻¹), 1644 (C=N); ¹H NMR (CDCl3, 293 K), δ 0.97 (d, 24H, 3J_H-H 6.9 CH(CH3)2), 0.97 (d, 6H, 3J_H-H 6.9, CH(CH3)2), 2.15 (s, 6H, (CH3)C=N), 2.64 (sept, 4H, 3J_H-H 6.9, CH(CH3)2), 2.83 (sept, 3J_H-H 6.9, 1H, CH(CH3)2), 5.39 (s, 1H, CH), 6.84 (dd, 4H, 3J_H-H, 4.8 4J_H-H 1.1, Ar-H), 7.06 (ddd, 4H, 3J_H-H 17.1, 8.4, 4J_H-H 1.8, Ar-H), 7.32 (ddd, 2H, 3J_H-H 5.0, 7.5, 4J_H-H 1.2, Py-H), 7.75 (ddd, 2H, 3J_H-H 1.8, 7.6, 7.9 4J_H-H 1.8, Py-H), 8.27 (ddd, 3J_H-H 7.5 4J_H-H 0.8, 0.9, 2H, Py-H), 8.60 (ddd, 2H, 3J_H-H 5.0 4J_H-H 0.8, 0.9, Ar-H); ¹³C {¹H} NMR (CDCl3, 293 K): δ 17.4 (s, CH3), 23.0 (s, CH3), 23.0 (s, CH3), 23.2 (s, CH3), 23.3 (s, CH3), 24.1 (s, CH3), 28.3 (s, CH), 23.7 (s, CH), 56.4 (s, CH2), 121.4 (s, Ar), 124.3 (s, Ar), 124.7 (s, Ar), 125.9 (s, Ar), 129.3 (s, Ar), 135.3 (s, Ar), 136.5 (s, Ar), 139.7 (s, Ar), 142.8 (s, Ar), 144.1 (s, Ar), 146.2 (s, Ar), 148.5 (s, Ar), 156.55 (s, Ar), 167.2 (s, C=N).
7.4 Synthesis of Complexes

7.4.1 Preparation of \([N-(\{10\}-phenanthrolin-2-yl)methylene]-2,6-R^1-4-R^2-benzenamine][M(II)dichloride [M = Fe (1), Co (2)]

(i) 1a: \(R^1 = \text{methyl; } R^2 = \text{hydrogen; } M = \text{Fe}\): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \(\text{FeCl}_2\) (0.110 g, 0.87 mmol) in \(n\)-BuOH (5 ml) and the contents stirred at 90 °C until the iron salt had completely dissolved. \(L_1\) (0.270 g, 0.87 mmol, 1 eq.) was added and the mixture heated to 90 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product. Following filtration, washing with hexane and drying under reduced pressure, 1a (0.075 g, 20%) was isolated as a pale green solid.

(ii) 1b: \(R^1 = R^2 = \text{methyl; } M = \text{Fe}\): Employing the method outlined in 7.4.1(i) using anhydrous iron dichloride (0.117 g, 0.92 mmol), \(n\)-butanol (5 ml) and \(L_2\) (0.300 g, 0.92 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 1b as a green solid (0.087 g, 21%).

(iii) 1c: \(R^1 = \text{isopropyl; } R^2 = \text{hydrogen; } M = \text{Fe}\): Employing the method outlined in 7.4.1(i) using anhydrous iron dichloride (0.047 g, 0.37 mmol), \(n\)-butanol (5 ml) and \(L_3\) (0.136 g, 0.37 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 1c as a brown solid (0.115 g, 63%).

(iv) 1d: \(R^1 = \text{isopropyl; } R^2 = \text{bromo; } M = \text{Fe}\): Employing the method outlined in 7.4.1(i) using anhydrous iron dichloride (0.109 g, 0.86 mmol), \(n\)-butanol (5 ml) and \(L_4\) (0.383 g, 0.586 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 1d as a brown solid (0.374 g, 76%).

(v) 1e: \(R^1 = \text{isopropyl; } R^2 = \text{cyano; } M = \text{Fe}\): Employing the method outlined in 7.4.1(i) using anhydrous iron dichloride (0.110 g, 0.87 mmol), \(n\)-butanol (5 ml) and \(L_5\) (0.341 g, 0.87 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 1e as a brown solid (0.378 g, 84%).

(vi) 2a: \(R^1 = \text{isopropyl; } R^2 = \text{hydrogen; } M = \text{Co}\): Employing the method outlined in 7.4.1(i) using anhydrous cobalt dichloride (0.112 g, 0.88 mmol), \(n\)-butanol (5 ml) and
L3 (0.393 g, 0.88 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 2a as a brown solid (0.403 g, 80%). Recrystallisation of 2a from acetonitrile afforded crystals suitable for a single crystal X-ray diffraction study that has confirmed the structural type of 2a, details can be found in Table 4.

Anal. Calcd for \( \text{C}_{25}\text{H}_{26}\text{N}_{3}\text{BrCoCl}_{2} \): C, 50.26; H, 4.02; N 7.03. Found: C 50.19, H 3.99, N 7.02%

(vii) 2b: \( R^{1} = \text{isopropyl} \); \( R^{2} = \text{cyano} \); \( M = \text{Co} \): Employing the method outlined in 7.4.1(i) using anhydrous cobalt dichloride (0.112 g, 0.88 mmol), \( n \)-butanol (5 ml) and L5 (0.345 g, 0.88 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 2b as a brown solid (0.297 g, 65%). Recrystallisation of 2b from acetonitrile afforded crystals suitable for a single crystal X-ray diffraction study that has confirmed the structural type of 2b, details can be found in Table 4.

### 7.4.2 Preparation of \([N-(2,2'-\text{bipyridin-6-yl})-\text{R-methylene}-2,6-\text{R}^{1}2-4-\text{R}^{2}-\text{benzenamine}]\text{iron(II)dichloride (3)}\)

(i) 3a: \( R = \text{hydrogen} \); \( R^{1} = \text{isopropyl} \); \( R^{2} = R = \text{hydrogen} \): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \( \text{FeCl}_{2} \) (0.110 g, 0.87 mmol) in \( n \)-BuOH (5 ml) and the contents stirred at 90 °C until the iron salt had completely dissolved. L6 (0.298 g, 0.87 mmol, 1 eq.) was added and the mixture heated to 90 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product. Following filtration, washing with hexane and drying under reduced pressure, 3a (0.183 g, 45%) was isolated as a pale green solid.

(ii) 3b: \( R = \text{methyl} \); \( R_{1} = \text{isopropyl} \); \( R_{2} = \text{hydrogen} \): Employing the method outlined in 7.4.2(i) using anhydrous iron dichloride (0.110 g, 0.87 mmol), \( n \)-butanol (5 ml) and L8 (0.310 g, 0.87 mmol, 1 eq.) at a temperature of 90 °C overnight, gave 3b as a dark blue (0.206 g, 62%).

### 7.4.3 Preparation of \([N-(1-(2,2'-\text{bipyridin-6-yl})\text{ethylidene}-2,6-\text{diisopropylbenzenamine}]\text{nickel(II)dibromide (4)}\)

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \([\text{DME}]\text{NiBr}_{2} \) (0.550 g,
1.78 mmol) and dichloromethane (25 ml) and the contents stirred at room temperature 
for two days with L8 (0.636 g, 1.78 mmol, 1 eq.). The suspension was concentrated and 
washed several times with hexane and diethyl ether and dried under reduced pressure to 
give 4 as a black powder (0.545 g, 53%). Recrystallisation of 4 from acetonitrile 
afforded crystals suitable for a single crystal X-ray diffraction study that has confirmed 
the structural type of 4, details can be found in Table 4.

Anal. Calcd for (C19H24N2Br2Ni): C, 45.89; H, 5.01; N, 4.86. Found: C 45.74, H 
4.81, N 5.02%

7.4.4 Preparation of \([N-(2-(2,6-diisopropylphenyl)imino)-1-methyl-
propylidene)-2,3,5,6-tetramethyl-benzene-1,4-diamine]nickel(II)dibromide (5)\)
To a suspension of [DME]NiBr₂ (0.550 g, 1.78 mmol) in dichloromethane (25 ml) was 
added L8 (0.70 g, 1.78 mmol, 1 eq.). The mixture was stirred under nitrogen at ambient 
temperature for two days. The suspension was concentrated and washed several times 
with hexane and diethylether and dried under reduced pressure to give 5 as a black 
powder (0.58 g, 53%). Recrystallisation of 5 from dichloromethane afforded crystals 
suitable for a single crystal X-ray diffraction study that has confirmed the structural type 
of 5, details can be found in Table 4.

Anal. Calcd for (C26H37N2Br2Ni): C, 58.8; H, 6.98; N, 7.92. Found C, 58.75; H, 7.08; 
N, 7.86%

7.4.5 Preparation of \([N-(pyridin-2-yl)- R-methylene-R₂ -
benezamine]nickel(II)dichloride (6)\)
(i) 6a: \(R = \text{hydrogen}; R' = \text{methyl}; R² = \text{hydrogen}\): An oven-dried Schlenk flask 
equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask 
was charged with anhydrous NiCl₂ (0.143 g, 1.10 mmol) in n-BuOH (10 ml) and the 
contents stirred at 110 °C until the nickel salt had completely dissolved. L9 (0.231 g, 
1.10 mmol, 1 eq.) was added and the mixture heated to 110 °C overnight. On cooling to 
ambient temperature, hexane was added to induce precipitation of the product. 
Following filtration, washing with hexane and drying under reduced pressure, 6a (0.292 
g, 78%) was isolated as a pale green solid.

(ii) 6b: \(R = \text{hydrogen}; R' = R² = \text{methyl}\): Employing the method outlined in 7.4.5(i) 
using anhydrous nickel dichloride (0.135 g, 1.04 mmol), n-butanol (20 ml) and L10
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(0.233 g, 1.04 mmol, 1 eq.) at a temperature of 110 °C overnight, gave 6b as a green solid (0.261 g, 71%).

(iii) 6c: \( R = \text{hydrogen}; R' = R^2 = \text{isopropyl} \): Employing the method outlined in 7.4.5(i) using anhydrous nickel dichloride (0.073 g, 0.56 mmol), \( n \)-butanol (10 ml) and \( L_{11} \) (0.150 g, 0.56 mmol, 1 eq.) at a temperature of 110 °C overnight, gave 6c as a green solid (0.156 g, 71%).

(v) 6d: \( R = R' = R^2 = \text{methyl} \): Employing the method outlined in 7.4.5(i) using anhydrous nickel dichloride (0.072 g, 0.56 mmol), \( n \)-butanol (10 ml) and \( L_{12} \) (0.148 g, 0.56 mmol, 1 eq.) at a temperature of 110 °C overnight, gave 6d as a green solid (0.112 g, 51%).

(vi) 6e: \( R = \text{methyl}; R' = R^2 = \text{isopropyl} \): Employing the method outlined in 7.4.5(i) using anhydrous nickel dichloride (0.073 g, 0.56 mmol), \( n \)-butanol (10 ml) and \( L_{13} \) (0.150 g, 0.56 mmol, 1 eq.) at a temperature of 110 °C overnight, gave 6e as a green solid (0.112 g, 53%).

7.4.6 Preparation of \([N-(1-(pyridin-2-yl)ethylidene)-2,3,5,6-tetramethylbenzene-1,4-diamine]nickel(II)dibromide (6f)\)
An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \([\text{DME}]\text{NiBr}_2\) (0.150 g, 0.486 mmol) in \( n \)-BuOH (10 ml) and the contents stirred at 90 °C until the nickel salt had completely dissolved. \( L_{14} \) (0.129 g, 0.486 mmol, 1 eq.) was added and the mixture heated to 90 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product. Following filtration, washing with hexane and drying under reduced pressure, 6f (0.143 g, 61%) was isolated as a brown green solid.

7.4.7 Preparation of \([N-((pyridin-2-yl)R-methylene)-N'-(pyridin-2-yl)-R'-methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine]\)
dinickel(II)tetrabromide (7)
(i) 7a: \( R = R' = \text{hydrogen} \): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \([\text{DME}]\text{NiBr}_2\) (0.180 g, 0.58 mmol) in \( n \)-butanol (10 ml) and the contents stirred at 110 °C until the nickel salt had completely dissolved. \( L_{15} \) was added (0.100 g, 0.29 mmol,
0.5 eq.) and the mixture was heated to 110 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 7a (0.143 g, 63%) was isolated as a pale green solid.

(ii) 7b: \( R = R' = \text{methyl} \): Employing the method outlined in 7.4.7(i) using anhydrous \([\text{DME}]\text{NiBr}_2\) (0.170 g, 0.55 mmol), \( n \)-butanol (10 ml) and \( \text{L16} \) (0.100 g, 0.28 mmol, 0.5 eq.) at a temperature of 110 °C overnight, gave 7b as a green solid (0.156 g, 70%).

(iii) 7c: \( R = \text{hydrogen}; R' = \text{methyl} \): Employing the method outlined in 7.4.7(i) using anhydrous \([\text{DME}]\text{NiBr}_2\) (0.180 g, 0.58 mmol), \( n \)-butanol (10 ml) and \( \text{L17} \) (0.100 g, 0.29 mmol, 0.5 eq.) at a temperature of 110 °C overnight, gave 7c as an orange solid (0.129 g, 56%).

7.4.8 Preparation of \([N,N'\text{-bis((pyridin-2-yl)methylene}-2,3,5,6\text{-tetramethylbenzene-1,4-diamine})\text{dinickel(II)tetrachloride (7d)}\]

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \( \text{NiCl}_2 \) (0.100 g, 0.77 mmol) in \( n \)-butanol (10 ml) and the contents stirred at 110 °C until the nickel salt had completely dissolved. \( \text{L15} \) was added (0.132 g, 0.39 mmol, 0.5 eq.) and the mixture was heated to 110 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 7d (0.204 g, 68%) was isolated as an orange solid.

7.4.9 Preparation of \([N\text{-((pyridin-2-yl)-R-methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine})\text{dinickel(II)tetrabromidehexakis-Ar ,Ap-dimethylformamide (7')}\]

(i) 7a': Layering of a \( N,N' \)-dimethylformamide (DMF) solution of 7a with diethyl ether gave red crystals of the DMF adduct of 7a, \([\{(\text{C}_5\text{H}_4\text{N})\text{CH(N(2,3,5,6-Me}_4\text{C}_6)}\text{NHC(C}_3\text{H}_4\text{N})\}(\text{DMF})_2\text{Ni}_2\text{Br}_2\)]\( \text{Br}_2 \) (7a'), suitable for a single crystal X-ray diffraction study, details can be found in Table 4.
(ii) \(7b'\): Layering of a N,N'-dimethylformamide (DMF) solution of \(7b\) with diethyl ether gave red crystals of the DMF adduct of \(7b\), \([\{(\text{C}_2\text{H}_4\text{N})\text{CMeN(2,3,5,6-Me}_4\text{C}_6)\text{NMeC(C}_3\text{H}_4\text{N}\}\})\text{DMF})_6\text{Ni}_2\text{Br}_2\text{Br}_2\) \((7b')\), suitable for a single crystal X-ray diffraction study, details can be found in Table 5.

Anal. Calcd for \((\text{C}_{36}\text{H}_{70}\text{N}_8\text{Br}_4\text{O}_{12}\text{Ni}_2)\): C, 34.75; H, 5.68; N, 8.81. Found: C, 34.92; H, 5.92; N, 8.81%.

(iii) \(7c'\): Layering of a N,N'-dimethylformamide (DMF) solution of \(7c\) with diethyl ether gave red crystals of the DMF adduct of \(7c\), \([\{(\text{C}_2\text{H}_4\text{N})\text{CHN(2,3,5,6-Me}_4\text{C}_6)\text{NMeC(C}_3\text{H}_4\text{N}\})\text{DMF})_6\text{Ni}_2\text{Br}_2\text{Br}_2\) \((7c')\), suitable for a single crystal X-ray diffraction study, details can be found in Table 5.

7.4.10 Preparation of \([N,N'-\text{bis((pyridin-2-yl)methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine}]\text{dinickel(II)tetrachlorideterakis-N,N'-dimethylformamide (7d')}

Layering of a N,N'-dimethylformamide (DMF) solution of \(7d\) with diethyl ether gave red crystals of the DMF adduct of \(7d\), \([\{(\text{C}_2\text{H}_4\text{N})\text{CHN(2,3,5,6-Me}_4\text{C}_6)\text{NHC(C}_5\text{H}_4\text{N})(\text{NiCl}_2)_2\text{(DMF})_4\}]\) \((7d')\), suitable for a single crystal X-ray diffraction study, details can be found in Table 5.

7.4.11 Preparation of \([N,N'-\text{bis((2,2'-bipyridin-6-yl)-R-methylene)-2,3,5,6-tetramethylbenzene-1,4-diamine}]\text{diiron(II)tetrachloride (9)}

(i) \(9a\ R = \text{hydrogen}\): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl\(_2\) (0.052 g, 0.41 mmol) in \(n\)-butanol (5 ml) and the contents stirred at 90 °C until the nickel salt had completely dissolved. \(\text{L19}\) was added (0.102 g, 2.10 mmol, 0.5 eq.) and the mixture was heated to 90 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, \(9a\) (0.085 g, 55%) was isolated as olive green powder.

(ii) \(9b\ R = \text{methyl}\): Employing the method outlined in 7.4.11(i) using anhydrous FeCl\(_2\) (0.034 g, 0.27 mmol), \(n\)-butanol (10 ml) and \(\text{L20}\) (0.070 g, 0.13 mmol, 0.5 eq.) at a temperature of 110 °C overnight, gave \(9b\) as a grey / black solid (0.059 g, 57%).
7.4.12 Preparation of \([N,N^\prime\text{-bis}([1,10]\text{-phenanthroline-2-yl}])\text{methylene}-2,3,5,6\text{-tetramethylbenzene-1,4-diamine}]\text{diiron(II)tetrachloride (10)}\)

Under an atmosphere of nitrogen, anhydrous iron dichloride (0.051 g, 0.41 mmol) was dissolved in \(n\)-butanol (5 ml) by stirring at 110 °C for 30 minutes. To this blue solution, \(L_{23}\) (0.110 g, 0.20 mmol, 0.5 eq.) was added and the mixture stirred at 110 °C for a further 30 minutes. On cooling to ambient temperature, hexane was added to induce precipitation of the product. Following filtration and washing with more hexane, complex 10 was isolated as a dark powder (0.101 g, 62%).

7.4.13 Preparation of \([N,N^\prime\text{-bis}([\text{pyridin-2-yl}]\text{-R-methylene})-3,5-R_12-3',5'-R_2-4,4'\text{-diaminodiphenylmethane}]\text{dinickel(II)tetrachloride (13)}\)

(i) \(13a\) \(R = \text{hydrogen}; R' = R_2 = \text{methyl}\): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous \(\text{NiCl}_2\) (0.092 g, 1.56 mmol) in \(n\)-butanol (15 ml) and the contents stirred at 120 °C until the nickel salt had completely dissolved. \(L_{22}\) was added (0.200 g, 0.79 mmol, 0.5 eq.) and the mixture was heated to 120 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, \(13a\) (0.152 g, 52%) was isolated as a black solid powder.

(ii) \(13b\) \(R = \text{hydrogen}; R' = R_2 = \text{isopropyl}\): Employing the method outlined in 7.4.13(i) using anhydrous \(\text{NiCl}_2\) (0.238 g, 1.84 mmol), \(n\)-butanol (15 ml) and \(L_{23}\) (0.500 g, 0.92 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(13b\) as a green solid (0.413 g, 56%).

(iii) \(13c\): \(R = \text{hydrogen}; R' = \text{isopropyl}; R_2 = \text{methyl}\): Employing the method outlined in 7.4.13(i) using anhydrous \(\text{NiCl}_2\) (0.110 g, 0.85 mmol), \(n\)-butanol (10 ml) and \(L_{24}\) (0.207 g, 0.42 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(13c\) as a green solid (0.183 g, 58%).

(iv) \(13d\): \(R = R' = R_2 = \text{methyl}\): Employing the method outlined in 7.4.15(i) using anhydrous \(\text{NiCl}_2\) (0.110 g, 0.85 mmol), \(n\)-butanol (10 ml) and \(L_{25}\) (0.195 g, 0.42 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(13d\) as a green solid (0.216 g, 51%).
(v) **13e** \( R = \text{methyl}; R^1 = R^2 = \text{isopropyl} \): Employing the method outlined in 7.4.13(i) using anhydrous NiCl\(_2\) (0.110 g, 0.85 mmol), \( n \)-butanol (10 ml) and \( L_{28} \) (0.243 g, 0.42 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \( 13e \) as a green solid (0.180 g, 51%).

### 7.4.14 Preparation of \([N,N'\text{-bis((pyridin-2-yl)methylene)}-3,5,3',5'-\text{tetraisopropyl}-4,4'\text{-diaminodiphenylmethane}]\) dinickel(II) tetrabromide (13f)

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous [DME]NiBr\(_2\) (0.183 g, 0.59 mmol, 0.5 eq.) in dichloromethane (10 ml) and the contents stirred at 50 °C until the nickel salt had completely dissolved. \( L_{23} \) was added (0.161 g, 0.29 mmol, 0.5 eq.) and the mixture was heated to 120 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, \( 13e \) (0.238 g, 82%) was isolated as green powder.

### 7.4.15 Preparation of \( [(L_{23})_2(\text{NCMe})_4]\)Ni\(_4\)Cl\(_8\) (13b')

Prolonged standing of an acetonitrile solution of \( 13b \) gave crystals of the acetonitrile adduct of \( 13b \), \( [(L_{23})_2(\text{NCMe})_4]\)Ni\(_4\)Cl\(_8\) (13b'), suitable for X-ray diffractometry studies, details can be found in Table 5.

### 7.4.16 Preparation of \( [(L_{26})_2(\text{NCMe})_2]\)Ni\(_4\)Cl\(_8\) (13e')

Prolonged standing of an acetonitrile solution of \( 13e \) gave crystals of the acetonitrile adduct of \( 13e \), \( [(L_{26})_2(\text{NCMe})_2]\)Ni\(_4\)Cl\(_8\) (13e'), suitable for X-ray diffractometry studies details can be found in Table 5.

### 7.4.17 Preparation of \([N,N'\text{-bis([2,2'\text{-bipyridin-6-yl}]-R\text{-methylene})-3,5,3',5'\text{-R}^14,4'\text{-diaminodiphenylmethane]}\)diiron(II) tetrachloride (14)

(i) **14a** \( R = \text{hydrogen}, R^1 = \text{isopropyl} \): An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl\(_2\) (0.073 g, 0.58 mmol) in \( n \)-butanol (5 ml) and the contents stirred at 90 °C until the iron salt had completely dissolved. \( L_{28} \) was added (0.200 g, 0.29 mmol) and the mixture was heated to 100 °C overnight. On cooling to ambient...
temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 14a (0.027 g, 10%) was isolated as a dark blue powder.

(ii) 14b $R = \text{methyl}$, $R' = \text{methyl}$: Employing the method outlined in 7.4.17(i) using anhydrous FeCl$_2$ (0.083 g, 0.66 mmol) $n$-butanol (5 ml) and L29 (0.202 g, 0.33 mmol, 0.5 eq.) at a temperature of 100 °C overnight, gave 14b as a blue solid (0.151 g, 53%).

(iii) 14c: $R = \text{methyl}$, $R' = \text{isopropyl}$: Employing the method outlined in 7.4.17(i) using anhydrous FeCl$_2$ (0.070 g, 0.56 mmol), $n$-butanol (5 ml) and L30 (0.200 g, 0.28 mmol, 0.5 eq.) at a temperature of 100 °C overnight, gave 14c as a dark blue green solid (0.166 g, 61%).

7.4.18 Preparation of $[N,N'$-bis([1,10]-phenanthroline-2-yl)methylene]-3,5,3',5'-R',R'-4,4'-diaminodiphenylmethaneM(II)$_2$tetrachloride [$M = \text{Fe (15)}, \text{Co (16)}$]

(i) 15a $R' = \text{methyl}$, $M = \text{Fe}$: An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous FeCl$_2$ (0.040 g, 0.32 mmol) in $n$-butanol (5 ml) and the contents stirred at 90 °C until the iron salt had completely dissolved. L32 was added (0.100 g, 0.16 mmol) and the mixture was heated to 100 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 15a (0.102 g, 73%) was isolated as a dark blue powder.

(ii) 15b $R' = \text{isopropyl}$, $M = \text{iron}$: Employing the method outlined in 7.4.18(i) using anhydrous FeCl$_2$ (0.035 g, 0.28 mmol), $n$-butanol (5 ml) and L33 (0.103 g, 0.14 mmol, 0.5 eq.) at a temperature of 100 °C overnight, gave 15b (0.89 g, 65%) as a blue solid.

(iii) 16 $R' = \text{isopropyl}$, $M = \text{Co}$: Employing the method outlined in 7.4.18(i) using anhydrous CoCl$_2$ (0.035 g, 0.27 mmol) $n$-butanol (5 ml) and L33 (0.100 g, 0.14 mmol, 0.5 eq.) at a temperature of 100 °C overnight gave 16 (0.102 g, 76%) as a dark green solid.
7.4.19 Preparation of \([N,N'-\text{bis}((\text{pyridin-2-yl})-\text{R-methylene})-3,5,3',5'-\text{R}^1-\text{biphenyl}-4,4'-\text{diamine}]\text{dinickel(II)}\text{tetrachloride} \) (17)

(i) 17a \( R = \) hydrogen; \( R^1 = \) methyl: An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous NiCl\(_2\) (0.238 g, 1.84 mmol) in n-butanol (15 ml) and the contents stirred at 120 °C until the nickel salt had completely dissolved. L33 was added (0.499 g, 0.92 mmol, 0.5 eq.) and the mixture was heated to 120 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 17a (0.412 g, 56%) was isolated as green powder.

(ii) 17b \( R = \) methyl; \( R^1 = \) isopropyl: Employing the method outlined in 7.4.19(i) using anhydrous NiCl\(_2\) (0.110 g, 0.85 mmol), n-butanol (10 ml) and L35 (0.243 g, 0.42 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave 17b as a green solid (0.180 g, 51%).

7.4.20 Preparation of \([N,N'-\text{bis}((\text{pyridin-2-yl})-\text{R-methylene})-4,4'-\text{amino}-3,3',5,5'-\text{tetraisopropyl}-4''-\text{Y-triphenylmethine}]\text{dinickel(II)}\text{tetrachloride} \) (18)

(i) 18a \( R = Y = \) hydrogen: An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with anhydrous NiCl\(_2\) (0.110 g, 0.77 mmol) in n-butanol (10 ml) and the contents stirred at 120 °C until the nickel salt had completely dissolved. L36 was added (0.239 g, 0.39 mmol, 0.5 eq.) and the mixture was heated to 120 °C overnight. On cooling to ambient temperature, hexane was added to induce precipitation of the product and the suspension was concentrated and washed several times with hexane. Following filtration, washing with hexane and drying under reduced pressure, 18a (0.217 g, 64%) was isolated as a green powder.

(ii) 18b \( R = \) hydrogen; \( Y = \) hydroxy: Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), n-butanol (10 ml) and L37 (0.245 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave 18b (0.238 g, 69%) as a red solid.
(iii) \(18c\) \(R = \text{hydrogen}; \ Y = \text{bromo}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L38\) (0.269 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18c\) (0.270 g, 73%) as a blue solid.

(iv) \(18d\) \(R = \text{hydrogen}; \ Y = \text{isopropyl}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L39\) (0.255 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18d\) (0.234 g, 66%) as a green-blue solid.

(v) \(18e\) \(R = \text{hydrogen}; \ Y = \text{allyl}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L40\) (0.255 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18e\) (0.194 g, 55%) as a green-blue solid.

(vi) \(18f\) \(R = \text{hydrogen}; \ Y = \text{nitro}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L41\) (0.256 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18f\) (0.220 g, 62%) as a green solid.

(vii) \(18g\) \(R = \text{methyl}; \ Y = \text{hydrogen}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L42\) (0.250 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18g\) (0.276 g, 79%) as a yellow-green solid.

(viii) \(18h\) \(R = \text{methyl}; \ Y = \text{hydroxy}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L43\) (0.255 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18h\) (0.257 g, 72%) as a dark red solid.

(ix) \(18i\) \(R = \text{methyl}; \ Y = \text{isopropyl}\): Employing the method outlined in 7.4.20(i) using anhydrous NiCl\(_2\) (0.100 g, 0.77 mmol), \(n\)-butanol (10 ml) and \(L44\) (0.266 g, 0.39 mmol, 0.5 eq.) at a temperature of 120 °C overnight, gave \(18i\) (0.292 g, 80%) as a blue solid.
Chapter Seven

7.4.21 \([N,N'\text{-bis(4-(pyridin-2-yl)methylene)-4,4'\text{-amino-3,3',5,5'-tetraisopropyl-4''-PS-triphenylmethine]}\text{dinickel(II)}\text{tetrachloride (19)}\]

An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with a suspension of \(18e\) (0.200 g, 0.22 mmol) in toluene (24 ml) at 80 °C and was stirred with AIBN (0.090 g, 6.6 mmol, 3 eq.) and styrene (4 ml) overnight. After cooling to ambient temperature, the solvent was removed under reduced pressure to afford a blue solid (2.251 g).
## Table 1 FAB-MS, IR and Magnetic measurements for complexes 1a –18i

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<th>Complex</th>
<th>FAB mass spectra</th>
<th>u(C=N) (cm⁻¹)</th>
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7.5 Crystallography

Data for 3,3',5,5'-tetraisopropyl biphenyl-4,4'-diamine, 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyldiphenylmethane, 4,4'-diamino-3,3',5,5'-tetraisopropyl-4''-hydroxytriphenylmethine, 1-methoxy,1-(4-nitrophenyl),1-(3,5-diisopropyl, 4-amino-phenyl)methane, L15, L22, L33, L36, L38 L42, 2a, 2b, 4, 5, 7a', 7b', 7c', 7d', 13b' and 13e' were collected on a Bruker APEX 2000 CCD diffractometer. Details of the data collection, refinement and crystal data are listed in Tables 2-5. The diffractometer used a graphite-monochromated molybdenum Kα radiation: λ = 0.7107. The data were corrected for Lorenz-polarisation effects and empirical absorption corrections were based on ψ scans. Structure solution by Patterson methods and structure refinements on F2 employed by SHELXTL version 6.10.14 Hydrogen atoms were included in calculated positions (C-H = 0.96 Å) riding on the bonded atoms and 1.2 Ueq(C) for all other atoms. All non-hydrogens atoms were refined with anisotropic displacement parameters.
### Table 2 Crystallographic and data processing parameters for compounds 3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine, 4,4'-diamino-3,5-diisopropyl-3',5'-dimethyl-diphenylmethane and 4,4'-diamino-3,3',5,5'-tetraisopropyl-4'-hydroxy-triphenylmethine

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<th>Compound</th>
<th>3,3',5,5'-tetraisopropylbiphenyl-4,4'-diamine</th>
<th>4,4'-diamino-3,5-diisopropyl-3',5'-dimethyl-diphenylmethane</th>
<th>4,4'-diamino-3,3',5,5'-tetraisopropyl-4'-hydroxy-triphenylmethine</th>
<th>1-methoxy,1-(4-nitrophenyl),1-(3,5-diisopropyl,4-amino-phenyl)methane</th>
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</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>99.776(3) °</td>
<td>105.482(4) °</td>
<td>95.341(5) °</td>
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<tr>
<td>γ (°)</td>
<td>120</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>U(Å³)</td>
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<td>1782.9(5) Å</td>
<td>6267(2) Å</td>
<td>959.9(5) Å</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>4</td>
<td>8</td>
<td>2</td>
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<tr>
<td>Dc (Mg m⁻³)</td>
<td>0.990</td>
<td>1.157</td>
<td>1.064</td>
<td>1.185</td>
</tr>
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<td>F(000)</td>
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<td>2200</td>
<td>368</td>
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<tr>
<td>μ(Mo-Kα) (mm⁻¹)</td>
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<td>5489</td>
<td>3222</td>
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<td>5489 / 0 / 314</td>
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<td>1.102</td>
<td>1.034</td>
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</table>

Data in common: temperature 150(2) K, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å; R₁ = Σ||F₀||-|F₁||/Σ|F₀||, wR₂ = [Σw(F₀²-F₁²)²/Σw(F₀²)²]¹/₂, w⁻¹=|σ²(F₀²)+(aP)²|, P = [max (F₀²,0) + 2(F₁²)]/3 where a is a constant adjusted by the program; goodness of fit = [Σ(F₀²-F₁²)²/(n-p)]¹/₂ where n is the number of reflections and p the number of parameters.
### Table 3 Crystallographic and data processing parameters for L4, L15, L22, L33, L36, L38 and L40

<table>
<thead>
<tr>
<th>Compound</th>
<th>L4</th>
<th>L15</th>
<th>L22</th>
<th>L33</th>
<th>L36</th>
<th>L38</th>
<th>L40</th>
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<tr>
<td>Formula</td>
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<td>$C_{25}H_{32}N_{4}$</td>
<td>$C_{28}H_{32}N_{4}$</td>
<td>$C_{33}H_{32}N_{4}$</td>
<td>$C_{33}H_{32}BrN_{4}$</td>
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<tr>
<td>M</td>
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<td>342.44</td>
<td>432.55</td>
<td>418.53</td>
<td>620.85</td>
<td>639.96</td>
<td>660.92</td>
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<td>Crystal size (mm$^3$)</td>
<td>$0.24 \times 0.18 \times 0.08$</td>
<td>$0.21 \times 0.11 \times 0.09$</td>
<td>$0.24 \times 0.15 \times 0.06$</td>
<td>$0.19 \times 0.23 \times 0.08$</td>
<td>$0.35 \times 0.88 \times 0.23$</td>
<td>$0.42 \times 0.08 \times 0.04$</td>
<td>$0.16 \times 0.09 \times 0.04$</td>
</tr>
<tr>
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<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Orthonhobic</td>
</tr>
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<td>P2(1)/c</td>
<td>P-1</td>
<td>C2/c</td>
<td>P-1</td>
<td>P-1</td>
<td>Pnma</td>
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<td>34.646(5)</td>
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<td>12.565(3)</td>
<td>10.1322(17)</td>
<td>10.214(3)</td>
<td>18.320(3)</td>
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<tr>
<td>b ($\AA$)</td>
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<td>9.208(6)</td>
<td>11.4671(9)</td>
<td>11.368(2)</td>
<td>13.239(2)</td>
<td>13.003(4)</td>
<td>25.569(5)</td>
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<tr>
<td>c ($\AA$)</td>
<td>43.7827(1)</td>
<td>9.273(6)</td>
<td>12.5057(10)</td>
<td>17.102(4)</td>
<td>14.475(2)</td>
<td>14.750(5)</td>
<td>8.2381(14)</td>
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<td>11.4671(9)</td>
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<td>90</td>
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<td>90.0</td>
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<tr>
<td>$\beta$ (°)</td>
<td>108.448(3)</td>
<td>101.821(12)</td>
<td>107.023(3)</td>
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<td>90</td>
<td>91.865(10)</td>
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<td>13733(4)</td>
<td>877.3(9)</td>
<td>1191.12(17)</td>
<td>2335.9(8)</td>
<td>1825.3(5)</td>
<td>1846.3(10)</td>
<td>3859.0(12)</td>
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<td>Z</td>
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<td>4</td>
<td>2</td>
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<td>4</td>
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<td>D$_m$ (Mg m$^{-3}$)</td>
<td>1.295</td>
<td>1.296</td>
<td>1.206</td>
<td>1.190</td>
<td>1.130</td>
<td>1.259</td>
<td>1.138</td>
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<td>364</td>
<td>460</td>
<td>888</td>
<td>668</td>
<td>736</td>
<td>1473</td>
</tr>
<tr>
<td>a(Mo-K$_{a1}$) (mm$^{-1}$)</td>
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<td>0.079</td>
<td>0.072</td>
<td>0.071</td>
<td>0.066</td>
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<td>0.066</td>
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<td>8622</td>
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<td>14218</td>
<td>24400</td>
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<tr>
<td>Independent</td>
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<td>1533</td>
<td>4149</td>
<td>2056</td>
<td>6373</td>
<td>7132</td>
<td>3108</td>
</tr>
<tr>
<td>R$_{int}$</td>
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<td>0.0719</td>
<td>0.0539</td>
<td>0.0389</td>
<td>0.0410</td>
<td>0.0665</td>
<td>0.2002</td>
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<tr>
<td>R$_{int}$/I</td>
<td>13489 / 0 / 796</td>
<td>1533 / 0 / 120</td>
<td>2056 / 0 / 147</td>
<td>6373 / 0 / 432</td>
<td>7132 / 0 / 441</td>
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<td></td>
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<tr>
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<td>R$_1$ = 0.0565</td>
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<td>wR$_2$ = 0.1084</td>
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</table>

Data in common: temperature 150(2) K, graphite-monochromated Mo-K$_{a1}$ radiation, $\lambda = 0.71073$ ; $\text{R} = \Sigma F_{o} - |F_{c}| \Sigma F_{o}$, $\text{wR} = \Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})$, $\text{w} = \sqrt{\sigma(F_{o}^{2} + aP)}$, $P = [\max(F_{o}^{2}, 0) + 2(F_{c}^{2})]/3$ where $a$ is a constant adjusted by the program; goodness of fit = $[\Sigma(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)/[\Sigma w(F_{c}^{2})]^{1/2}$ where $n$ is the number of reflections and $p$ the number of parameters.
<table>
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<tr>
<th>Compound</th>
<th>2a</th>
<th>2b</th>
<th>4</th>
<th>5</th>
<th>7a'</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{25}$H$</em>{32}$Cl$_2$CoN$_3$</td>
<td>C$<em>{26}$H$</em>{32}$Cl$_2$CoN$_4$</td>
<td>C$<em>{49}$H$</em>{52}$Br$_4$N$_3$C$_2$O</td>
<td>C$<em>{60}$H$</em>{72}$Br$_4$N$_3$Co</td>
<td>C$<em>{61}$H$</em>{72}$Br$_{12}$Ni$_2$O$_8$</td>
</tr>
<tr>
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<td>522.32</td>
<td>1152.03</td>
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<td>0.33 x 0.21 x 0.09</td>
<td>0.28 x 0.26 x 0.04</td>
<td>0.32 x 0.23 x 0.09</td>
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</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
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<td>Pbca</td>
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<td>P2/c</td>
<td>P-1</td>
<td>P-1</td>
</tr>
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<td>9.457(3)</td>
<td>31.086(3)</td>
<td>14.0554(16)</td>
<td>9.6479(15)</td>
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<tr>
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<td>14.7357(17)</td>
<td>11.4550(17)</td>
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<td>9.736(3)</td>
<td>15.6922(12)</td>
<td>16.8925(19)</td>
<td>13.926(2)</td>
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<tr>
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<td>90</td>
<td>90</td>
<td>110.864(2)</td>
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<tr>
<td><strong>β (°)</strong></td>
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<td>94.597(5)</td>
<td>111.555(2)°</td>
<td>91.460(2)</td>
<td>82.197(3)</td>
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<tr>
<td><strong>γ (°)</strong></td>
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<td>90</td>
<td>90</td>
<td>116.515(2)</td>
<td>79.326(3)</td>
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<td>2</td>
<td>4</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td><strong>D$_c$ (Mg m$^{-3}$)</strong></td>
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<td>538</td>
<td>3949</td>
<td>9938</td>
<td>698</td>
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<tr>
<td><strong>μ(Mo-Kα) (mm$^{-1}$)</strong></td>
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<td>0.907</td>
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<td>2056</td>
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<td>5041</td>
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<td><strong>R(flat)</strong></td>
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<td>13489 / 796</td>
<td>2056 / 147</td>
<td>6373 / 432</td>
<td>5041 / 335</td>
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<td><strong>Goodness-of-fit on F$^2$</strong></td>
<td>0.969</td>
<td>0.902</td>
<td>0.851</td>
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Data in common: temperature 150(2) K, graphite-monochromated Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å; $R_1 = \Sigma ||F_0|| - |F_E||/\Sigma|F_0|$, wR$_2 = \{\Sigma w(F_E^2 - F_0^2)^2/\Sigma w(F_0^2)\}^{1/2}$, w$^{-1} = [a^2(F_E^2) + (dP)^2]$, P = [max($F_E^2$,0) + 2(F$_C^2$)]/3 where a is a constant adjusted by the program; goodness of fit = $\{\Sigma(F_E^2 - F_0^2)^2/2(n-p)\}^{1/2}$ where n is the number of reflections and p the number of parameters.
<table>
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<th>7b'</th>
<th>7c'</th>
<th>7d'</th>
<th>13b'</th>
<th>13d'</th>
</tr>
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<tbody>
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<td>Formula</td>
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<td>C₄₄H₃₅Br₄Cl₄N₁₂O₅Ni₂</td>
<td>C₄₄H₃₅Br₄Cl₄N₁₂O₅Ni₂</td>
<td>C₄₄H₃₅Br₄Cl₄N₁₂O₅Ni₂</td>
<td>C₄₄H₃₅Br₄Cl₄N₁₂O₅Ni₂</td>
</tr>
<tr>
<td>M</td>
<td>483.57</td>
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<td>P1</td>
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<td>P2(1)/n</td>
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<td>b (Å)</td>
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<td>20.154(3)</td>
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<td>80.9160(10)</td>
<td>23.807(8)</td>
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<td>β (°)</td>
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<td>80.7570(10)</td>
<td>98.983(6)</td>
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<td>112.293(3)</td>
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<td>γ (°)</td>
<td>90</td>
<td>77.8680(10)</td>
<td>90</td>
<td>77.7670(10)°</td>
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<td>F(000)</td>
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<td>18181</td>
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<td>10798</td>
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<td>Independent reflections</td>
<td>4680</td>
<td>5737</td>
<td>9441</td>
<td>7613</td>
<td>8446</td>
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<td>R&lt;sub&gt;int&lt;/sub&gt;</td>
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<td>0.0206</td>
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<td>5737 / 0 / 345</td>
<td>9441 / 3 / 303</td>
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Data in common: temperature 150(2) K, graphite-monochromated Mo-Kα radiation, λ = 0.71073; R₁ = Σ||F₀|| - |F₁||/Σ|F₀||, wR₂ = [Σw(F₀² - F₁²)²/ΣwF₀²]¹/², w = [max (F₀²,0) + 2(F₁²)]/3 where a is a constant adjusted by the program; goodness of fit = [Σ(F₀² - F₁²)²/2(n-p)]¹/² where n is the number of reflections and p the number of parameters.
7.6 Ethylene Polymerisation
The precatalysts (0.01 mmol) was added to a Schlenk vessel, dissolved or suspended in toluene (40 ml) and MAO (4.0 mmol, 400 equiv.). MAO was allowed to react with the precatalyst for 5 minutes. The vessel was purged with ethylene and the contents stirred under 1 bar ethylene at room temperature for the duration of the test. After 1 hr, the test was terminated by the addition of dilute aqueous hydrogen chloride (5 ml). Any solid polymer was collected by filtration, washed with methanol and dried under reduced pressure at 40 °C overnight. The organic phase was separated and analysed by GC. The oligomeric portion was obtained after removal of the solvent by distillation and was used for further analyses.
7.7 References

2 F. E. Mabbs and D. J. Machin, Magnetism and Transition Metal Complexes, 1973, Chapman and Hall.
9 P. Bamfield and P. M. Quan, Synthesis, 1978, 537.
14 G. M. Sheldrick, program for crystal structure refinement, University of Göttingen, Germany, 1993.
Appendices
8.1 Determination of the structural index parameter

The structural index parameter has been determined by using the formula reported by Addison et al.\textsuperscript{1} The structure of a five-co-ordinate system can be a distorted intermediate between a square-pyramidal and a trigonal-bipyramidal geometry (Figure 1). In an ideal square pyramidal, the angles \( \alpha \) and \( \beta \) that are formed by the ligand of the plane of the square pyramidal are equal (viz., \( \alpha = \beta = 180^\circ \)). In a perfectly trigonal-bipyramidal geometry, \( \alpha \) becomes 120° and BMC the principal axis. The geometric parameter (Equation 1) is applicable to five-co-ordinate structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal and rectangular pyramidal. For a perfectly tetragonal geometry \( r \) is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry.

\[ \tau = \frac{(\beta - \alpha)}{60} \]

\textbf{Equation 1: Formula for structural index determination}

\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Complex} & \textbf{\( \alpha \)} & \textbf{\( \beta \)} & \textbf{\( \tau \)} \\
\hline
2a & 148.23(7) N(1)-Co(1)-N(3) & 137.49(5) N(2)-Co(1)-Cl(2) & 0.179 \\
2b & 149.6(2) N(1)-Co(1)-N(3) & 132.58(19) N(2)-Co(1)-Cl(1) & 0.283 \\
4 & 154.88(9) N(2)-Ni(1)-Br(2) & 151.12(11) N(1)-Ni(1)-N(3) & 0.063 \\
13d' & Ni(1) & 167.84(6) N(1)-Ni(1)-Cl(1) & 137.34(3) Cl(2)-Ni(1)-Cl(1) & 0.508 \\
& Ni(2) & 170.80(9) N(3)-Ni(2)-N(5) & 129.85(4) Cl(3)-Ni(2)-Cl(4) & 0.682 \\
\hline
\end{tabular}

8.2 Magnetic measurements

The magnetic moment were determined with an Evans Balance and the equations below.

\[ \chi_g = \frac{c l}{10^5 m(R - R_0)} \]

Equation 1 Determination of the magnetic susceptibility \( \chi_g \).

Where:
- \( \chi_g \) = magnetic susceptibility
- \( c \) = constant 1.030
- \( l \) = length of Evans tube (cm)
- \( m \) = mass of sample (g)
- \( R \) = final Evans balance reading
- \( R_0 \) = initial Evans balance reading

\[ \chi_m' = \left( \frac{\chi_g}{M_w} \right) + \chi_d \]

Equation 2 Determination of the corrected molar magnetic susceptibility \( \chi_m' \).

Where:
- \( \chi_g \) = corrected molar magnetic susceptibility plus diamagnetic correction \( \chi_d \)
- \( M_w \) = molecular weight of the sample

Diamagnetic corrections (x 10^6 mol\(^{-1}\)) = pyridine \(-49\)
- \( = \) NH\(_3\) \(-18\)
- \( = \) OH\(^-\) \(-12\)
- \( = \) First row TM \(-12.8\)
- \( = \) Cl\(^-\) \(-23\)
- \( = \) Br\(^-\) \(-34\)

\[ \mu_{\text{eff}} = 2.828\sqrt{\chi_m'T} \]

Equation 3 Determination of effective magnetic moment \( \mu_{\text{eff}} \).

Where:
- \( \mu_{\text{eff}} \) = effective magnetic moment

Ideal Effective magnetic moment for iron, cobalt, and nickel centres.
\[ \mu_{\text{eff}} = 2.828 \sqrt{\chi_n T} = \sqrt{n(n+2)} \]

and \[ \chi_n T = \frac{g^2}{8N(S+1)} \]

Where:

- \( G \) = gyromagnetic ratio
- \( N \) = the number of metal centres
- \( S \) = the spin state
- \( n \) = number of unpaired electrons

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<th>Ferromagnetically coupled metal centres</th>
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<td></td>
<td>([g=2, S=0])</td>
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<td>(\mu_{\text{eff}} = 0 \text{ BM})</td>
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<td><strong>Cobalt</strong></td>
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8.3 Postgraduate record

APG - Postgraduate Training Activities, Lectures, Modules and Examinations

18/9/01 Pre-Session Demonstrator Training
24/9/01 Departmental Induction
25/9/01 Introduction to Key Techniques and Equipment
26/9/01 Graduate School Induction
27/9/01 Faculty Induction
17/10/01 Information Skills for Chemists Session 1, An Introduction to Chemical Information Databases
24/10/01 Information Skills for Chemists Session 2, Advanced Searching in Crossfire
5/12/01 Developing a Personal Skills Portfolio - Royal Society of Chemistry
12/6/02 Advanced Scientific Writing for Chemists
12/6/02 Applications of Endnote
31/10/01 1D-NMR Spectroscopy
28/11/01 2D-NMR Spectroscopy
30/1/02 The nOe Effect
5/6/02 Presentation of NMR data
6/3/02 Chemdraw, Molecular Modelling and Powerpoint
4/3/02, 11/3/02, 13/3/02 Skills
6/2/02, 13/3/02 Writing Skills
1/5/02 Presentation Skills - Powerful Spoken and Poster Presentations
29/5/02 Developing Skills for a Future Career
13/5/02 IPR, Patent Protection and Commercialisation

Symposia, Conferences and Poster Sessions Attended

9/7/03 - Coordination Chemistry Discussion Group (CCDG) conference, Royal Society of Chemistry; Dalton Division, UK, Manchester, Manchester University
Poster Title: Blending 2-Pyridine Alcohols with Bifunctional Carboxylates on Paramagnetic Transition Metal Centres (Awarded First Prize)
23/2/04 Half-Day Symposium: Catalysis 2004
University of Leicester

12/7/04 - Coordination Chemistry Discussion Group (CCDG) conference,
14/7/04 Royal Society of Chemistry; Dalton Division, UK, Leicester,
Leicester University
Flash Presentation and Poster 1 Title: Derivatised Porous Nanoballs Based on Secondary Building Units (SBU)
Poster 2 Title: Paramagnetic Chains, Cubes and Open-Cubes Featuring Benzilate Ligands; Syntheses and Magnetic Properties

Personal Internal Seminars and Literature Discussion Session Presentations

<table>
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<tr>
<th>Date</th>
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<tr>
<td>8/11/01</td>
<td>PhD first year project outline</td>
<td>'Paramagnetic Assemblies Based on Imido Ligand Scaffolds'</td>
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<td>18/2/02</td>
<td>PhD first year project</td>
<td>'Towards Nano-Scale Assemblies'</td>
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<td>14/11/02</td>
<td>PhD second year project outline</td>
<td>'Paramagnetic Oxo- and/or Imido-Transition Metal Assemblies.'</td>
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<td>PhD second year project</td>
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<td>4/12/03</td>
<td>PhD third year project</td>
<td>'Blending 2-Pyridine Alcohols with Bifunctional Carboxylate Ligands on Paramagnetic Transition Metal Centres'</td>
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<td>22/6/04</td>
<td>Final Year Presentation</td>
<td>'Controlled Synthesis of Paramagnetic Copper Assemblies'</td>
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Internal Seminars – External Speakers

1/10/01  Royal Society of Chemistry Centenary Lecture
Professor Kyriacos Nicolaou – Scripps Research Institute, California
‘Enabling Technologies for Biology and Medicine Arising from Endeavours in Total Synthesis’

4/10/01  Royal Society of Chemistry Lecture
Dr Peter O’Brien – University of York
‘Basic Instinct: New Synthetic Adventures with Chiral Bases’

10/10/01  Dr Didier Bourrissou – Université Paul Sabatier, Toulouse
‘Stable Carbenes and Diradicals: New Stabilisation and Bonding Mod

22/10/02  Royal Society of Chemistry Student Chemical Society Lecture
Dr Anthony Hooper – Institute of Arable Crops, Rothamstead
‘Sex, Bugs and Rock and Roll: Identification and Synthesis of Semiochemicals and Exploitation of the Ecological Interactions they Regulate as an Approach to Pest Management’

14/11/01  Royal Society of Chemistry Joseph Chatt Lecture
Professor Vernon C. Gibson – Imperial College, London
‘Designing Catalysts for Polymer Synthesis’

10/12/01  Dr Jonathan McMaster – University of Nottingham
‘The Electronic Structure of the Active Sites of Molybdenzymes’

14/12/02  Professor Peter Fleckier – Johannes Gutenberg University, Mainz
‘Dissecting Intramolecular versus Intermolecular Protein Recognition

28/1/02  Professor Judith Howard – University of Durham
‘The Application of Very Low Temperature Crystallography to Chemic Problems’

11/2/02  Dr Robin Bedford – University of Exeter
‘High Activity Catalysts for C-C Bond Formation’

25/2/02  Professor John Nixon – University of Sussex
‘The New World of Phospha-Organometallic Chemistry’

4/3/02  Dr Holger Braunschweig – Imperial College, London
‘Compounds with Novel Boron Containing Ligands: Transition Metal Complexes of Boron and [1] Bora – Metalloacenophanes’
Appendices

6/3/02 Dr Richard Shutt – ExxonMobil, Belgium
'Supercritical Phase Phenomena in Ethylene Polymerisation and Poly
Separation'

8/5/02 Dr Nick Long – Imperial College, London
'Ferrocene – Ligand Design'

20/5/02 Dr Martyn Coles – University of Sussex
'Anionic and Neutral Guanidine – based Ligands in Coordination
Chemistry and Catalysis'

Internal Seminars and Literature Discussion Sessions – Internal Speakers Project
Seminars
11/10/01 Christopher J. Davies – PhD second year project outline
1/11/01 Sukhvinder K. Kandola, Toby Reeve and Samuel Suhard – PhD
second year project outlines
29/10/01 MChem project outlines
8/11/01 Alice Hickman – PhD first year project outline
22/11/01 Jérémie D. Pelletier and Omar Duaij – PhD first year project outlines
3/12/01 Dr. G. A. Solan and Dr. P. W. Dyer – Current Projects
6/12/01 Martin Hanton – PhD third year project outline
4/2/02 Alice Hickman, Jérémie D. Pelletier and Katie Sharpe – PhD first year
18/2/02 Andrew West and Omar Duaij – PhD first year projects
18/3/02 Dr. E. Raven and Dr. D. Davies – Current projects
19/3/02 MChem final presentations

Final Year PhD Presentations attended
27/5/02 Martin Hanton
17/6/02 Neesha Patel
24/6/02 Ben. Croxtall and James Sherrington

Literature Discussion Sessions
29/10/01 Speakers: M. Hanton and N. Patel, Chair: C. J. Davies
Questioners: B. Croxtall and J. Sherrington
5/11/02 Speakers: P. Griffith and D. Harding, Chair: M. Dix
Questioners: M. Giardiello and G. Barth
26/11/01 Speaker: G. Barth, Chair: M. Hanton
Questioners: P. Griffith and D. Harding
Appendices

Questioners: C. J. Davies, S. Suhard and M. Hanton

25/3/02 Speakers: C. J. Davies, S. Suhard and J. Sherrington, Chair: B. Croxtal
Questioners: S. K. Kandola, T. Reeve and N. Patel

24/4/02 Speakers: A. Hickman, A. West and J. D. Pelletier, Chair: N. Patel
Questioners: R. K. Chaggar, K. Sharp and O. Duaij

13/5/02 Speakers: O. Duaij, K. Sharp and R. K. Chaggar, Chair: S. K. Kandola
Questioners: A. Hickman and A. West

13/11/03 Speakers: Y. Champouret, R. K. Chaggar and O. A. Duaij

11/12/03 Speakers: A. Gregory and E. A. Sabban

PhD Second and Third year Seminars

Internal Seminars – External and Internal Speakers

21/10/02 Dr Paul Raithby – University of Bath
‘Adventures in Organometallic Polymer Chemistry’

28/10/02 Dr Clive Metcalfe – University of Leicester
‘Transition Metal Complexes and their Interaction with DNA’

18/11/02 Dr Mike Turner – University of Sheffield
‘Synthesis of Conjugated Polymers for Polarised Electroluminescence and Polymer Electronics’

9/12/02 Prof. Todd Marder – University of Durham
‘The Role of Transition Metal Boryl Complexes in Catalysed Borylations including Rhodium Catalysed C-H Bond Functionalisation’

17/2/03 Prof. V. McKee – University of Loughborough
‘Manipulating Metal Arrays within Macrocycles’

10/3/03 Prof. Duncan Bruce – University of Exeter
‘Metallomesogens by Design’

28/4/03 Prof. Kingsley Cavell – University of Cardiff
‘Reactions of Heterocyclic Carbene Complexes: Important Ramifications for their Application in Catalysis’

30/5/03 Dr Carine Aubrey – University of Leicester
‘Synthèse, Analyse Stucturale et Activité Biologique d’analogues Rigidès d’un Antagoniste de l’octadecaneuropeptide (ODN)’

2/6/03 Dr Sarah Heath – University of Manchester
‘Shedding Light on Biological Systems: the Development of...’
Dinuclear Lanthanide Probes'

Inaugural Lecture

3/6/03 Prof. Jonathan Percy – Appointed as Professor of Chemistry at the University of Leicester

'Against Nature: Unnatural Products in the Service of Humanity'

9/6/03 Dr Alan Spivey – Imperial College, London

'Catalytic Asymmetric Acylation – Studies towards the Total Synthesis of Polyol Sesquiterpenes'

29/9/03 Dr Zoe Pikramenou – University of Birmingham

'Luminescent Supramolecular Architectures: from Shape to Function'

6/10/03 Dr Chris Richards – Queen Mary, University of London

'Palladium and Platinum Metallacycles for Organic Synthesis'

The Second Tim Norwood Memorial Lecture

8/10/03 Prof. Ian Campbell – University of Oxford

'NMR and Proteins'

20/10/03 Dr Sandie Dann – University of Loughborough

'Something Old, Something New Something Borrowed and Something Blue: Complex Oxides and Sulphides'

27/10/03 Dr Chris Hayes – University of Nottingham

'Natural and non-Natural Products: Total Synthesis and Biological Applications'

3/11/03 Prof. Helen Fielding – University College London

'Controlling Electrons and Molecules using Light'

17/11/03 Prof. Chris Binns – Department of Physics University of Leicester

'Building High-Performance Magnetic Materials by Assembling Nanoclusters'

1/12/03 Prof. Richard Winpenny – University of Manchester

'Synthetic Studies of Metal Wheels and other Cages'

8/12/03 Prof. Peter Hore – University of Oxford

'Bird Navigation: a Photochemical Magnetic Compass?'

19/1/04 Prof. Bill Levason – University of Southampton

'Recent Developments in the Chemistry of Antimony Ligands'

9/2/04 Dr Michael Whittlesey – University of Bath

'Stoichiometric and Catalytic Small Molecule Activation by
Appendices

*Ruthenium N-Heterocyclic Carbene Complexes*

8/3/04 Dr Chris Kay – Free University of Berlin

‘Applications of Electron Spin Resonance Spectroscopy to Biological Problems’
Royal Society of Chemistry – East Midlands Local Section sponsored seminar

15/3/04 Prof. David Schiffrin – University of Liverpool

‘Connectivity of Functionalised Nanoparticles and their Arrays’
Royal Society of Chemistry – East Midlands Local Section

26/4/04 Dr Graham Sandford – University of Durham

‘Polyfunctional Heterocycles and Macrocycles’

10/5/04 Dr Dominic Wright – University of Cambridge

‘Cation and Anion Coordination using ‘Torocyclic’ Ligands’

7/6/04 Prof. Peter Scott – University of Warwick

‘Catalysis with Chiral Metal Complexes’

Internal Seminars and Literature Discussion Sessions – Internal Speakers Project Seminars

24/10/02 Jérémie Pelletier and Alice Hickman (PhD project update)

31/10/02 MChem project introductions

7/11/02 MChem / MSc project introductions

14/11/02 Rajinder Kaur Chaggar and Omar Al-Duaij (PhD project update)

28/11/02 Yohan Champouret and Ishaq Dadhiwala (PhD project outlines)

5/12/02 Samuel Suhard and Sukvinder Kandola (PhD project update)

12/12/02 Christopher Davies and Toby Reeve (PhD project update)

25/3/03 Projects seminar

Yohan Champouret (1st year PhD), Jérémie Pelletier (2nd year PhD),
Ishaq Dadhiwala (1st year PhD), Carly Anderson (MSc), Omar Al-Duaij (2nd year PhD), Rajinder Kaur Chaggar (2nd year PhD), Alice Hickman (2nd year PhD), Duncan Harding (1st year PhD), Andrew West (2nd year PhD), Nektaria Papadopoulou (1st year PhD)

26/11/03 MChem Introductory Presentations

27/11/03 Projects Seminar 3rd Year PhD

Jérémie Pelletier and Omar Al-Duaij
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<td>Projects Seminar</td>
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<td>MChem and 1st year PhD Projects Seminar</td>
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<td>E. A. Sabban, R. Griffin, M. Gourlay, J. Bennett, B. Parmar, M. Giardiello and P. Villuendas</td>
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**ExxonMobil project report**

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<td>Project report I, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt</td>
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<td>Sep. 2002</td>
<td>Project report II, Oral presentation and written report, ExxonMobil, Notre-Dame de Gravenchon</td>
<td>Dr R. Shutt</td>
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<td>Oct. 2002</td>
<td>Project report II, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt, Dr D. McConville</td>
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<td>Mar 2003</td>
<td>Project report III, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt</td>
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<td>Project report IV, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt</td>
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<td>Mar 2004</td>
<td>Project report V, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt</td>
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<tr>
<td>Sep. 2004</td>
<td>Project report VI, Oral presentation and written report, University of Leicester</td>
<td>Dr R. Shutt</td>
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