3d Transition Metal Complexes of N-Heterocyclic Carbene Ligands and N-Heterocyclic Ligands

A thesis submitted to The University of Manchester for the degree of Master of Philosophy in the Faculty of Engineering and Physical Sciences, 2015

Kieran Weldon

School of Chemistry

The University of Manchester
# Table of Contents

Table of Contents .......................... 2  
List of Figures .............................. 4  
Abstract ................................... 6  
Declaration .................................. 7  
Copyright Statement ......................... 7  
Acknowledgement ............................ 9  
Terms and Abbreviations ................. 11

**Chapter 1: Introduction** ............... 13  
1.1 N-Heterocyclic Carbene Ligands .... 14  
1.2 Tripodal N-Heterocyclic Carbene Ligands ............. 18  
1.3 Tetrapodal N-Heterocyclic Carbene Ligands ....... 20  
1.4 Synthetic Routes to Bis- and Tris- N-Heterocyclic Carbenes ......... 21  
1.5 Catalysis ................................ 25  
1.6 NHC Ligands Compared with Phosphine Ligands .. 27  
1.7 N-Donor Ligands ......................... 29  
1.8 Project Proposal ......................... 32

**Chapter 2: Results and Discussion** ... 35  
2.1 Metal Amide Complexes ................. 36  
2.2 Metal Amide Complexes and Reactions with Alcohols .......... 48  
2.3 Metal Amide Complexes and Reactions with Imidazolium Chlorides .... 53  
2.4 Tetrapodal Ligands – Preparation and Reactions .......... 62
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>P(V) Bridged N-Heterocyclic Carbenes</td>
<td>66</td>
</tr>
<tr>
<td>2.6</td>
<td>Conclusion and Future Work</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>Chapter 3: Experimental Section</td>
<td>77</td>
</tr>
<tr>
<td>3.1</td>
<td>General Considerations</td>
<td>78</td>
</tr>
<tr>
<td>3.2</td>
<td>Preparation of Metal Amide Complexes</td>
<td>79</td>
</tr>
<tr>
<td>3.3</td>
<td>Preparation of Metal Amide [RO] Complexes</td>
<td>82</td>
</tr>
<tr>
<td>3.4</td>
<td>Preparation of Metal Amide Imidazole Complexes</td>
<td>83</td>
</tr>
<tr>
<td>3.5</td>
<td>Preparation and Reactions of Tetrapodal ligands</td>
<td>85</td>
</tr>
<tr>
<td>3.6</td>
<td>Preparation of P(V) Bridged N-Heterocyclic Carbene Complexes</td>
<td>88</td>
</tr>
<tr>
<td>3.7</td>
<td>Crystallographic Details for Compounds</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>Chapter 4: References</td>
<td>98</td>
</tr>
</tbody>
</table>
List of Figures

Chapter 1: Introduction

**Figure 1** - Examples of commonly used NHCs 14

**Figure 2** - An orbital diagram to illustrate a singlet carbene 15

**Figure 3** - An Arduengo carbene (IAd) 15

**Figure 4** - The structure of \textit{trans}-Pd(1,3-diethylbenzimidazol-2-ylidene)$_2$Cl$_2$ 24

**Figure 5** - Schematic of an NHC bis-carbene showing the constituents that affect the electronics and steric 28

**Figure 6** - The structure of 1-tert-butyl-2-diphenylphosphino-imidazole 28

**Figure 7** - Examples of NHCs and N-donor heterocycles targeted for use in this project 33

**Figure 8** - Examples of tetrapodal NHC ligands targeted for use in this project 34

Chapter 2: Results and Discussion

**Figure 9** - Structure of $\left[\left(\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\right)_2(\text{bipyrimidine})\right]$ 37

**Figure 10** - Structure of $\left[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2(\text{phenanthroline})\right]$ 39

**Figure 11** - Structure of $\left[\left(\text{Co}\{\text{N(SiMe}_3\}_2\}_2\right)_2(\text{bipyrimidine})\right]$ 43

**Figure 12** - Structure of $\left[\text{Co}\{\text{N(SiMe}_3\}_2\}_2(\text{phenanthroline})\right]$ 46

**Figure 13** - Structure of $\left[\left(\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\right)_3(\text{HAN})(\text{IPr.HCl})\right]$ from previous work undertaken by the Layfield Group 54

**Figure 14** - Structure of $\left[\left(\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\right)_3(\text{HAN})(\text{ItBu.HCl})\right]$ 57
Figure 15 - Possible products for the reaction between POCl₃ and t-butylimidazole in THF

Figure 16 - Structure of [Mn(tBuIm)₂(OTf)₂(THF)₂]
Abstract

The synthesis of two new \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}_2]\) complexes; \([[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(bipyrimidine)}](2.1)\) and \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(phenanthroline)}](2.2)\) are discussed. These complexes have been analysed by NMR spectroscopy and the additional solid-state structures have been obtained using X-ray crystallography. The corresponding \([\text{Co}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}_2]\) complexes; \([[\text{Co}\{\text{N(SiMe}_3\}_2\}_2\text{(bipyrimidine)}](2.4)\) and \([\text{Co}\{\text{N(SiMe}_3\}_2\}_2\text{(phenanthroline)}](2.5)\), have been synthesised and isolated. These are discussed and have been analysed by NMR spectroscopy, the additional solid-state structures for both these compounds were obtained using X-ray crystallography. Complex 2.1 was reacted with a number of alcohols and imidazolium chlorides. Complex 2.2 was reacted with selected imidazole chlorides. Both sets of reactions for complexes 2.1 and 2.2 are discussed. No further reactions were carried out with complexes 2.4 and 2.5.

\(\text{[Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(hexaazatrinaphthalene)}](2.3)\), was synthesised and further reactions with numerous imidazole chlorides were carried out and these are discussed. Successful reaction of \([[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(hexaazatrinaphthalene)}]\) and \(\text{I}^\text{Bu}^\text{HCl}\), resulted in the formation of a new complex (2.15), the structure of which has been obtained through X-ray crystallography. The reaction needs to be repeated in order to obtain full characterisation.

A tetrapodal ligand (2.21) was synthesised according to an established literature procedure. This ligand was reacted with \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}_2]\) and manganocene in THF, the reactions produced insoluble solids. NMR spectroscopy has been attempted on both products. A reaction with \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}_2]\) in bromobenzene was also carried out, producing an insoluble solid, NMR spectroscopy was attempted using benzene-\(d_6\) but this has so far been unsuccessful.

The synthesis of a new P(V) bridged NHC, \([\text{O}\equiv\text{P}\{\text{NHC}\{\text{H}\}_3\}]^3^+\) [OS(=O)\(\text{CF}_3\)]\(^3\) complex (2.29), is discussed. This new tripodal NHC has been characterised using NMR spectroscopy and elemental analysis. Characterisation via X-ray crystallography was not possible, as explained in the results and discussion chapter. \([\text{O}\equiv\text{P}\{\text{NHC}\{\text{H}\}_3\}]^3^+\) [OS(=O)\(\text{CF}_3\)]\(^3\) was reacted with manganocene to produce a new octahedral manganese complex (2.30), which is discussed. The complex has been characterised by NMR spectroscopy and elemental analysis. Additionally a solid-state structure has been obtained through X-ray crystallography.
Declaration

That no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Copyright statement

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time.

This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property
and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.
Acknowledgement

First and foremost I would like to thank Dr Richard A. Layfield for allowing me into his group for the duration of my MPhil. His help and support has been a great source of encouragement to me throughout the duration of this project. Without his ideas, persistence and enthusiasm this thesis would have failed to exist.

Special thanks need to be extended to Dr Ben Day whose support, encouragement and patience have inspired me throughout this degree. I wish to further thank him for his work with my crystallography. To Dr Thomas Pugh, again for his encouragement and support, as well as the endless amusement he has provided throughout my time in the lab. I would also like to thank him for his previous work with the [(Fe{N(SiMe$_3$)$_2$})$_2$](HAN)] complex which greatly aided my project. To Dr Kuntal Pal for his help with numerous aspects of my experimental work. Finally, I would like to thank Dr Jani Moilanen for his help and guidance with my project. I would also like to thank the remainder of the Layfield group for making me feel welcome, as well as for ensuring that my time spent here has been both a pleasant and enjoyable experience. Further acknowledgement needs to be extended to the occupants of my office and to the members of the Ingleson group who have made the duration of my degree both an entertaining and worthwhile experience.
Finally, I wish to thank my family and friends for their constant support and encouragement, which has helped me to remain positive and focused throughout the duration of my project.
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anal. Calcd</td>
<td>combustion elemental analysis calculated</td>
</tr>
<tr>
<td>'Bu</td>
<td>tertiary butyl</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>chloroform-$d$ (99.8 % atom D)</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>acetonitrile-$d_3$ (99.8 % atom D)</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
<td>benzene-$d_6$ (99.8 % atom D)</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>HAN</td>
<td>hexaazatrinaphthalene</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>IBuMe</td>
<td>1-butyl-3-methylimidazol-2-ylidene</td>
</tr>
<tr>
<td>IPr</td>
<td>1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene</td>
</tr>
<tr>
<td>IMes</td>
<td>1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene</td>
</tr>
<tr>
<td>ITol</td>
<td>1,3-bis(4-methylphenyl)imidazol-2-ylidene</td>
</tr>
<tr>
<td>KN(SiMe$_3$)$_2$</td>
<td>potassium bis(trimethylsilyl)amide</td>
</tr>
<tr>
<td>LiN(SiMe$_3$)$_2$</td>
<td>lithium bis(trimethylsilyl)amide</td>
</tr>
<tr>
<td>Me</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-trimethylphenyl</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>TIMEN</td>
<td>tris-[2-(3-aryl-imidazol-2-ylidene)ethyl]amine</td>
</tr>
<tr>
<td>δ/ppm</td>
<td>chemical shift in parts per million</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction
1.1 N-Heterocyclic Carbene Ligands

In the early 1990s the ability to finally isolate stable N-heterocyclic carbenes (NHCs) laid the foundations for vigorous research into these ligands.\(^1\) Before this, many carbenes synthesised were short lived and unable to be isolated.\(^2\) In recent years there has been a growing interest in NHCs,\(^3\) and this chemistry has proved to be a lot more complex than previously thought. NHCs have a wide number of applications in both inorganic and organometallic chemistry and their ability to bind to a number of transition metals and main group elements, as both Lewis acids and bases, has made them a highly desirable set of ligands.\(^4\)

Numerous examples of NHCs currently exist with common examples including, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol), and 1-butyl-3-methylimidazol-2-ylidene (IBuMe) as shown in figure 1.

![Figure 1 Examples of commonly used NHCs.](image)

NHCs are electron rich carbenes that are stabilised predominantly by electronics, with stericstics playing a role in some cases. The main reason for their electronic stability is due to \(\pi\) donation from the electron rich system (N-C=C-N) found in the ring to the \(p\) orbital that lies perpendicular to the carbene.\(^5\) For singlet carbenes that are in the ground state, a pair of electrons will occupy the \(\sigma\) orbital, this in turn results in the \(p\) orbital being formally vacant, as shown in figure 2.\(^2\)
In order to stabilise carbenes it is therefore necessary for electrons to be donated from the nitrogen atoms. Amino groups are also very useful for stabilising carbenes, due to them being highly effective donor groups.\(^2\) 1,3-diadamantylimidazol-2-ylidene (IAd), a structure for which is shown in figure 3, was the first isolated crystalline diaminocarbene and was reported by Arduengo in 1991. This carbene proved to be stable in the absence of both air and moisture, with both thermodynamic and kinetic properties allowing for it to be easily isolated.\(^5\)

NHCs are extremely versatile ligands, a large number have now been synthesised and there are numerous examples available for use in the synthesis of metal complexes,\(^6\) or for potential catalytic applications. The use of these ligands, particularly in catalysis,\(^7\) offers many alternative and more efficient synthetic routes to those currently known, facilitating the need to isolate these highly desirable compounds. NHCs are highly tuneable ligands and they can be conveniently synthesised when needed,\(^6\) the ability to modify NHCs stems from the use of a
number of different substituents, which can further enhance their use in chemistry. NHCs (and carbenes in general) dissolve very well in both polar and non-polar solvents, DCM and chloroform have sometimes had limited success due to solubility issues with the carbenes.

Free NHCs are often formed through deprotonation of their imidazolium precursors an example of which is shown in scheme 1. Deprotonating the NHC makes it easier to bond to the corresponding metal salt, successfully forming a metal complex.

![Scheme 1 Deprotonation of an imidazolium precursor](image)

Deprotonation of chelating bis-imidazolium salts is difficult, as the deprotonated NHC tends to dimerise due to the Wanzlick equilibrium, which is in favour of the dimer, therefore making the synthesis of this variety of carbene non-trivial. Where acidic triazolium salts are involved, it is quite common to use triethylamine in THF as the main base for deprotonation. The deprotonation will usually take place in the presence of a metal salt or a complex, essentially providing in situ deprotonation. NHCs reacted in this way can bind in the agostic mode (although this is not very common) or potentially add oxidatively to the metal centre.
present.\textsuperscript{3} Agostic bonding involves the interaction between a co-ordinately unsaturated metal and a C-H bond. Two electrons from the C-H bond are able to enter the empty orbital on the transition metal, which in turn results in a three centre two-electron bond forming (where three atoms share two electrons).

It is possible for an NHC to bind to virtually all metals in high and low oxidation states,\textsuperscript{12} there are however some exceptions to this. In order for an NHC to bind to a metal it has to undertake covalent bonding, therefore metals such as the lanthanides, which predominately undergo ionic bonding, are less likely to react with NHCs to form metal complexes. Due to NHC ligands being both $\sigma$ donating and $\pi$ accepting, this results in them being used alongside a variety of metal complexes that have high and low valency.\textsuperscript{8} NHC ligands are potentially capable of accepting $\pi$-backbonding from a metal centre, allowing for electron-rich metal centres to be stabilised.\textsuperscript{13} Examples of this exist as early as 1975, when the existence of $\pi$-backbonding was exhibited in a number of ruthenium(II)-NHC complexes.\textsuperscript{14} Recent studies have shown that $\pi$-backbonding from electron rich metal centres can contribute to approximately 20 – 30 % of orbital bonding interactions, which is exhibited in some palladium complexes,\textsuperscript{15} as well as iridium complexes such as $[\text{Cp(NHC)}\text{Ir=CH}_2]$, where NHC stands for imidazol-2-ylidene.\textsuperscript{16}

Varying the type of NHC used in the reaction can alter the reactivity of metal complexes possessing NHC ligands.\textsuperscript{8} Substituents such as 2,4,6-trimethylphenyl (Mes) or methyl vary vastly in size and can influence the properties and reactivity of NHC ligands,\textsuperscript{17} with steric demand varying considerably across the range of NHCs
available. It has been found that ligands with extra steric bulk will greatly affect the bond length between the metal centre and the NHC\textsuperscript{18} as well as the bond energy, with bulkier ligands causing lower observed bond energies.\textsuperscript{7} Due to this there have been cases where extremely bulky NHC ligands have been shown to have a destabilising effect on some metal bonds.\textsuperscript{18} Rotation around the metal centre is influenced by steric bulk and it is possible to use NMR spectroscopy to show how the barrier of rotation in a metal complex can be very high.\textsuperscript{19} In many NHCs, rotation around the metal centre is a factor that strongly contributes to the chemistry of the complex.\textsuperscript{3}

\subsection*{1.2 Tripodal N-Heterocyclic Carbene Ligands}

Tripodal ligands have gained increased importance in transition metal coordination chemistry. As with NHCs, tripodal ligands are important in catalysis and are able to promote a number of catalytic transformations.\textsuperscript{6} These ligands have many unique steric and electronic affects offering a number of stabilising properties, one known example being their ability to stabilise functional groups, such as iron nitride groups, making them desirable ligands to use in synthesis.\textsuperscript{18} One ligand known for its stabilising properties is \textit{tris}-(2-(3-aryl-imidazol-2-ylidene)ethyl)amine, commonly abbreviated to TIMEN. This ligand is often added to complexes due to its ability to stabilise metals in high or low states. The synthesis of this ligand is shown below in scheme 2.\textsuperscript{8} An example of the use of the TIMEN ligand includes the synthesis of a [(TIMEN\textsuperscript{R})Fe(N)]\textsuperscript{+} complex by photolysis.\textsuperscript{8}
The structural arrangement of tripodal ligands can result in the inhibition of decomposition pathways, which would usually result in the cleavage of NHCs from metal centres.\textsuperscript{1} Recently there have been developments into both bi- and tri-dentate NHCs and a large number of these ligands are being used in the synthesis of metal complexes, with a number of new and interesting structural arrangements having arisen from the use of these ligands. They can also be used to alter properties like chirality, steric hindrance and bite angle. The chelating effect of these ligands has resulted in the production of complexes with higher stability when compared to those that have been synthesised using mono-dentate NHCs.\textsuperscript{19}
1.3 Tetrapodal N-Heterocyclic Carbene Ligands

Tetrapodal ligands are formed using NHCs which tend to be rigid imidazolium acceptors, often using both benzyl and mesityl substituents. These ligands have a large number of potential applications, particularly in catalysis and as reactants in host-guest chemistry. The formation of metal-carbon bonds in tetrapodal ligands means that the isolation of different metallocages is possible regardless of the alkyl group that has been used as a substituent; these cages result in host-guest chemistry being achievable due to the available geometry.\textsuperscript{20}

There are a number of properties that affect the products generated in reactions to form tetrapodal ligands; these include ligand flexibility, steric hindrance and coordination modes.\textsuperscript{20} The twisting of the planarity of the ligand alongside the formation of a metal-carbon(NCN) bond\textsuperscript{20} is itself enough to have an effect on the geometries of the tetradeinate ligand, generally these ligands can form molecular cylinders and again alkyl substituents tend to have no effect on the resulting geometry. Scheme 3 shows one possible synthetic method for the formation of a tetrapodal ligand. R\textsubscript{1} could be a benzyl, methyl or ethyl group for example.\textsuperscript{20}

\begin{ Scheme}
\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\includegraphics[width=0.4\textwidth]{tetrapodal_ligand.png}};
\end{tikzpicture}
\end{center}
\end{ Scheme}
1.4 Synthetic Routes to Bis- and Tris-N-Heterocyclic Carbenes

In the preparation of N-heterocyclic carbene complexes it is very common to use N-alkyl or -aryl imidazolium salts as starting materials, these precursors are easy to synthesise as well as being readily available from commercial sources.\(^\text{19}\) A bis- or tris- imidazolium salt is commonly prepared by undertaking a reaction directly between the corresponding precursors, an example of which is shown in scheme 4.\(^\text{21}\) This type of reaction is important as it provides a simple synthetic method, resulting in the ability to synthesise a large number of bidentate NHC precursors. It is possible to adapt and modify these precursors through the use of a number of different N-substituents as well as changing the linkers used between the two imidazoles.\(^\text{19}\)

![Scheme 4 Synthesis of a bis-imidazolium salt.](image)

There are many reported methods that have proved to be successful in synthesising chelating NHC complexes. The methods most commonly used are;

i. The insertion of a metal into a C=C bond of electron rich olefins

ii. In situ deprotonating of bisimidazolium salts with bases which can be added to the reaction mixture in the presence of a metal precursor

iii. Transmetallation from silver(I)-NHC complexes

iv. Oxidative addition of the C-H bond of an imidazolium cation.\(^\text{19}\)
The isolation of free bis-carbenes is a synthetic route that very often gives high yields. The liquid ammonia route in scheme 5 is a classic example of high yielding free carbene isolation. With reference to scheme 5 it is sometimes required for the reaction to be carried out via an alternative route, such as the deprotonation of the corresponding imidazolium dibromide, this method produces a similar ligand to the method shown, but results in much poorer yields.

Scheme 5 The isolation of a bis-free carbene.

A synthetic route that was extensively researched by Lappert in the 1980s involves the insertion of a metal centre into a C=C bond of electron rich olefins. His research led to the use of electron rich olefins as N-heterocyclic carbene precursors; these are referred to in his reports as carbenoids. This resulted in the synthesis of a number of new transition metal complexes as well as a variety of new transition metal adducts. Using this synthetic route and carrying out a reaction between an electron rich olefin and a metal complex, it is possible to create a number of different mono-, bis-, and tris-carbene complexes. Any NHC that is synthesised in this method will be saturated. Scheme 6 is an example of an insertion of a metal into a C=C bond.
The main advantage for preparing a chelating NHC complex via in situ deprotonation of an azolium salt is that there is no need to isolate the NHC.\textsuperscript{19} Scheme 7 is an example of a chelating bis-NHC that has been obtained through the reaction of a bisimidazolium salt with palladium acetate.\textsuperscript{24}

Transmetallation from a silver(I) NHC complex was originally reported as a synthetic method for the production of a number of gold and palladium complexes.\textsuperscript{25} This method of synthesis involves the use of an imidazole salt which is reacted with silver(I) oxide in order to produce the corresponding mono- or bis-NHC silver complex, as shown in scheme 8.
The resulting silver complex from this reaction is very stable and can either be isolated or used in situ in subsequent reactions, using the silver complex in situ makes it possible to form the related M-NHC. An example of a complex formed using a silver carbene transfer agent is trans-Pd(1,3-diethylbenzimidazol-2-ylidene)Cl₂, the structure for this complex is given in figure 4.

Transmetallation reactions can be carried out in aerobic conditions, this type of reaction is very successful with a large variety of transition metals, including cobalt, iron and ruthenium. With transmetallation it is often possible to create different compounds depending on the reaction conditions. The relative size of the N- substituents also contributes to the type of complex formed, and it is known that N- substituents can affect the geometry of the final compound.
A recently developed method for synthesising metal complexes is the oxidative addition of the C-H bond of an imidazolium cation. Not many examples of this synthesis currently exist in the literature due to it being relatively new and underdeveloped. The synthetic method predominantly involves the direct oxidation of a mono-imidazolium C2-H bond to a low valent transition metal compound.

1.5 Catalysis

Recent years have seen a strong push for the development of catalysts based on metal-NHC complexes, predominantly due to these catalysts having some of the highest catalytic activity in their respective field. The variety of NHC ligands that are currently available has resulted in the synthesis of many new and exciting catalysts; their versatility means that there is potential to design selective catalysts and NHCs have also been known to improve reactivity and tolerance. The strong metal-carbon bonds that are exhibited in metal-NHC complexes mean that degradation of the catalyst is less common; this results in a much longer lifespan together with a higher tolerance of harsh reaction conditions. Numerous metals can be used when creating metal complexes for catalysts, with examples including both ruthenium and palladium, but at present iron is growing increasingly popular. Iron is cheaper, less toxic and much more abundant, therefore making it a safer and more economically viable metal when compared to the more traditional transition metals previously used in catalysis.
Metal-NHC complexes have the potential to be developed into catalysts able to aid carbon-carbon bond formation as well as carbon-heteroatom bond formation. Scheme 9 shows an example of C-C bond formation, which is catalysed by a palladium-NHC complex.

![Scheme 9](image)

In the case of carbon-carbon bond formation it has been found that it is often better for the NHC to be formed in situ and so far this appears to be the most effective method to use. In particular iron-NHC catalysts have proven to be versatile and offer many alternative routes in synthesis, these catalysts produce much higher yields and have better reactivity than those previously used, such as those involving phosphines. Low coordinate iron complexes for example play a significant role in a number of bond forming reactions. NHCs have been found to be less susceptible to oxidative ligand degradation, a problem that is quite common in phosphine ligands.
Iron-NHC complexes can have a number of different Fe-C bond lengths with steric repulsion being the predominant reason for this. Different sized ligands will result in different bond lengths, bulkier ligands for example will cause longer bond distances in order to accommodate the size of the ligand. This can cause some problems for catalytic activity as the longer bond length shows a hindered approach of the carbene carbon to the iron centre. Reactions involving iron-NHC complexes can be repeated using other elements that exhibit similar reactivity. Cobalt, tin and vanadium all have the potential to react in a similar way to iron, creating a number of analogous compounds.

1.6 NHC Ligands Compared with Phosphine ligands

Phosphine ligands have been extensively studied in chemistry and a number of them are now commonly used in the creation of homogeneous catalysts. Although some NHCs are preferable in areas such as homogenous catalysis and in certain synthetic reactions, there are still a number of phosphines that remain in common use due to them not being as degradable and as such they still retain this one benefit over NHCs. It is possible to alter the electronic and steric properties of phosphines, allowing for catalysts to be optimised depending on the reaction they are needed for. However more often than not it is very difficult to change each property independently, with changes to one characteristic normally resulting in changes to another as well. With NHCs it is easy to synthesise and isolate the free carbene, but the wide commercial availability of phosphines has resulted in there being many applications for them.
Figure 5 gives a brief outline of the different constituents of NHC biscarbenes that can influence the electronic and steric effects of these ligands.\textsuperscript{19} R1 (wingtips) optimises steric properties,\textsuperscript{35} R2 (linker) determines the ring orientation\textsuperscript{36} and R3 (backbone) helps modulate the electronic properties.\textsuperscript{37}

\begin{center}
\includegraphics[width=0.5\textwidth]{figure5.png}
\end{center}

\textbf{Figure 5} Schematic of an NHC bis-carbene showing the constituents that affect the electronics and sterics.\textsuperscript{19}

Currently there is interest in reactions of phosphines that have imidazole groups as their substituents as these are easily obtained through a number of reactions. Figure 6 shows 1-tert-butyl-2-diphenylphosphino-imidazole, which is an example of a phosphine with an attached imidazole substituent.\textsuperscript{38}

\begin{center}
\includegraphics[width=0.3\textwidth]{figure6.png}
\end{center}

\textbf{Figure 6} The structure of 1-tert-butyl-2-diphenylphosphino-imidazole.\textsuperscript{38}

One of the most common synthetic methods used is to react an N-H imidazole derivative with a diorganochlorophosphane in the presence of a base such as triethylamine.\textsuperscript{38} It has been noted that the N-substituent on the imidazole can
influence how the reaction takes place, with the size of the substituent being an important factor. However there still needs to be further studies into this area in order to research its full effects.38

1.7 N-Donor Ligands

N-Donor ligands are used in a number of organic and inorganic syntheses.39 Many examples of these ligands exist; including polypyridyls such as 2,2-bipyridine,40 and ligands such as; 2,2-bipyridimidine, 2,2-bi(imidazole), phenanthroline, and hexaaazatrinaphthalene.39 Polypyridyls tend to be bases and are classed as a number of pyridine rings that are linked, but not fused together; often they are linked via a C-C bond which results in a significant degree of free rotation,40 however the pyridine groups themselves are planar.41 Aromatic ligands such as the ones mentioned, tend to be very stable in both strong acids and bases39 and can often withstand very harsh reaction conditions.42 Ligands such as 2,2-bipyrimidine and 2,2-bi(imidazole) are sometimes referred to as binucleating,43 or biomimetic ligands,44 and they are synthesised via the Ullman coupling reaction.5,45 Scheme 10 shows an example of Ullman synthesis, which is used to create the 2,2-bipyrimidine ligand.39
The Ullman synthesis is often carried out using a copper catalyst and at high temperatures,\textsuperscript{46} nickel is occasionally used but the reaction yields are not as high as when a copper catalyst is utilised.\textsuperscript{39} High temperatures result in the reactions being difficult to control,\textsuperscript{43} and it is often hard to reproduce the reaction yields previously obtained.\textsuperscript{42} Any substituents present on the heterocyclic ring or attached to the nitrogen atoms can also affect the reaction and yields.\textsuperscript{47} Despite the limitations with temperature control, Ullman synthesis can in principle give very high yields of the desired product, hence its use in the synthesis of ligands such a 2,2-bipyrimidine.\textsuperscript{45} The synthesis of 2,2-bipyrimidine is an example of aryl-aryl bond formation, this predominantly happens via Ullman coupling, scheme 11 shows an example of how it is possible to use palladium based complexes as catalysts in homocoupling reactions to form an aryl-aryl bond.\textsuperscript{45}
2,2-bi(imidazole) has many uses in biological processes and a number of reactions are undertaken with copper to produce copper imidazoles that are often demonstrated in a number of proteins.\textsuperscript{48} The imidazole group is also present in a number of amino acids and biological compounds\textsuperscript{49} such as histidine.\textsuperscript{44} Reactions undertaken using bi(imidazole) can often mirror reactions that take place at biological sites such as enzymes.\textsuperscript{44} The general synthesis of 1-substituted imidazoles is shown below in scheme 12,\textsuperscript{49} after the imidazole is obtained it is then possible to use homocoupling or Ullman synthesis to produce the required bi(imidazole).

\begin{scheme}
\chemfig{\textcolor{blue}{\text{N}}(\text{R})\text{H}_2 + \text{\textcolor{red}{'\text{\textcolor{black}{O}}}} + \text{\textcolor{green}{'\text{\textcolor{black}{O}}}} \rightarrow \text{R}\text{\textcolor{blue}{\text{\textcolor{black}{N}}}(\text{'\text{\textcolor{black}{O}}})} \quad \text{35\% Formatedehyde, 25\% NH}_2\text{H}_2\text{O, 70\°C, 5 - 15 hours}}
\end{scheme}

\textbf{Scheme 12} Synthesis of 1-substituted imidazoles.\textsuperscript{49}

Halogen derivatives of N-donor ligands such as pyridines and pyrimidines produce relatively high product yields when they undergo Ullman synthesis.\textsuperscript{45} These derivatives are very useful as intermediates in the synthesis of important compounds.
with biological activity.\textsuperscript{50} The chemistry of chloro-N donor ligands is well known and well documented,\textsuperscript{42} and many reactions have been undertaken using these derivatives. Bromo-N donor ligands however, are very underdeveloped and there has been a lack of investigation into the reactivity or chemistry of these ligands.\textsuperscript{42} Recently, work has been undertaken to develop reactions involving iodo-aryl compounds, and a number of these are now possible to produce using Ullman coupling.\textsuperscript{39}

1.8 Project Proposal

Although there have been a large number of metal-NHC complexes synthesised already, few contain low coordinate iron or cobalt. Iron-NHC chemistry is underdeveloped and needs to be further investigated. It is therefore necessary to extend reactions involving iron and cobalt as well as the range of ligands involved. This thesis will aim to isolate a number of new metal-NHC complexes containing metals such as iron, cobalt and manganese. It is hoped that these will produce interesting new geometries, as well as develop the reactivity of metal-NHC complexes for potential use in catalysis or biochemical reactions.

It is planned to carry out reactions involving 2,2-bipyrimidine, phenanthroline and \( t \)-butylimidazole. An example of the structures of some of these molecules is given in figure 7. These will be reacted with [Fe\{N(SiMe\(_3\))\(_2\}\}\{\mu\text{-}N(SiMe\(_3\))\(_2\}\}\text{\_2}\) and [Co\{N(SiMe\(_3\))\(_2\}\}\{\mu\text{-}N(SiMe\(_3\))\(_2\}\}\text{\_2}\], as well as undertaking reactions with manganocene.
Current work in the Layfield group has involved the reaction of HAN with $[\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2$ to produce a novel metal complex. This project plans to build on the initial reactions carried out, allowing for a deeper understanding of the reactivity of these types of complexes to be developed, as well as investigating how they could potentially be utilised in catalysis or in biochemical studies.

Any resulting metal complexes aim to be reacted with several different alcohols and/or imidazolium chlorides in order to test reactivity and study their potential as reactants in further chemical reactions.

Reactions shall be carried out with phosphorus oxychloride and $t$-butyl imidazole with the aim to synthesise a novel P(V) bridged tripodal NHC. If successful, it is planned to react this resulting complex with $[\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2$ and manganocene, with the view of synthesising a number of new complexes.
New developments in the area of tetrapodal NHC ligands has led to the need to further investigate the reactivity of a number of new ligands such as the ones shown in figure 8.

![Figure 8 Examples of tetrapodal NHC ligands targeted for use in this project.](image)

Reactions are planned to be carried out utilising $[\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2$ and manganocene, in the hope of producing a number of metal complexes.
Chapter 2
Results and Discussion


2.1 Metal Amide Complexes

Metal amide complexes were generated through the addition of the required amount of metal amide to a suspension of the respective ligand in toluene.

The addition of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\) to 2,2-bipyrimidine resulted in the formation of metal complex 2.1 in a yield of 32 % as shown in scheme 13.

![Scheme 13](image)

**Scheme 13** Synthesis of \([(\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\)(bipyrimidine)] (N'' = N(SiMe)_3).

The addition of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\) to 2 equivalents of phenanthroline resulted in the formation of metal complex 2.2 in a yield of 45 % as shown in scheme 14.

![Scheme 14](image)

**Scheme 14** Synthesis of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\)(phenanthroline)] (N'' = N(SiMe)_3).
In both cases upon the addition of [Fe{N(SiMe$_3$)$_2$}$_2$]$_2$ to the corresponding ligand in toluene there was an instantaneous colour change from bright green to black. Black crystals of 2.1 and 2.2 suitable for X-ray diffraction were obtained from saturated toluene solutions after cooling at -30 °C making it possible to obtain solid-state structures for these complexes, these are shown in figure 9 and figure 10.

The molecular structure of 2.1 was determined via X-ray crystallography and features a bimetallic dinuclear structure with two 4 coordinate iron centres in a distorted tetrahedral geometry. The crystallographic data for this complex showed two sets of Fe-N bond lengths. The bonds from the bipyrimidine ligand to the iron centre have bond lengths of 2.2335(17) and 2.2493(17) Å, whilst the bonds from the
iron centre to the N(SiMe₃)₂ groups have bond lengths of 1.9506(17) and 1.9552(17) Å. N-Fe-N angles range from 73.19(6) – 132.89(7)° with the acute angle for this complex being the bite angle at 73.19(6)°.

The metal amide used as a starting material, [Fe{N(SiMe₃)₂}{µ-N(SiMe₃)₂}]₂, is a dimer and exhibits two distinct Fe-N bond lengths. The bonds from the iron centre to the bridging nitrogen atoms have an average bond length of 2.085 Å, the bonds from the iron centre to the terminal nitrogens have an average bond length of 1.925 Å.³³ When these are compared with the bond lengths from the iron centre to the N(SiMe₃)₂ groups in the [(Fe{N(SiMe₃)₂})₂(bipyrimidine)] complex, there has been both an increase and decrease respectively so that both bonds are almost equal with an average length of 1.9529 Å. For the starting material, the N-Fe-N bond angle from the bridging to the terminal nitrogen is 127.7(1)°.³³ In the [(Fe{N(SiMe₃)₂})₂(bipyrimidine)] complex the bond angle has increased to 132.89(7)° the additional space available in this complex has made it possible for the bulky SiMe₃ groups to have moved further apart and reduce the steric repulsion between them.

¹H NMR spectroscopy was also carried out for complex 2.1, showing that the complex is paramagnetic, the NMR spectroscopy data for this complex showed three different proton environments, which was consistent with the structure obtained. The protons present in the N(SiMe₃)₂ groups, resulted in a very broad singlet at 14.10 ppm, the protons attached to the carbon atoms in the rings of the bipyrimidine ligand resulted in broad singlets at 30.20 ppm and 90.77 ppm.
The molecular structure of 2.2 was determined via X-ray crystallography and features an orthorhombic structure with a 4 coordinate iron centre in a distorted tetrahedral geometry. The crystallographic data for this complex shows two sets of Fe-N bond lengths. The bonds from the phenanthroline ligand to the iron centre have bond lengths of 2.190(5) and 2.198(5) Å, whilst the bonds from the iron centre to the N(SiMe$_3$)$_2$ groups have bond lengths of 1.962(5) and 1.954(4) Å. N-Fe-N angles range from 75.64(6) – 130.93(7)$^\circ$ with the acute angle for this complex being the phenanthroline ligand bite angle at 75.64(6)$^\circ$. 

![Figure 10 Molecular structure of [Fe{N(SiMe$_3$)$_2$}(phenanthroline)] (2.2), selected bond lengths (Å) and angles (°). Hydrogen atoms have been removed for clarity. Blue = nitrogen, green = iron, grey = carbon, pink = silicon. Fe(1)-N(1) 2.198(5), Fe(1)-N(2) 2.190(5), Fe(1)-N(3) 1.962(5), Fe(1)-N(4) 1.987(4), Fe(2)-N(5) 2.173(5), Fe(2)-N(6) 2.217(5), Fe(2)-N(7) 1.982(5), Fe(2)-N(8) 1.954(4). N(1)-Fe(1)-N(2) 75.64(18), N(3)-Fe(1)-N(1) 121.33(17), N(3)-Fe(1)-N(2) 99.46(18), N(3)-Fe(1)-N(4) 130.93(17), N(4)-Fe(1)-N(1) 96.78(18), N(4)-Fe(1)-N(2) 120.59(18), N(5)-Fe(2)-N(6) 75.16(18), N(7)-Fe(2)-N(5) 120.83(16), N(7)-Fe(2)-N(6) 95.95(19), N(8)-Fe(2)-N(5) 99.62(17), N(8)-Fe(2)-N(6) 129.77(19).]
[Fe{N(SiMe₃)₂₂}{µ-N(SiMe₃)₂₂}]₂ was utilised as a starting material in this reaction. This complex exists as a dimer, displaying two distinct Fe-N bond lengths. Comparing these with the bond lengths from the iron centres to the N(SiMe₃)₂ groups in the [Fe{N(SiMe₃)₂}_2(phenanthroline)] complex, there has been an increase and decrease in the respective bonds, resulting in the bonds being almost equidistant in length. The asymmetric unit for this crystal contains two identical molecules. The N-Fe-N bond angle from the bridging to the terminal nitrogen for the starting material is 127.7(1)°, in the [(Fe{N(SiMe₃)₂}_2)_2(phenanthroline)] complex the bond angle has increased to 130.93(7)°, implying that the additional space available in this complex has made it possible for the bulky SiMe₃ groups to have moved further apart.

The complex was analysed via ¹H NMR spectroscopy, this indicated that the complex is paramagnetic. The NMR spectroscopy data for complex 2.2 showed four different proton environments present. From the structure obtained six proton environments would be expected, however due to this being a paramagnetic complex it is possible that some environments may overlap or not be present in the spectra. The methyls in the N(SiMe₃)₂ groups resulted in a very broad singlet at 13.01 ppm. The remaining protons were difficult to directly assign to the peaks present in the NMR spectra, but they would correspond to the protons in the phenanthroline ring, these peaks were a broad singlet at 22.06 ppm, a broad singlet at 52.79 ppm and a final broad singlet at -17.84 ppm.
The addition of 1.5 equivalents of $[\text{Fe}\{\text{N(SiMe}_3\}_2\}{\mu-}\text{N(SiMe}_3\}_2\}]_2$ to hexaazatrinapthalene (HAN) resulted in the formation of metal complex 2.3, shown in scheme 15.

Scheme 15 Synthesis of $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_3\text{(HAN)}]$ ($\text{N}'' = \text{N(SiMe}_3\}_2\}$).

As with all previous reactions involving the addition of $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\{\mu-\text{N(SiMe}_3\}_2\}]_2$ to a N-heterocyclic ligand, there was an instantaneous colour change. Concentration of the reaction mixture in vacuo, followed by cooling to -30 °C yielded dark brown/black crystals of 2.3 suitable for X-ray diffraction in a yield of 35 %. The crystallographic and NMR data for this complex had previously been collected by Dr Thomas Pugh of the Layfield group, from his earlier work with the HAN ligand.
The addition of \([\text{Co}\{\text{N(SiMe}_3\}_2\}_2\{\text{bipyrimidine}\}]\) \((N'' = \text{N(SiMe}_3\}_2)\) to a suspension of 2,2-bipyrimidine in toluene (scheme 16) resulted in the formation of the cobalt complex, \textbf{2.4}, which is analogous to the iron based complex \textbf{2.1}. Like the \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\{\mu-\text{N(SiMe}_3\}_2\}]\) reactions there was an instantaneous colour change, which resulted in a dark brown solution. Concentration of the reaction mixture \textit{in vacuo}, followed by cooling to -30 °C yielded dark brown/black crystals of \textbf{2.4} in a yield of 41 %. The solid-state structure was obtained via X-ray crystallography, which is shown in figure 11.
X-ray crystallography was used to determine the molecular structure of complex 2.4. The complex features a bimetallic monoclinic structure containing two 4 coordinate cobalt centres that are arranged in a distorted tetrahedral geometry. The crystallographic data showed that this complex has two sets of Co-N bond lengths. The bond lengths from the ligand to the cobalt centre are 2.166(3) and 2.168(3) Å, whilst the bonds from the cobalt centre to the N(SiMe$_3$)$_2$ groups have bond lengths of 1.937(3) and 1.936(3) Å. N-Co-N angles range from 75.71(11) – 133.60(12)$^\circ$ with the acute angle for this complex being the bite angle at 75.71(12)$^\circ$. This structure is isostructural to the [(Fe{N(SiMe$_3$)$_2$})$_2$(bipyrimidine)] complex, however as expected due to cobalt being smaller in size than iron, the complex displayed shorter metal-nitrogen bond lengths.
[Co\{N(SiMe$_3$)$_2$\}$_2$\{µ-N(SiMe$_3$)$_2$\}]$_2$ also exists as a dimer and like [Fe\{N(SiMe$_3$)$_2$\}$_2$\{µ-N(SiMe$_3$)$_2$\}]$_2$ it too demonstrates two distinct Co-N bond lengths. The length of the bonds from the cobalt centre to the bridging nitrogen atoms averages at 2.086 Å, the bond length from the cobalt centre to the terminal nitrogens averages at 1.916 Å. Comparing these with the bond lengths from the cobalt centre to the N(SiMe$_3$)$_2$ groups in the [(Co\{N(SiMe$_3$)$_2$\})$_2$(bipyrimidine)] complex, the bonds have increased and decreased respectively, till they are almost equal in length, with a mean bond distance of 1.937 Å. For the starting material, the N-Co-N bond angle from the bridging to the terminal nitrogen is 128.8(1)$^\circ$. In the [(Co\{N(SiMe$_3$)$_2$\})$_2$(bipyrimidine)] complex the bond angle has increased to 133.60(7)$^\circ$, due to the additional space available the SiMe$_3$ groups have been able to move further apart which has resulted in a reduction of the steric repulsion between them.

Analysis of this complex, which included $^1$H NMR spectroscopy, showed that the complex was paramagnetic, the data obtained from the NMR spectroscopy presented three different proton environments and this was consistent with the structure obtained. The presence of the protons in the methyls forming the N(SiMe$_3$)$_2$ groups, resulted in a very broad singlet at 5.61ppm, the protons attached to the carbon atoms in the rings of the bipyrimidine ligand resulted in very broad singlets at 40.90 ppm and 72.77 ppm.
The addition of $[\text{Co}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2$ to a suspension of 2 equivalents of phenanthroline in toluene (scheme 17), resulted in the formation of metal complex 2.5. An instantaneous colour change occurred resulting in a dark brown solution, showing similarities between this reaction and the reaction of $[\text{Co}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2$ and 2,2-bipyridine. Concentration of the reaction mixture in vacuo, followed by cooling to -30 °C yielded dark brown/black crystals of 2.5 in a yield of 19 %. The solid-state structure was obtained via X-ray crystallography, which is shown in figure 12.
The molecular structure of 2.5 was determined via X-ray crystallography displaying a monoclinic structure with a 4 coordinate cobalt centre in a distorted tetrahedral geometry. Two sets of Co-N bond lengths were apparent from the results of the crystallographic data. The bonds from the phenanthroline ligand to the cobalt centre have lengths of 2.108(3) and 2.142(3) Å, whilst the length of the bonds from the cobalt centre to the N(SiMe₃)₂ groups are 1.957(3) and 1.966(3) Å. N-Co-N angles range from 78.41(13) – 127.40(12)° with the angle of 78.41(13)° being the acute angle for this complex as well as the bite angle. This structure is isostructural to the [(Fe{N(SiMe₃)₂})₂(phenanthroline)] complex, but as cobalt is smaller than
iron shorter metal-carbon bond lengths were displayed. The asymmetric unit for this crystal contains two identical molecules.

Comparison of the bond lengths of the starting material and the bond lengths of the complex shows that the bonds from the cobalt centre to the N(SiMe$_3$)$_2$ groups have increased and decreased respectively resulting in bonds that are almost equal, with a length of 1.962 Å. For the starting material, the N-Co-N bond angle from the bridging to the terminal nitrogen is 128.8(1)$^\circ$. In the [(Co{N(SiMe$_3$)$_2$)$_2$(phenanthroline)}] complex the bond angle has decreased to 127.40(7)$^\circ$.

The results of $^1$H NMR spectroscopy carried out on this complex showed that it is paramagnetic as well as displaying four different proton environments. The structure obtained crystallographically exhibited 6 proton environments, as this complex is paramagnetic it would be expected that some environments may overlap or not be present in the spectra. The methyl groups bound to the silicon atoms in the N(SiMe$_3$)$_2$ groups resulted in a very broad singlet at 10.02 ppm, the remaining protons were difficult to directly assign due to the paramagnetic nature of the complex, broad singlets are present at 40.88 ppm, 57.99 ppm and -22.14 ppm and these are most likely to correspond to the protons present on the phenanthroline ligand.
2.2 Metal Amide Complexes and Reactions with Alcohols

The complexes which had been synthesised through the reaction between the required amount of \([\text{Fe}\{\text{N(SiMe}_3\}_2}\{\mu-\text{N(SiMe}_3\}_2]\}_2\) or \([\text{Co}\{\text{N(SiMe}_3\}_2}\{\mu-\text{N(SiMe}_3\}_2]\}_2\) and the respective ligands (2.1, 2.2, 2.3, and 2.4) were utilised as starting materials in reactions with the following alcohols; 1,3-benzenediol (2.6), 1,2-dihydroxy benzene (2.8), and 2,7-dihydroxynaphthalene (2.9).

It was hoped that through these reactions, it would be possible to form a chain of metal complexes linked via alcohol bridges; a suggested structure for this can be seen in 2.7. Eventually these reactions may have the potential of being able to link multiple metal complexes together.

2 equivalents of \([\text{Fe}\{\text{N(SiMe}_3\}_2}\}_{2}\text{(bipyrimidine)}] \text{ (2.1)}\) was added to a suspension of 1,3-benzenediol (2.6). The reaction was attempted a number of times using diethyl ether, THF and toluene as solvents (scheme 18). These reactions were firstly carried out through stirring at room temperature overnight, repeat reactions involving THF and toluene were also heated to reflux. Initial observations of the reactions suggested that the 1,3-benzenediol did not dissolve in diethyl ether or THF, however in the set of reactions where toluene was used after a number of hours stirring all 1,3-benzenediol dissolved.
Overnight stirring resulted in slightly cloudy mixtures; no obvious colour changes were observed throughout the course of the reactions, with the solutions remaining dark brown/black in colour. The volumes of each reaction were reduced in vacuo and subsequently cooled to -30  °C. After a number of days at this temperature no crystals had formed, the volumes were further reduced and this resulted in the formation of a solid precipitate overnight.

For the reaction involving THF overnight stirring resulted in the formation of a solid precipitate, which was insoluble in all solvents tried including toluene, DCM and diethyl ether. The filtrate that had been removed from the solid was also reduced and placed into the freezer, however no crystals or solid precipitate formed after the solution had been cooled at -30  °C for over a week. The repeat reaction was refluxed at 70  °C. After several hours it was possible to see the formation of a solid precipitate, which suggested that heating to reflux was speeding up the reaction. A number of solubility tests were carried out on this solid and it was found to be insoluble in toluene, DCM and diethyl ether. The filtrate that had been removed was

---

**Scheme 18** Synthetic procedure for the reaction between \([(\text{Fe}(\text{N(SiMe}_3)_2)_2)(\text{bipyrimidine}))\] and 1,3-benzenediol, including the proposed structure for the product of this reaction. (N'' = N(SiMe)_3).
concentrated and cooled to -30 °C, however no crystals or solid precipitate formed after the solution had been left for over a week.

The reaction that utilised toluene as a solvent was heated to reflux at 110°C overnight, this resulted in the formation of a solid precipitate. Numerous solubility tests were carried out on this solid and as with previous reactions it was found to be very insoluble in THF, DCM and diethyl ether. The filtrate was concentrated in vacuo and cooled to -30 °C; however no crystals or solid precipitate formed.

The ineffectiveness of any of these solvents in producing a product that could be easily recrystallised, or soluble enough to carry out any analysis, meant that work with metal complexes 2.2, 2.3, 2.4 and 2.5 was not continued. Instead all efforts were focused on trying to find successful reactions between metal complex 2.1 and the stated alcohols.

Problems with the reactions previously tried resulted in it being necessary to use an alternative alcohol in place of 1,3-benzenediol. Due to its similar molecular structure 1,2-dihydroxy benzene (2.8) was used instead (scheme 19).

![Scheme 19](image)

**Scheme 19** Synthetic procedure for the reaction between [(Fe\{N(SiMe\_3)\_2\})\_2(bipyrimidine)] and 1,2-dihydroxy benzene, including the proposed structure for the product of this reaction. (N" = N(SiMe\_3)\_2).
The close proximity of the alcohol groups (being situated on the 1- and 2-positions of the benzene ring) meant that the formation of a chain of metal amide complexes was unlikely. Instead the alcohol should be able to substitute in place of the amide groups, as shown in 2.9. The reaction was attempted in both THF and toluene; the reaction with THF as a solvent was stirred overnight at room temperature, whilst the reaction with toluene was stirred with overnight refluxing.

For the reaction utilising THF as a solvent, 1,2-dihydroxy benzene showed good solubility. Initial observations concluded that no precipitate had formed and overnight stirring resulted in a cloudy mixture with no obvious colour change. Again the problem seemed to be the production of a very poorly soluble product that crashed out of solution during the course of the reaction. A number of attempts were made to recrystallise the solid, but these have so far been unsuccessful and further investigations need to be carried out. The filtrate removed from the solid was concentrated in vacuo and cooled to -30 °C. After several days a powdery solid precipitate had formed but this was unable to be analysed crystallographically.

1,2-dihydroxy benzene was found to be not particularly soluble in toluene. After several hours of refluxing a solid precipitate had started to form, which continued to precipitate out overnight. As before it was necessary to carry out a number of solubility tests and this solid was found to be insoluble in THF, DCM and diethyl ether. The filtrate that had been removed from the solid was also reduced in vacuo and cooled to -30 °C, this resulted in a further amount of powdery solid forming, which again had solubility issues.
Problems with solubility in the reaction between \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(bpyrimidine)}]\) and 1,2-dihydroxy benzene (scheme 19), resulted in it being necessary to try an alternative alcohol. 2,7-dihydroxynaphthalene \((2.9)\) was used (scheme 20) as a substitute. The larger distance between both alcohol groups in theory should make the formation of metal complex chains easier, the lack of steric hindrance should mean that it would be possible to use these alcohols as ‘linkers’ between two or more metal complexes, a structure for such a complex being proposed in \(2.10\).

The reactions using 2,7-dihydroxynaphthalene were treated in the same way as the other alcohol reactions mentioned in this section. Both THF and toluene were used as solvents, with both reactions being heated to reflux overnight. 2,7-dihydroxynaphthalene was insoluble in THF and toluene. Addition of the required amount of \([\text{Fe}\{\text{N(SiMe}_3\}_3\}_2\text{(bpyrimidine)}]\) appeared to cause a reaction to form a more soluble product. Heating the reactions at reflux overnight resulted in the
formation of a solid precipitate. Investigations into the solubility of these solids proved inconclusive; solvents tried included toluene, THF, DCM and diethyl ether. Both filtrates from the THF and toluene reactions were concentrated and cooled to -30 ºC, producing a powdery solid.

Time restraints meant that it was necessary to side-line any further research into the reactions between metal complexes and alcohols and instead focus on a different area of research. It was thought that these reactions would result in the formation of polymetallic systems, which would be very insoluble. As a number of the reactions attempted resulted in insoluble products it is possible to argue that a polymetallic system had been formed. The inconclusive results that have been obtained so far mean it is necessary for this area of research to be revisited and studied in more depth, ideally full characterisation would need to be carried out on all products that were obtained, however solubility issues may make it difficult to obtain NMR spectroscopy data.

2.3 Metal Amide Complexes and Reactions with Imidazolium Chlorides

After reacting the required amount of metal complex (2.1, 2.2, 2.3, 2.4 and 2.5) with the respective alcohol. It was decided to conduct a series of reactions with imidazolium chlorides; reactions were carried out using 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr.HCl), 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (IMes.HCl), and 1,3-di-tert-butylimidazolium chloride (ItBu.HCl), (2.10, 2.11 and 2.12). The required amount of
metal complex was added drop wise to the respective imidazolium chloride in toluene.

Previous work in the Layfield group\textsuperscript{52} involving the reaction between $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]$ and IPr.HCl set a precedence for the work undertaken with this set of reactions. The addition of 3 equivalents of IPr.HCl to $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]$ resulted in the following crystal structure shown in figure 13 (2.13). This positive result set the foundation for the investigations into the reactions between $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]$ and a number of other imidazolium chlorides, as well as investigation into how metal complexes synthesised in this project would react.

**Figure 13** Molecular structure produced from the reaction of $[\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]$ and IPr.HCl, structure (2.13).\textsuperscript{52}
The structure obtained from this reaction was quite a surprise; it was initially thought that all three imidazoles would substitute in place of the amide groups, as suggested in 2.17. However, the observed solid-state structure clearly shows that only two imidazole chlorides were able to substitute onto the metal complex. Closer study of the structure appears to suggest that sterics is a major issue. The large bulk of the IPr.HCl ligand means that space for a third IPr.HCl to substitute onto the complex was limited as currently shown in figure 13; the two imidazolium chlorides have arranged themselves above and below the metal complex. When studying the structure it is clear to see that the majority of free space is taken up by these two ligands, and substitution of a third ligand would not have been possible given the space available.

Previous reactions involved the addition of [(Fe\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}(bipyrimidine)] to the respective alcohol in toluene. This set of reactions focused on reacting [(Fe\{N(SiMe\textsubscript{3})\textsubscript{2}\}\textsubscript{2}(hexaazatrinaphthalene)] (2.3) with the required imidazolium chloride, this metal complex has very good solubility in toluene and it was hoped that this would enable a number of successful reactions with imidazolium chlorides to take place.
The first reaction attempted was the addition of the required amount of 
$[(\text{Fe} \{\text{N(SiMe}_3\}_2\}_2\text{HAN})]$ to 3 equivalents of a suspension of ItBu.HCl, (2.12) in 
toluene (scheme 21).

![Scheme 21](image)

Scheme 21  Synthetic procedure for the reaction between $[(\text{Fe} \{\text{N(SiMe}_3\}_2\}_2\text{HAN})]$ and $\text{t}$-butylimidazole chloride. ($N'' = \text{N(SiMe}_3\}_2$).

Drop wise addition of $[(\text{Fe} \{\text{N(SiMe}_3\}_2\}_2\text{HAN})]$ resulted in no initial colour 
change, and none was observed throughout the course of the reaction with the 
solution remaining dark brown in colour. The reaction was filtered, concentrated in 
vacuo before being cooled to -30 °C, yielding brown crystals which were able to be 
analysed via X-ray crystallography giving a solid state structure of the complex, as 
shown in figure 14 (2.15).
What was most surprising about this structure was the fact that it appeared that \([(\text{Fe}\{\text{N}({\text{SiMe}}_3)_2\}_2\text{HAN})]\) had dissociated, as none of the HAN ligand was present in the obtained structure. Instead it appears that a reaction occurred between the \([\text{Fe}\{\text{N}({\text{SiMe}}_3)_2\} \{\mu\text{-N}({\text{SiMe}}_3)_2\}]_2\) and the imidazolium chloride; how this occurred it is not yet possible to say. There are yet to be any NMR spectroscopy or elemental analysis studies of this reaction and a repeat of it is necessary in order to obtain this data.
Investigations into this reaction were carried out using an alternative imidazolium chloride, IMes.HCl (2.11) was chosen and 3 equivalents were used in this reaction (scheme 22), a potential product is suggested in 2.16.

![Scheme 22](image)

**Scheme 22** Synthetic procedure for the reaction between [(Fe{N(SiMe$_3$)$_2$})$_3$(HAN)] and IMes.HCl. (N" = N(SiMe$_3$)$_2$).

All previous reaction conditions were kept the same in order to ensure continuity. It was therefore necessary to continue with the drop wise addition of [(Fe{N(SiMe$_3$)$_2$})$_3$(HAN)] to the suspension of the imidazolium chloride in toluene. This resulted in no significant colour change, and the reaction mixture remained a dark brown colour. Unlike the reaction with ItBu.HCl, after stirring the reaction mixture for 2 – 3 hours no solid precipitate had formed. This was taken as a positive sign and suggested that if any reaction had taken place, the product had remained in solution and would hopefully recrystallise. The reaction was filtered, which resulted in a small amount of dark precipitate that was assumed to be unreacted starting material. The volume of the filtrate was reduced and cooled to -30 °C, after being left for several days no crystals had formed, after approximately a week a small
amount of powdery solid was present but this was unable to be used in crystallographic studies.

It was necessary to repeat the reaction that had been tried with \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]\) and 3 equivalents of IPr.HCl, (2.10) (scheme 23) in order to obtain full characterisation of the original product formed in figure 13 (2.13).

\[
\begin{align*}
\text{2.3} & + \text{3 H}^+ \rightarrow \text{2.17}
\end{align*}
\]

**Scheme 23** Synthetic procedure for the reaction between \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]\) and IPr.HCl \((\text{N}'' = \text{N(SiMe}_3\}_2)\).

Like the reactions involving both IMes.HCl and ItBu.HCl it was necessary to ensure that reaction conditions were kept the same. Again it was required to add \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]\) drop wise to the suspension of the imidazolium chloride in toluene. Throughout the course of the reaction no colour change was observed and as with the previous reaction involving ItBu.HCl no solid precipitate was formed. It was hoped that any product produced would have remained in solution, resulting in crystals that could potentially provide a solid-state structure. The reaction was filtered, concentrated *in vacuo* before being cooled to -30 °C, but after several days
no crystals had formed and a repeat of this reaction is needed to obtain the necessary data for characterisation.

Building on the previous success of the reaction between \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{HAN}\}]\) and 3 equivalents of IPr.HCl, it was decided to expand the investigation to include reactions with \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{bipyrimidine}\}]\) and \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{phenanthroline}\}]\). It was postulated that the \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{phenanthroline}\}]\) complex, which is comparable to \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_3\text{HAN}\}]\), would react in a similar way and produce equivalent results to either of the two crystal structures already obtained.

It was attempted to react \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{phenanthroline}\}]\) with one equivalent of IPr.HCl (the reaction working on the principle of one imidazolium chloride per iron centre) with toluene being used as a solvent (scheme 24), a product for this reaction is suggested in 2.18.

![Scheme 24](image_url)

Scheme 24 Synthetic procedure for the reaction between \([\text{Fe}\{\text{N(SiMe}_3\}_2\text{)}_2\text{phenanthroline}\}]\) and IPr.HCl (\(N^\equiv = \text{N(SiMe}_3\}_2\)).
Drop wise addition of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2(\text{phenanthroline})]\) to the suspension of the \(\text{IPr.HCl}\) in toluene was carried out in the same manner as all previous reactions involving imidazolium chlorides. This led to no significant colour change, and the reaction mixture remained dark green in colour, all of the imidazolium chloride appeared to have dissolved into solution during the course of the reaction. After the reaction had been left stirring for 2 – 3 hours there was still no colour change. No precipitate had formed either suggesting that any product had remained in solution. This was very promising as it appeared that the reaction had followed the same course as the \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_3(\text{HAN})]\) complex. The same work up that was followed in the \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_3(\text{HAN})]\) reactions was followed, and cooling to -30 °C produced no crystals or solid precipitate.

Another set of reactions was also attempted, this time looking into how \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2(\text{bipyrimidine})]\) would react with both \(\text{IPr.HCl}\) and \(\text{IMes.HCl}\) (scheme 25 and scheme 26), products for these reactions are suggested in 2.19 and 2.20.

\[
\text{Scheme 25} \text{ Synthetic procedure for the reaction between } [\text{Fe}\{\text{N(SiMe}_3\}_2\}_2(\text{bipyrimidine})] \text{ and IPr.HCl. (N'' = N(SiMe}_3\}_2).}
\]
These reactions were carried out in the same way as all previous reactions involving imidazolium chlorides and the synthesised metal complexes. Initial observations of these reactions suggested that the imidazolium chloride had reacted to form a more soluble product in solution, but after a number of attempts at recrystallisation no solid precipitate or crystals had formed.

Time restraints meant that it was necessary too sideline any further investigations into the reactions between metal complexes and imidazolium chlorides and instead focus on a different area of research. The initial successes with the \([\text{[(Fe\{N(SiMe_3)_2\}_2)_2(bpyrimidine)]]} + 3 \text{ equivalents of IMes.HCl}}\) reaction, mean that this is an area of research that requires a lot more in depth study in order to work out the nature of the reaction that is happening.

### 2.4 Tetrapodal Ligands – Preparation and Reactions

Recent developments with tetrapodal ligands, including the recent synthesis of a silver carbene cage, has led to the need to further study these ligands and develop reactions involving transition metals such as iron, cobalt and manganese.
The tetrapodal ligand (2.21) used in these reactions was synthesised according to a literature procedure\(^{20}\) and reacted with 2 equivalents of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\) (scheme 27), a structure for the product of this reaction is suggested in 2.22.

![Scheme 27 Synthetic procedure for the reaction between a tetrapodal ligand and \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\) including the proposed structure for the product of this reaction. (N'' = N(SiMe)_3).](image)

Solubility issues with this reaction were apparent from the start as the tetrapodal ligand used (2.21) was insoluble in all solvents tried. It was hoped that through choosing a suitable solvent that dissolves \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\) the resulting product of this reaction would be soluble enough to remain in solution. THF was tried as a solvent due to it being able to dissolve \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\). Most of the solid appeared to dissolve and the reaction displayed a colour change from green to dark brown. From previous work carried out in the group on reactions involving a similar ligand and \([\text{Fe}\{\text{N(SiMe}_3\}_2\}\{\mu-\text{N(SiMe}_3\}_2\}]_2\), the reaction was initially stirred at -78 °C, before being allowed to slowly heat up to room temperature, this was preferably carried out overnight. The initial low temperature suggested that on addition of the reactants, the reaction was not instantaneous and it was only through the slow rise in temperature that a reaction was able to take place. Overnight stirring produced a brown precipitate, this was unable to be dissolved in THF, toluene or acetonitrile and therefore recrystallisation...
was not possible. NMR spectroscopy in benzene-$d_6$ was attempted, but has so far been unsuccessful due to solubility issues.

The reaction was repeated using the same reaction conditions and solvents, but this time 4 equivalents of manganocene were reacted (scheme 28), a product for this reaction is suggested in 2.23.

![Scheme 28](image)

**Scheme 28** Synthetic procedure for the reaction between a tetrapodal ligand and manganocene, including the proposed structure for the product of this reaction. ($\text{Cp} = \text{C}_5\text{H}_5$)

The reaction in toluene appeared to be unsuccessful as no dissolution of the reactants appeared to take place, and both reactants exhibited poor solubility in toluene. Switching the solvent to THF proved to be much more effective for the reaction. Manganocene was successfully dissolved in THF and the required amount of this reactant was added to a suspension of tetrapodal ligand in THF. The mixture was stirred at -78 °C and left to rise slowly to room temperature overnight. The solid tetrapodal ligand appeared to react to form a more soluble product as the temperature rose with most solid appearing to remain in solution. The solution was filtered to remove any unreacted starting material; the filtrate was concentrated *in vacuo* and cooled to -30 °C, after leaving over the weekend no crystals had formed. The solvent was removed, and the resultant solid was dissolved toluene. The solution was further
concentrated, but after cooling to -30 °C this still proved unsuccessful in providing a set of crystals for solid-state analysis. The solvent was therefore removed and the resultant solid was analysed via NMR spectroscopy. NMR spectroscopy in benzene-

\( d_6 \) was attempted, but has so far been unsuccessful.

The tetrapodal ligand (2.21) used in these reactions was synthesised according to a literature procedure\(^\text{20}\) and reacted with 2 equivalents of \([\text{Fe}\{\text{N(SiMe}_3\text{)}_2\}\{\mu-\text{N(SiMe}_3\text{)}_2\}\}_2\) (scheme 29).

![Scheme 29 Synthetic procedure for the reaction between a tetrapodal ligand and \([\text{Fe}\{\text{N(SiMe}_3\text{)}_2\}\{\mu-\text{N(SiMe}_3\text{)}_2\}\}_2\), including the proposed structure for the product of this reaction. \( \text{N}'' = \text{N(SiMe}_3\text{)}_2 \).](image)

Previous reactions where THF and toluene had been used as a solvent had produced a solid, which proved to be insoluble, making both crystallisation and analysis extremely difficult. It was decided to try bromobenzene as a solvent, it was hoped that its high refluxing temperature, would enable a more soluble product or crystals to potentially form as the reaction cooled down after reflux. Initial addition of the \([\text{Fe}\{\text{N(SiMe}_3\text{)}_2\}\{\mu-\text{N(SiMe}_3\text{)}_2\}\}_2\) to a suspension of the tetrapodal ligand suggested that no reaction took place, on heating the reaction to 160 °C there was a slow colour change from green to dark brown, and most of the solid tetrapodal ligand appeared to react to form a more soluble product. The reaction was refluxed
overnight resulting in a brown/black solid. Solubility tests concluded that this solid would not dissolve in THF, toluene or acetonitrile; therefore it was not possible to obtain a solid-state structure of this product. NMR spectroscopy in benzene-$d_6$ has been attempted but has so far been unsuccessful due to the product not dissolving.

2.5 P(V) Bridged N-Heterocyclic Carbenes

There are a number of examples in literature of tripodal complexes and tripodal NHCs. Aside from working with metal complexes the other area of this project was to focus on the synthesis of a new P(V) bridged tripodal NHC complex. This was to be carried out through the reaction of phosphorus oxychloride (POCl$_3$) (2.24), and $t$-butylimidazole (2.25). Due to the novel nature of this reaction it was necessary to try a number of different synthetic routes in order to produce the desired compound, such as utilising a number of different solvents and reaction conditions in order to create the optimised synthetic route.
The first reaction attempted (scheme 30), was the drop wise addition of POCl$_3$ to a solution of 3 equivalents of $t$-butylimidazole, which had been dissolved in THF.

![Scheme 30](image)

**Scheme 30** Synthetic procedure for the reaction between POCl$_3$ and $t$-butylimidazole.

Initial addition of POCl$_3$ resulted in the formation of a white/yellow precipitate, which quickly dissolved back into solution on stirring. The reaction was refluxed at 70 °C for 2 - 3 hours resulting in the formation of a light yellow solid, which was dried and washed with hexane. One of the main concerns with this synthesis was ensuring that the reaction conditions were adequate enough to cause all three of the chlorides to be replaced with the $t$-butylimidazole ligands, with the aim of producing the desired product shown in **2.26**. With $^{13}$C and $^1$H NMR spectroscopy not being suitable to assign the number of $t$-butylimidazole ligands present in the complex, it was necessary to rely predominantly on $^{31}$P NMR spectroscopy and mass spectrometry analysis. For the reaction shown in scheme 30, $^{31}$P NMR spectroscopy showed two peaks in the -25.00 ppm region, showing the presence of a P(V) bridged NHC complex, the two peaks suggest that two products had formed and the reaction had not gone to completion, possible products are suggested in figure 15 as compounds **2.27** and **2.28** (see experimental section for details).
In order to try and drive the reaction to completion it was necessary to increase the reaction time. 2 - 3 hours had proved to be an insufficient amount of time, and the reaction was therefore heated at reflux for approximately 4 – 6 hours. The solvent was also changed to ethyl acetate due to an unsuccessful reaction involving THF. The reaction (scheme 31) again produced a white/yellow precipitate, which formed after a number of hours of stirring. Analysis of this solid using $^{31}$P NMR spectroscopy again suggested that two P(V) compounds had formed and further refinement of the synthetic method was needed.

**Figure 15** Possible products for the reaction between POCl$_3$ and $t$-butylimidazole in THF (scheme 30).

Due to the previous unsuccessful reactions, it was necessary to look through the literature to try and see if there had been any precedent for the formation of P(V)
bridged carbenes. Previous reactions involving PCl₃ and quinuclidine³¹ show that it is possible to form these types of compounds. The aforementioned reaction used trimethylsilyl trifluoromethane sulfate (TMSOTf) this would hopefully form trimethylsilyl chloride (TMSCl) and stop any reaction between the chloride counter ions and the P(V) bridged NHC complex. TMSCl is also volatile so would be easily removed in vacuo to leave the pure compound. Like previous reactions, POCl₃ and t-butylimidazole were first stirred together in ethyl acetate. After approximately 15 minutes, TMSOTf was slowly added drop wise with continuous stirring; the reaction (scheme 32) was refluxed at 80 °C and left for a minimum of 24 hours, as suggested by the literature.⁵³

![Scheme 32](image)

**Scheme 32** Synthetic procedure for the reaction between POCl₃ and t-butylimidazole.

Overnight refluxing resulted in the formation of a solid, which appeared to be dark brown in colour, the reaction mixture was filtered and the remaining solid was dried under reduced pressure to ensure that all TMSCl had been removed.¹H and ¹³C NMR spectroscopy showed all the peaks required for the t-butylimidazole groups.³¹P NMR spectroscopy, showed a peak at -0.01 ppm, which was not in the correct region for a P(V) bridged NHC, this suggested that the reaction had been unsuccessful and that none of the desired product had been formed in this reaction.
Further investigations into literature resulted in the discovery of a much more recent paper\textsuperscript{54} which also used TMSOTf in the reaction of a P(V) tripodal ligand complex, as well as undertaking a second reflux of the reaction in diethyl ether. Adapting this synthesis (scheme 33), \(t\)-butylimidazole was first dissolved in toluene before POCl\(_3\) was added drop wise to the stirring mixture. This mixture was left for around 15 minutes after which TMSOTf was slowly added drop wise; this formed a small amount of precipitate on the initial addition that quickly dissolved back into solution as the reaction mixture was stirred. After complete addition had taken place, the reaction was refluxed at 110 °C and following the precedence set in literature, was left refluxing at this temperature overnight.

![Scheme 33](image.png)

**Scheme 33** Synthetic procedure for the reaction between POCl\(_3\) and \(t\)-butylimidazole.

Overnight refluxing resulted in the formation of a light yellow solid, toluene was removed via cannula filtration and the solid was left to dry under reduced pressure for several hours. As stated in the literature the reaction was then refluxed in diethyl ether for 1 – 2 hours at 35 °C, the diethyl ether was removed via cannula filtration and again the solid was dried. Recrystallisation was attempted at -30 °C using dichloromethane (DCM) which resulted in the formation of pale yellow crystals. A number of attempts to obtain a solid-state structure were carried out. However, it appeared that there was solvent locked into the crystal lattice, as the
crystals desolvated before they could be analysed via X-ray crystallography. As the solvent was removed *in vacuo* the crystals formed desolvated into a microcrystalline powder, which was used for elemental analysis and to collect NMR spectroscopy data. $^1$H and $^{13}$C NMR spectroscopy exhibited all the peaks necessary to show the presence of the $t$-butylimidazole ligand. $^{31}$P NMR spectroscopy showed one peak in the -25.00 ppm region which suggested the presence of a P(V) compound, the existence of only one peak was also very promising as it showed that only one compound had been formed from this reaction. $^{19}$F NMR spectroscopy was also utilised, and this displayed one peak at around -78.00 ppm suggesting that the triflate counter ion was present in the compound as expected. Elemental analysis further confirmed that the correct compound had formed as all CHN data that was calculated matched the results that had been obtained, (see experimental section for data). Despite the absence of a solid-state structure, the analytical data obtained suggested that the desired complex had been formed, and that the reaction was successful.

After the successful synthesis of a P(V) bridged tripodal NHC, it was necessary to carry out reactions with this product to further test reactivity, with the potential to form a number of new complexes. A reaction was attempted between the complex and 1.5 equivalents of manganocene in THF as shown in scheme 34.
Scheme 34 Synthetic procedure for the reaction between a tripodal P(V) bridged NHC and managanocene.

The required amount of P(V) tripodal NHC in THF was added drop wise to a solution of managanocene in THF, the reaction mixture was stirred, before being heated to reflux and left overnight. After overnight heating the reaction mixture was filtered, the volume reduced in vacuo before being cooled to -30 °C. After leaving at this temperature overnight, this resulted in the formation of brown/orange crystals of complex 2.30. These were analysed via X-ray crystallography, giving a solid-state structure for the product of this reaction as shown in figure 16. The structure obtained was quite surprising as it did not contain any phosphorus, but instead was a manganese complex of THF, the t-butylimidazole ligands and the triflate counter ions. The formation of this product would suggest that the previously synthesised P(V) bridged NHC is unstable and had decomposed throughout the duration of the reaction.
The molecular structure of 2.30 was determined via X-ray crystallography and features an orthorhombic structure with a 6 coordinate manganese centre in an octahedral geometry. The Mn-N bonds were equidistant at 2.183(2) Å. Mn-O bond lengths range from 2.1750(18) – 2.2164(18) Å. The N-Mn-N bond angle for this
complex is 180.00(10)°, the O-Mn-O bond angles range from 86.38(8) – 180.00(8)° and the O-Mn-N bond angles range from 89.10(3) – 90.90(8). Each set of ligands is *trans*- to each other along their respective bonds.

**2.6 Conclusion and Future Work**

The synthesis of [Fe{N(SiMe$_3$)$_2$}$_2$]{µ-N(SiMe$_3$)$_2$}] complexes, 2.1 and 2.2 was completed and the structures were confirmed via X-ray crystallography, as well as via elemental analysis and NMR spectroscopy data. The [Co{N(SiMe$_3$)$_2$}$_2$]{µ-N(SiMe$_3$)$_2$}]$_2$ versions of the 2,2-bipyrimidine and phenanthroline complexes, 2.4 and 2.5, were also synthesised and these were successfully confirmed via X-ray crystallography, elemental analysis and NMR spectroscopy. The reaction between [Co{N(SiMe$_3$)$_2$}$_2$]{µ-N(SiMe$_3$)$_2$}]$_2$ and 2,2-bipyrimidine needs to be repeated in order to obtain data for elemental analysis. Successful reactions of [(Fe{N(SiMe$_3$)$_2$})$_3$(HAN)] with IPr.HCl or ItBu.HCl produced two structures (2.13 and 2.15) that have both been confirmed via crystallography. The synthesis of a P(V) bridged tripodal NHC (2.29), was completed and the structure was successfully confirmed via $^{13}$C, $^1$H and $^{31}$P NMR spectroscopy, as well as by elemental analysis. Successful reactions between 2.29 and manganocene successfully produced a novel manganese complex (2.30) the structure of which has been confirmed via X-ray crystallography, $^1$H NMR spectroscopy and elemental analysis.

For the reactions between metal amide complexes and alcohols, the reactions need to be repeated and further investigations into the reaction conditions need to be carried out to optimise this set of reactions. Solubility of the products proved to be a
serious problem, and further investigations need to be carried out in order to obtain proper analysis of the compounds. Ideally, investigations into forming crystals need to be carried out, as a solid state structure from these reactions would be very useful in determining what happens throughout the course of the reaction.

For the reactions between metal amide complexes and imidazolium chlorides, the reactions between [(Fe{N(SiMe$_3$)$_2$)$_2$}(HAN)] and IPr.HCl needs to be repeated in order for further characterisation, such as NMR spectroscopy and elemental analysis to be obtained. With regards to [(Fe{N(SiMe$_3$)$_2$)$_2$}(HAN)] and IMes.HCl, a solid was formed but time restraints led to this not being able to be characterised, this therefore needs to be worked up and further investigated. With reference to the iron and cobalt complexes synthesised, selected reactions were carried out between both [Fe{N(SiMe$_3$)$_2$}$_2$(bipyrimidine)] and [Fe{N(SiMe$_3$)$_2$}$_2$(phenanthroline)] and selected imidazolium chlorides. Further work needs to be carried out with the cobalt versions of these two complexes as time restraints resulted in no reactions being attempted.

For the reactions between tetrapodal ligands and both [Fe{N(SiMe$_3$)$_2$}$_2$]$_2$ and manganocene, the products obtained from the two successful reactions need to be characterised via NMR spectroscopy, elemental analysis and X-ray crystallography. Solubility issues need to be overcome in order to carry out the required analysis; previous tests have shown the products to be very insoluble in a number of solvents, making characterisation extremely difficult.
With regards to the synthesis of the P(V) bridged tripodal NHC complex, further work involves the need to attempt to find a suitable solvent or solvent system that could be used to grow crystals and obtain a solid state structure.
Chapter 3

Experimental Section
3.1 General Considerations

All syntheses for this project were carried out under conventional Schlenk techniques using a nitrogen line. Air sensitive chemistry was carried out in a glove box before being transferred to the Schlenk line. All solvents used were either refluxed over molten potassium (toluene and THF), calcium hydride (DCM) or NaK, a sodium potassium alloy, (hexane and Et₂O) and then degassed. 2,2-bipyrimidine,⁴² t-butylimidazole,⁴⁴ hexaazatriphenylene,⁵⁵ [Fe{N(SiMe₃)₂} {µ-N(SiMe₃)₂}]₂,⁵⁶ and [Co{N(SiMe₃)₂} {µ-N(SiMe₃)₂}]₂⁵⁷ were prepared according to literature procedures, all other reagents and solvents were used as purchased unless otherwise stated in the experimental method. All temperatures that have been quoted for heating sources are given in degrees celsius. NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer or a Bruker Ultrashield AVANCE III 400 MHz spectrometer for ¹H, ¹³C, ³¹P and ¹⁹F. Elemental Analysis was carried out on a Thermo Scientific (Carlo-Erba) Flash 2000 Elemental Analyser, which had been configured for %CHN, at the London Metropolitan University. It should be noted that due to the air sensitive nature of these compounds it is possible that decomposition may have occurred whilst in transit. Crystallographic studies were carried out on Agilent Technologies SuperNova, Single source at offset diffractometer.
3.2 Preparacion de Complejos de Amida de Metal

**Synthesis of FeBr$_2$(THF).** This was prepared according to a literature procedure.$^{58}$ FeBr$_2$ (15 g, 69.5 mmol) was extracted in THF via soxhlet extraction under an inert atmosphere; this was carried out for approximately 12 hours. After cooling, the solid was filtered, washed with Et$_2$O and dried *in vacuo*. (17.5 g, 48.6 mmol, 70 %)

**Synthesis of [Fe{N(SiMe$_3$)$_2$},µ-N(SiMe$_3$)$_2$]$_2$.** This was prepared according to a literature procedure.$^{56}$ [FeBr$_2$(THF)] (10 g, 27.7 mmol) was suspended in Et$_2$O. LiN(SiMe$_3$)$_2$ (12.5 g, 74.7 mmol) was also suspended in Et$_2$O. The suspension of LiN(SiMe$_3$)$_2$ was added drop wise to the suspension of FeBr$_2$(THF), the mixture was stirred for approximately 12 hours at 0 °C. Et$_2$O was removed *in vacuo* and the remaining solid was extracted using pentane. The solution was filtered and the filtrate was dried *in vacuo*. The remaining oil was distilled to leave a green liquid. (3.01 g, 7.99 mmol, 29 %)

**Synthesis of 2,2-Bipyrimidine.** This was carried out according to a literature procedure.$^{42}$ Triphenylphosphine (6.9 g, 26.0 mmol), nickel(II) chloride (1.5 g, 12.0 mmol) and zinc powder (0.86 g, 13.2 mmol) were added to DMF (127.5 mL) and stirred at room temperature for 1 hour. 2-chloropyrimidine (3.00 g, 26.2 mmol) was added to the stirring solution, the solution was stirred for a further hour at room temperature. The temperature was raised to 55 °C for approximately 50 hours. The solution was left to cool before being filtered through celite and washed with chloroform. The filtrate was evaporated *in vacuo* and the remaining solid was
suspended in a solution of ethylene diamine tetraacetic acid (EDTA) (11.3 g, 38.5 mmol) in aqueous ammonia (NH₃) (40 mL, 7%). The aqueous layer was extracted first with diethyl ether (Et₂O) and secondly with chloroform. The chloroform layer was dried over magnesium sulfate (MgSO₄) and evaporated to dryness in vacuo, yielding a yellow/orange solid. (0.722 g, 4.56 mmol, 18% yield) ¹H NMR (δ/ppm, 400 MHz, CDCl₃) 7.47, t, 2H, 9.05, d, 4H.

**Synthesis of [(Fe{N(SiMe₃)₂}₂)₂(bipyrimidine)] (2.1).** [Fe{N(SiMe₃)₂}₂{µ-N(SiMe₃)₂}]₂ (0.23 g, 0.6 mmol) was dissolved in toluene. 2,2-bipyrimidine (0.05 g, 0.3 mmol) was suspended in toluene. The solution of [Fe{N(SiMe₃)₂}₂{µ-N(SiMe₃)₂}]₂ was added to the suspension of 2,2-bipyrimidine, the mixture was stirred at room temperature for approximately 30 minutes. The solution was left to settle before being filtered by cannula. The reaction was concentrated in vacuo and cooled to -30 °C, resulting in dark black crystals. (0.088 g, 0.1 mmol, 32%) Anal. Calcd for C₃₂H₇₈Fe₂N₈Si₈; C 42.17, H 8.63, N 12.29; found C 41.99, H 8.55, N 12.16 ¹H NMR (δ/ppm, 400 MHz, C₆D₆) 14.10, s, 72H, 9 x SiMe₃, very broad; 30.20, s, 4H, very broad; 90.77, s, 2H, broad.

**Synthesis of [(Co{N(SiMe₃)₂}₂)₂(bipyrimidine)] (2.4).** [Co{N(SiMe₃)₂}₂{µ-N(SiMe₃)₂}]₂ (0.06 g, 0.16 mmol) was dissolved in toluene. 2,2-bipyrimidine (0.013 g, 0.08 mmol) was suspended in toluene. The solution of [Co{N(SiMe₃)₂}₂{µ-N(SiMe₃)₂}]₂ was added to the suspension of 2,2-bipyrimidine, the mixture was stirred at room temperature for approximately 30 minutes. The solution was left to settle before being filtered by cannula. The reaction was concentrated in vacuo and
cooled to -30 °C resulting in dark black crystals. (0.03 g, 0.03 mmol, 41 %) $^1$H NMR ($\delta$/ppm, 400 MHz, C$_6$D$_6$) 5.61, s, 72H, 9 x SiMe$_3$, very broad; 40.90, s, 4H, broad; 72.77, s, 2H, broad.

**Synthesis of [(Fe{N(SiMe$_3$)$_2$})$_2$(phenanthroline)] (2.2).** [Fe{N(SiMe$_3$)$_2$} {$\mu$-N(SiMe$_3$)$_2$}]$_2$ (0.15 g, 0.39 mmol) and phenanthroline (0.07 g, 0.39 mmol) were suspended in toluene. The solution of [Fe{N(SiMe$_3$)$_2$} {$\mu$-N(SiMe$_3$)$_2$}]$_2$ was added drop wise to the suspension of phenanthroline, the mixture was stirred at room temperature for approximately 30 minutes. The solution was filtered by cannula. The reaction was concentrated in vacuo and cooled to -30 °C, resulting in dark green crystals. (0.098 g, 0.18 mmol, 45 %) Anal. Calcd for C$_{24}$H$_{44}$FeN$_4$Si$_4$; C 51.77, H 7.97, N 10.06; found C 50.28, H 7.34, N 10.52. $^1$H NMR ($\delta$/ppm, 400 MHz, C$_6$D$_6$) NMR ($\delta$/ppm, 400 MHz, C$_6$D$_6$) 13.01, s, 72H, 9 x SiMe$_3$, very broad; 22.06, s, broad; 52.79, s, broad, -17.84, s, broad.

**Synthesis of [(Co{N(SiMe$_3$)$_2$})$_2$(phenanthroline)] (2.5).** [Co{N(SiMe$_3$)$_2$} {$\mu$-N(SiMe$_3$)$_2$}]$_2$ (0.15 g, 0.39 mmol) was dissolved in toluene. Phenanthroline (0.07g, 0.39 mmol) was also suspended in toluene. The solution of [Co{N(SiMe$_3$)$_2$} {$\mu$-N(SiMe$_3$)$_2$}]$_2$ was added to the suspension of phenanthroline, the mixture was stirred at room temperature for approximately 30 minutes. The solution was filtered by cannula, concentrated in vacuo and cooled to -30 °C, resulting in dark green crystals. (0.041 g, 0.07 mmol, 19 %) Anal. Calcd for C$_{24}$H$_{44}$CoN$_4$Si$_4$; C 51.48, H 7.91, N 10.01; found C 51.40, H 7.80, N 9.90. $^1$H NMR ($\delta$/ppm, 400 MHz, C$_6$D$_6$) 10.02, s, 72H, 9 x SiMe$_3$, very broad; 40.88, s, broad; 57.99, s, broad, -22.14, s, broad.
Synthesis of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{HAN}]\) (2.3). \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\{\mu-\text{N(SiMe}_3\}_2\}\] (0.9 g, 2.4 mmol) was dissolved in toluene. HAN (0.3 g, 0.78 mmol) was suspended in toluene. The solution of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\{\mu-\text{N(SiMe}_3\}_2\}\] was added to the suspension of HAN and left to stir overnight at room temperature. The solution was filtered via cannula, concentrated \textit{in vacuo} and cooled to -30 °C, resulting in black crystals. (0.486 g, 0.32 mmol, 41%)

3.3 Preparation of Metal Amide [RO] Complexes

Reaction of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) and 1,3-benzenediol. \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) (0.1 g, 0.11 mmol) and 1,3-benzenediol (0.012 g, 0.11 mmol) were dissolved in THF. The solutions were stirred until all solid had dissolved. The solution of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) was added drop wise to the solution of 1,3-benzenediol and stirred at room temperature for 24 hours. The solution was filtered via cannula, concentrated \textit{in vacuo}, and cooled to -30 °C.

Reaction of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) and 1,2-dihydroxy benzene. \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) (0.1 g, 0.11 mmol) was dissolved in THF. 1,2-dihydroxy benzene (0.01 g, 0.11 mmol) was dissolved in THF. The solutions were stirred until all solid had dissolved. The solution of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{bipyrimidine}]\) was added drop wise to the solution of 1,2-dihydroxy benzene and stirred at room temperature for 24 hours. The solution was filtered via cannula, concentrated \textit{in vacuo}, and cooled to -30 °C.
Reaction of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(bipyrimidine)}]\) and 2,7-dihydroxynaphthalene. 

\([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(bipyrimidine)}]\) (0.1 g, 0.11 mmol) was dissolved in THF. 2,7-dihydroxynaphthalene (0.02 g, 0.12 mmol) was dissolved in THF. The solutions were stirred until all solid had dissolved. The solution of \([\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(bipyrimidine)}]\) was added drop wise to the solution of 2,7-dihydroxynaphthalene, and stirred at room temperature for 24 hours. The solution was filtered via cannula, concentrated \textit{in vacuo} and cooled to -30 °C.

3.4 Preparation of Metal Amide Imidazole Complexes

\begin{align*}
\text{Reaction of } & [\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(HAN)}] \text{ and } \text{ItBu.HCl}. & \quad \text{[Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(HAN)}] \\
\text{of } & (0.10 \text{ g}, 0.07 \text{ mmol}) \text{ was dissolved in toluene. } \text{ItBu.HCl} & \quad \text{dissolved in toluene. The two solutions were added together and left to stir} \\
\text{overnight. The mixture was filtered by cannula, concentrated } \textit{in vacuo} & \text{and cooled to } -30 ^\circ \text{C}. \\
\end{align*}

\begin{align*}
\text{Reaction of } & [\text{Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(HAN)}] \text{ and } \text{IMes.HCl}. & \quad \text{[Fe}\{\text{N(SiMe}_3\}_2\}_2\text{(HAN)}] \\
\text{of } & (0.1 \text{ g}, 0.07 \text{ mmol}) \text{ was dissolved in toluene. } \text{IMes.HCl} & \quad \text{dissolved in toluene. The two solutions were added together and left to stir} \\
\text{overnight. The mixture was filtered by cannula concentrated } \textit{in vacuo} & \text{and cooled to } -30 ^\circ \text{C}. \\
\end{align*}
Reaction of [(Fe{N(SiMe$_3$)$_2$)$_2$(HAN)} and IPr.HCl. [(Fe{N(SiMe$_3$)$_2$)$_2$(HAN)} (0.1 g, 0.07 mmol) was dissolved in toluene. IPr.HCl (0.07 g, 0.17 mmol) was dissolved in toluene. The two solutions were added together and left to stir overnight. The mixture was filtered by cannula, concentrated in vacuo and cooled to -30 °C.

Reaction of [(Fe{N(SiMe$_3$)$_2$)$_2$(bipyrimidine)} and IMes.HCl. [(Fe{N(SiMe$_3$)$_2$)$_2$(bipyrimidine)} (0.05 g, 0.05 mmol) was dissolved in toluene. IMes.HCl (0.03 g, 0.09 mmol) was dissolved in toluene. The solutions were mixed together and stirred at room temperature for 24 hours. The solution was filtered via cannula, concentrated in vacuo, and cooled to -30 °C.

Reaction of [(Fe{N(SiMe$_3$)$_2$)$_2$(bipyrimidine)} and IPr.HCl. [(Fe{N(SiMe$_3$)$_2$)$_2$(bipyrimidine)} (0.02 g, 0.02 mmol) was dissolved in toluene. IPr.HCl (0.02 g, 0.04 mmol) was dissolved in toluene. The solutions were mixed together and stirred at room temperature for 24 hours. The solution was filtered via cannula, concentrated in vacuo, and cooled to -30 °C.

Reaction of [Fe{N(SiMe$_3$)$_2$}(phenanthroline)] and IPr.HCl. [Fe{N(SiMe$_3$)$_2$}(phenanthroline)] (0.23 g, 0.14 mmol) was dissolved in toluene. IPr.HCl (0.19 g, 0.11 mmol) was dissolved in toluene. The solution of IPr.HCl was added drop wise to the solution of [Fe{N(SiMe$_3$)$_2$}(phenanthroline)] and the
mixture was stirred at room temperature for approximately one hour. The solution was filtered via cannula, concentrated *in vacuo*, and cooled to -30 °C.

### 3.5 Preparation and Reactions of Tetrapodal Ligands

**Synthesis of 1,1′,1′′,1′′′-(benzene-1,2,4,5-tetryltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide.** 1,2,4,5–tertakis(bromomethyl)benzene (0.450 g, 1 mmol) was dissolved in acetonitrile, N-benzylimidazole (0.790 g, 5 mmol) was added and the mixture was stirred overnight and heated to reflux. The resulting white powder was washed with acetonitrile. (0.835 g, 0.55 mmol, 77%)

**Reaction of 1,1′,1′′,1′′′-(benzene-1,2,4,5-tetryltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide with Manganocene.** 1,1′,1′′,1′′′-(benzene-1,2,4,5-tetryltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide (0.100 g, 0.1 mmol) was suspended in toluene. Manganocene (0.0490 g, 0.2 mmol) was added and the mixture was stirred overnight. The solution was filtered via cannula, concentrated *in vacuo* before being cooled to -30 °C.

**Reaction of 1,1′,1′′,1′′′-(benzene-1,2,4,5-tetryltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide with Manganocene.** 1,1′,1′′,1′′′-(benzene-1,2,4,5-tetryltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide (0.10 g, 0.1 mmol) was suspended in toluene. Manganocene (0.049 g, 0.2 mmol) was
added and the mixture was stirred before being refluxed at 110 °C overnight. The
solution was filtered via cannula concentrated in vacuo and cooled to -30 °C.

**Reaction of 1,1',1'',1''''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-
benzyl-1H-imidazol-3-ium) bromide with Manganocene.** 1,1',1'',1''''-(benzene-
1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide
(0.100 g, 0.1 mmol) was suspended in toluene. Manganocene (0.121 g, 0.5 mmol)
was added and the mixture was stirred before being refluxed at 110 °C overnight.
The solution was filtered via cannula concentrated in vacuo and cooled to -30 °C.

**Reaction of 1,1',1'',1''''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-
benzyl-1H-imidazol-3-ium) bromide with [Fe{N(SiMe₃)₂}{µ-N(SiMe₃)₂}]₂.**
1,1',1'',1''''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-
imidazol-3-ium) bromide (0.100 g, 0.1 mmol) was suspended in toluene.
[Fe{N(SiMe₃)₂}{µ-N(SiMe₃)₂}]₂ (0.098 g, 0.2 mmol) was added and the mixture
was stirred overnight. The solution was filtered via cannula, concentrated in vacuo
and cooled to -30 °C.

**Reaction of 1,1',1'',1''''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-
benzyl-1H-imidazol-3-ium) bromide with [Fe{N(SiMe₃)₂}{µ-N(SiMe₃)₂}]₂.**
1,1',1'',1''''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-
imidazol-3-ium) bromide (0.100 g, 0.1 mmol) was suspended in toluene.
[Fe{N(SiMe₃)₂}{µ-N(SiMe₃)₂}]₂ (0.098 g, 0.2 mmol) was added and the mixture
was stirred before being refluxed at 110 °C overnight. The solution was filtered via cannula, concentrated in vacuo and cooled to -30 °C.

Reaction of 1,1',1'',1'''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide with [Fe{N(SiMe$_3$)$_2$}{$\mu$-N(SiMe$_3$)$_2$}]$_2$. [Fe{N(SiMe$_3$)$_2$}{$\mu$-N(SiMe$_3$)$_2$}]$_2$ (0.240 g, 0.4 mmol) was added to THF and stirred in order to create the THF adduct. The reaction mixture was cooled to -78 °C and 1,1',1'',1'''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide (0.100 g, 0.1 mmol) was added dropwise. The mixture was stirred and the temperature was kept at -78 °C for several hours before being allowed to heat slowly to room temperature overnight. After stirring overnight the solution was filtered via cannula, concentrated in vacuo and cooled to -30°C. (0.071 g, 0.03 mmol, 36 %)

Reaction of 1,1',1'',1'''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide with [Fe{N(SiMe$_3$)$_2$}{$\mu$-N(SiMe$_3$)$_2$}]$_2$. 1,1',1'',1'''-(benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-benzyl-1H-imidazol-3-ium) bromide (0.100 g, 0.1 mmol) was dissolved in bromobenzene. [Fe{N(SiMe$_3$)$_2$}{$\mu$-N(SiMe$_3$)$_2$}]$_2$ (0.098 g, 0.2 mmol) was added and the mixture was stirred and refluxed at 160 °C overnight. The solution was filtered via cannula and the resulting solid precipitate was dried in vacuo (0.058 g, 0.02 mmol, 30 %)
3.6 Preparation of P(V) Bridged N-Heterocyclic Carbene Complexes

Synthesis of 1-butylimidazole. This was carried out according to a literature procedure.\textsuperscript{44} Glyoxal (11.5 mL, 250 mmol) and formaldehyde (8.1 mL, 220 mmol) were mixed together. tert-Butylamine (10.6 mL, 100 mmol) and aqueous ammonia (6.8 mL, 290 mmol) were mixed together. The two solutions were added drop wise simultaneously to water and refluxed for 30 minutes. The mixture was cooled to room temperature and the water was removed via rotary evaporator. The crude product was distilled via vacuum distillation, to leave a pale yellow liquid. (7.39 g, 59.5 mmol, 60 %)

Synthesis of \([\text{O}=\text{P}\{\text{NHC(H)}\}_3]^3\text{Cl}^-\). POCl\(_3\) (0.31 mL, 3.3 mmol) was added to \(t\)-butylimidazole (1.24 g, 10 mmol). THF was added to the mixture which was refluxed for 2 hours at 80 °C. Solvent was removed \textit{in vacuo} to leave a pale yellow solid; this was washed with hexane and dried \textit{in vacuo}. \(31^P\) NMR, (δ/ppm, 400 Hz, CD\(_3\)CN), -21.84, s, sharp; -25.22, s, sharp.

Synthesis of \([\text{O}=\text{P}\{\text{NHC(H)}\}_3]^3\text{Cl}^-\). POCl\(_3\) (0.03 mL, 0.033 mmol) was dissolved in ethyl acetate. \(t\)-Butylimidazole (0.12 g, 0.1 mmol) was dissolved in ethyl acetate. The solution of POCl\(_3\) was slowly added drop wise to a stirring solution of \(t\)-butylimidazole and the mixture was refluxed for 3 - 4 hours at 80 °C. The solvent was removed \textit{in vacuo} to leave a pale yellow solid; this was washed with hexane and
subsequently dried. $^{31}$P NMR, ($\delta$/ppm, 400 MHz, CD$_3$CN), -21.60, s, sharp; -23.88, s, sharp.

**Synthesis of $[O=P\{\text{NHC(H)}\}_3]^3+$ $[\text{OS(=O)}_2\text{CF}_3]^-$.** POCl$_3$ (0.31 mL, 3.3 mmol) was dissolved in ethyl acetate. $t$-butylimidazole (1.24 g, 10 mmol) was dissolved in ethyl acetate. The solution of POCl$_3$ was slowly added drop wise to a stirring solution of $t$-butylimidazole. After 15 minutes, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (2.22 mL, 10 mmol) was added drop wise to the solution. The mixture was refluxed for 24 hours at 90 °C. The solvent was removed in vacuo, leaving a brown solid. $^{31}$P NMR, ($\delta$/ppm, 400 MHz, CD$_3$CN), -0.01, s, sharp.

**Synthesis of $[O=P\{\text{NHC(H)}\}_3]^3+$ $[\text{OS(=O)}_2\text{CF}_3]^-$.** POCl$_3$ (0.31 mL, 3.3 mmol) was dissolved in toluene. $t$-butylimidazole (1.24 g, 10 mmol) was dissolved in toluene. The solution of POCl$_3$ was slowly added drop wise to a stirring solution of $t$-butylimidazole. After stirring for 15 minutes, TMSOTf (2.22 mL, 10 mmol) was added drop wise to the solution. The mixture was refluxed for 24 hours at 110 °C. The solution was filtered via cannula and taken to dryness. Et$_2$O was added and the mixture was refluxed for 3 hours at 35 °C. The solvent was removed in vacuo, resulting in a white solid, which was dried in vacuo. (0.314 g, 0.36 mmol, 11 %) Anal. Calcd for C$_{66}$H$_{120}$FeN$_{12}$Si$_{12}$; C 33.26, H 4.19, N 9.70; found C 33.39, H 4.06, N 9.80. $^1$H NMR ($\delta$/ppm, 400 MHz, CDCl$_3$) 1.66, s, 9H, sharp, 3 x Me$_3$; 7.31, s, 1H, sharp; 7.58, s, 1H, sharp; 8.92, s, 1H, sharp. $^{13}$C NMR 29.96, s, 3C, sharp; 59.69, s, 1C, sharp; 118.27, s, 1C, sharp; 121.27, s, 1C, sharp; 133.07, s, 1C, sharp. $^{31}$P NMR, -26.99, s, sharp. $^{19}$F NMR, -78.61, s, sharp.
Reaction of $[\text{O=P}\{\text{NHC(H)}\}_3]^{3+}$ $[\text{OS(=O)}_2\text{CF}_3]^{-3}$ with Manganocene.

$[\text{O=P}\{\text{NHC(H)}\}_3]^{3+}$ $[\text{OS(=O)}_2\text{CF}_3]^{-3}$ (0.05 g, 0.058 mmol) and manganocene (0.033 g, 0.15 mmol) was dissolved in THF. The solution of manganocene was added drop wise to the solution of $[\text{O=P}\{\text{NHC(H)}\}_3]^{3+}$ $[\text{OS(=O)}_2\text{CF}_3]^{-3}$. The mixture was left to stir overnight at room temperature. The solution was filtered via cannula and the volume was reduced in vacuo. Cooling overnight to -30 °C resulted in the formation of small brown crystals. (0.057 g, 0.08 mmol) Anal. Calcd for C$_{24}$H$_{40}$F$_6$MnN$_4$O$_8$S$_2$; C 38.66, H 5.41, N 7.51; found C 38.47, H 5.36, N 7.47. $^1$H NMR ($\delta$/ppm, 400 MHz, C$_6$D$_6$) 2.68, s, broad; 5.27, s, very broad; 6.30, s, sharp; 6.49, s, sharp.
3.7 Crystallographic Details for Compounds

Crystals were mounted on thin glass fibres using perfluoropolyether oil and frozen in situ in a flow of cold nitrogen gas from a Cryostream instrument. Data was collected using an Agilent Technologies SuperNova, Single source at offset diffractometer, (compound 2.1, 2.2, 2.3, 2.4, 2.13 and 2.30). Using Olex2, the structures were solved using the ShelXS-2013 structure solution program using direct methods, and refined with the XL refinement package using Least Squares minimisation. The crystallography data for each complex was collected and calculated by Dr Benjamin Day of the Layfield group.
Crystal Data and Structure Refinement for Complex 2.1, 
\[(\text{Fe}\{\text{N(SiMe}_3\}_2\}_2)\text{bipyrimidine}\]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>(C_{32}H_{78}N_8\text{Si}_8\text{Fe}_2)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>911.44</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/n)</td>
</tr>
<tr>
<td>Unit Cell dimensions</td>
<td>(a = 8.1900(3) \text{ Å} \quad \alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 17.9004(6) \text{ Å} \quad \beta = 93.517(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 17.6674(6) \text{ Å} \quad \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>2585.24(16) \text{ Å}^3</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.171 mg/mm(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.776 mm(^{-1})</td>
</tr>
<tr>
<td>(F(000))</td>
<td>980.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.5 (\times) 0.1 (\times) 0.1 mm(^3)</td>
</tr>
<tr>
<td>2(\Theta) range for collection</td>
<td>6.064 to 52.744(^\circ)</td>
</tr>
<tr>
<td>Index range</td>
<td>(-10 \leq h \leq 10, -22 \leq k \leq 22, -22 \leq l \leq 14)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>11577</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5275 [(R_{int} = 0.0296, R_{sigma} = 0.0463)]</td>
</tr>
<tr>
<td>Completeness to (\Theta)</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Data/ restraints/ parameters</td>
<td>5275/0/238</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.050</td>
</tr>
<tr>
<td>Final (R) indices [I &gt; 2(\sigma(I))]</td>
<td>(R_1 = 0.0362, wR_2 = 0.0753)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.0485, wR_2 = 0.0809)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.32/-0.25 \text{ Å}^3</td>
</tr>
</tbody>
</table>
Crystal Data and Structure Refinement for Complex 2.2, [Fe{N(SiMe₃)₂}(phenanthroline)]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₄H₄₄FeN₄Si₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1065.64</td>
</tr>
<tr>
<td>Temperature</td>
<td>150.0 K</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pca₂₁</td>
</tr>
<tr>
<td>Unit Cell dimensions</td>
<td>a = 19.5301(5) Å, α = 90 °</td>
</tr>
<tr>
<td></td>
<td>b = 18.3989(7) Å, β = 90 °</td>
</tr>
<tr>
<td></td>
<td>c = 17.5884(6) Å, γ = 90 °</td>
</tr>
<tr>
<td>Volume</td>
<td>6320.1(4) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>5</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.400 mg/mm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.805 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>2860.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.3 x 0.2 x 0.1 mm³</td>
</tr>
<tr>
<td>2Θ range for collection</td>
<td>6.234 to 52.742°</td>
</tr>
<tr>
<td>Index range</td>
<td>-24 ≤ h ≤ 20, -22 ≤ k ≤ 11, -9 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13594</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>7954 [R_{int} = 0.0418, R_{sigma} = 0.0785]</td>
</tr>
<tr>
<td>Completeness to Θ</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Data/ restraints/ parameters</td>
<td>7954/1/619</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.063</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0510, wR₂ = 0.0810</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0690, wR₂ = 0.0886</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.36/-0.31 Å³</td>
</tr>
</tbody>
</table>
Crystal Data and Structure Refinement for Complex 2.4,

\[\text{[(Co}\{\text{N(SiMe}_3\}_2}\}2\text{(bipyrimidine)}]\]

Empirical formula \( \text{C}_{32}\text{H}_{78}\text{N}_8\text{Si}_8\text{Co}_2 \)
Formula weight 917.60
Temperature 150.02(10) K
Crystal system monoclinic
Space group \( \text{P2}_1/\text{n} \)
Unit Cell dimensions
\[a = 8.2590(6) \text{ Å} \quad \alpha = 90 \, ^\circ \]
\[b = 1707172(1) \text{ Å} \quad \beta = 93.361(6) \, ^\circ \]
\[c = 17.4926(1) \text{ Å} \quad \gamma = 90 \, ^\circ \]
Volume 2555.2(3) \( \text{Å}^3 \)
\(Z\) 2
Density (calculated) 1.193 mg/mm\(^3\)
Absorption coefficient 0.867 mm\(^{-1}\)
\(F(000)\) 984.0
Crystal size 0.2 \(\times\) 0.07 \(\times\) 0.07 mm\(^3\)
2\(\Theta\) range for collection 6.042 to 50.7\(^\circ\)
Index range \(-9 \leq h \leq 9, -21 \leq k \leq 12, -16 \leq l \leq 21\)
Reflections collected 8603
Independent reflections 4657 \([R_{\text{int}} = 0.0549, R_{\text{sigma}} = 0.0776]\)
Completeness to \(\Theta\) 99.7 %
Data/ restraints/ parameters 4657 /0 /238
Goodness of fit 1.036
Final \(R\) indices \([I > 2\sigma(I)]\)
\(R_1 = 0.0508, \text{wR}_2 = 0.1198\)
\(R\) indices (all data)
\(R_1 = 0.0740, \text{wR}_2 = 0.1334\)
Largest diff. peak and hole 0.68/-0.85 \(\text{Å}^3\)
### Crystal Data and Structure Refinement for Complex 2.5, [Co{N(SiMe$_3$)$_2$}$_2$(phenanthroline)]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$H$</em>{44}$CoN$_4$Si$_4$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>559.92</td>
</tr>
<tr>
<td>Temperature</td>
<td>150.01(11)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pca$_2_1$</td>
</tr>
<tr>
<td>Unit Cell dimensions</td>
<td>$a = 19.5039(7)$ Å, $\alpha = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 18.2498(5)$ Å, $\beta = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 17.5426(5)$ Å, $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>6244.2(3) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.1911 mg/mm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.722 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>2397.9</td>
</tr>
<tr>
<td>Crystal size</td>
<td>$0.2 \times 0.2 \times 0.1$ mm$^3$</td>
</tr>
<tr>
<td>$2\Theta$ range for collection</td>
<td>6.12 to 52.74 $^\circ$</td>
</tr>
<tr>
<td>Index range</td>
<td>$-24 \leq h \leq 8$, $-22 \leq k \leq 12$, $-17 \leq l \leq 21$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>18268</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>10248 [R$<em>{int} = 0.0332$, R$</em>{sigma} = 0.0598$]</td>
</tr>
<tr>
<td>Completeness to $\Theta$</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Data/ restraints/ parameters</td>
<td>10248/0/618</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.142</td>
</tr>
<tr>
<td>Final $R$ indices [$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.0418$, wR$_2 = 0.0785$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0533$, wR$_2 = 0.0824$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.36/-0.36 Å$^{-3}$</td>
</tr>
</tbody>
</table>
Crystal Data and Structure Refinement for Complex 2.13, 
[{Fe(IPr)(Cl)}₂{Fe[N(SiMe₃)₂](Cl)}(HAN)]

Empirical formula \( \text{C}_{46}\text{H}_{114}\text{N}_{8}\text{Si}_{8}\text{Cl}_{2}\text{Fe}_{2} \)
Formula weight 1283.75
Temperature 150.03(13)
Crystal system Triclinic
Space group P-1
Unit Cell dimensions 
\( a = 12.4812(5) \text{ Å} \quad \alpha = 85.551(3) ^\circ \)
\( b = 15.3920(6) \text{ Å} \quad \beta = 89.833(3) ^\circ \)
\( c = 21.4658(8) \text{ Å} \quad \gamma = 69.432(3) ^\circ \)
Volume 3848.0(3) Å³
Z 3
Density (calculated) 1.662 mg/mm³
Absorption coefficient 1.335 mm⁻¹
\( F(000) \) 1968.0
Crystal size 0.2 x 0.2 x 0.05 mm³
2Θ range for collection 6.13 to 57.746°
Index range -16 ≤ h ≤ 16, -15 ≤ k ≤ 20, -14 ≤ l ≤ 29
Reflections collected 24696
Independent reflections 16848 \([R_{int} = 0.0285, R_{sigma} = 0.0775]\)
Completeness to Θ 99.0 %
Data/ restraints/ parameters 16848/42/760
Goodness of fit 1.007
Final \( R \) indices [I > 2σ(I)] \( R_1 = 0.0493, wR_2 = 0.0851 \)
\( R \) indices (all data) \( R_1 = 0.0876, wR_2 = 0.0977 \)
Largest diff. peak and hole 0.34/-0.29 Å⁻³
Crystal Data and Structure Refinement for Complex 2.30,

\[\text{[Mn(tBuIm)\textsubscript{2}(OTf)\textsubscript{2}(THF)\textsubscript{2}]}\]

Empirical formula \(\text{C}_{24}\text{H}_{40}\text{N}_{4}\text{O}_{8}\text{F}_{6}\text{S}_{2}\text{Mn}\)

Formula weight \(745.66\)

Temperature \(150.03(10)\)

Crystal system orthorhombic

Space group \(\text{Pbca}\)

Unit Cell dimensions
\[\begin{align*}
    a &= 14.9999(7) \text{ Å} & \alpha &= 90 \degree \\
    b &= 11.8388(5) \text{ Å} & \beta &= 90 \degree \\
    c &= 19.2345(8) \text{ Å} & \gamma &= 90 \degree 
\end{align*}\]

Volume \(3415.7(2) \text{ Å}^3\)

\(Z\) \(4\)

Density (calculated) \(1.450 \text{ mg/mm}^3\)

Absorption coefficient \(0.589 \text{ mm}^{-1}\)

\(F(000)\) \(1548.0\)

Crystal size \(0.4 \times 0.3 \times 0.2 \text{ mm}^3\)

2\(\Theta\) range for collection \(6.884 \text{ to } 52.734 \degree\)

Index range \(-18 \leq h \leq 16, -14 \leq k \leq 14, -24 \leq l \leq 22\)

Reflections collected \(9339\)

Independent reflections \(3487 [R_{\text{int}} = 0.0300, R_{\text{sigma}} = 0.0412]\)

Completeness to \(\Theta\) \(99.8 \%\)

Data/ restraints/ parameters \(3487/112/245\)

Goodness of fit \(1.034\)

Final \(R\) indices \([I > 2\sigma(I)]\) \(R_1 = 0.0478, wR_2 = 0.1003\)

\(R\) indices (all data) \(R_1 = 0.0708, wR_2 = 0.1111\)

Largest diff. peak and hole \(0.36/-0.27 \text{ Å}^3\)
Chapter 4

References


19 J.A. Mata, M. Poyatos and E. Peris, *Coord. Chem Rev.*, 2007, **251**, 841-859


32 C.W.K. Gstöttmayr, V.P.W. Böhm, E. Herdtweck, M. Grosche, and


