The Synthesis, Reactivity and Electrochemical Study of Metallocene Substituted α-Diimine Ligands

Eleanor Magdzinski
The University of Western Ontario

Supervisor
Dr. Paul J. Ragogna
The University of Western Ontario

Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
© Eleanor Magdzinski 2013

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Part of the Inorganic Chemistry Commons

Recommended Citation
https://ir.lib.uwo.ca/etd/1615

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlsadmin@uwo.ca.
The Synthesis, Reactivity and Electrochemical Study of Metallocene Substituted 
α-Diimine Ligands

Thesis Format: Integrated-Article

by

Eleanor Magdzinski

Graduate Program in Chemistry

A thesis submitted in partial fulfillment 
of the requirements for the degree of 
Master of Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

© Eleanor Magdzinski 2013
Abstract

The synthesis of transition metal complexes containing redox-active ligands or ligands with redox-active substituents have been areas of ongoing interest in chemical research. To date, only a handful of examples involving redox-active ligands containing main group centres have been reported.

This thesis presents work on the development of novel redox-active ligands utilizing an assortment of nitrogen-based frameworks (diiminopyridine (DIMPY), 1,4-diaza-1,3-butadiene (DAB), N-heterocyclic carbene (NHC)) that contain metalloocene substituents (ferrocene and an understudied redox-active Co(III) moiety). Initially the syntheses of an N,N'-differocenyl diiminopyridine and its low-valent chalcogen (S^{2+}, Se^{2+}, Te^{2+}) and pnictogen (P^+) complexes are discussed. These complexes represent the first such examples of utilizing low-valent main group systems containing redox-active ligands with pendant ferrocenyl substituents. Other work focuses on the synthesis of the above listed nitrogen-based ligands containing novel mixed sandwich Co(III) substituents, and include comparative reactivity studies (SnCl₂ and GeCl₂•dioxane for DIMPY and SnCl₄ and Pt₂Me₄(SMe₂)₂ for DAB) of those ligands to their ferrocene derivatives. Electrochemical studies reveals an instability of the Co(III) containing complexes, leading to the continuous variation in the ligand framework towards a more stable compound.

Keywords

Nitrogen-based ligands • redox-active ligands • non-innocent ligands • N-heterocyclic carbenes • main group complexes • diiminopyridine • 1,4-diaza-1,3-butadiene
Co-Authorship Statement

This thesis includes material from one previously published manuscript presented in Chapter 2. This material was co-authored by E. Magdzinski, P. Gobbo, C. D. Martin, M. S. Workentin and P. J. Ragogna (Inorg. Chem., 2012, 51, 8425). All of the experimental work was performed by E. Magdzinski. X-ray diffraction data were solved by C. D. Martin and B. F. T. Cooper. E. Magdzinski wrote the manuscript except for the electrochemical details, where P. Gobbo was responsible for this work. P. J. Ragogna and M. S. Workentin edited the manuscript. Copyright approval can be found in the Appendix of this document (A.11).

This thesis also includes material from two submitted manuscripts presented in Chapter 3 and Chapter 4. The material in Chapter 3 was co-authored by E. Magdzinski, P. Gobbo, M. S. Workentin and P. J. Ragogna (Inorg. Chem., 2013, submitted). E. Magdzinski was responsible for the synthesis, characterizations and writing of the manuscript, with the exception of the electrochemical sections, which were performed and written by P. Gobbo. M. S. Workentin and P. J. Ragogna edited the manuscript.

The material in Chapter 4 was co-authored by E. Magdzinski, P. Gobbo, J. W. Dube, M. S. Workentin and P. J. Ragogna (Inorg. Chem., 2013, submitted). E. Magdzinski was responsible for the synthesis, characterizations and writing of the manuscript, with the exception of the electrochemical sections, which were performed and written by P. Gobbo. All of the diffraction data were collected and solved by J. W. Dube. P. J. Ragogna and M. S. Workentin edited the manuscript.
Acknowledgments

I would first like to thank Dr. Paul Ragogna for giving me the opportunity to work in his lab over the years. You always made time to help see me through the many issues I encountered in and out of the lab, for this I am truly grateful.

To Matt McCready, if you hadn’t called me during course registration the summer after 1st year I would have been a biologist. Thank you for being a great friend and talking some sense into me. My hat goes off next to the ever-changing Ragogna group for all the useful and not so useful discussions we would have in the lab, at the GC, Caleb’s house, Winks, or DTKB. Jonathan W. Dube played a huge role in my chemistry success by brightening up a dull day or sharing my enthusiasm with a great result. There isn’t anyone else I could imagine spending late nights with working in and out of the lab. Dr. Caleb D. Martin saw me through my 4490 thesis project. He taught me all about the fine balance between school and play—both necessary for success and maintaining sanity. I am privileged to have worked so closely with such an incredible chemist. To Dr. Jackie T. Price, my running buddy: “To keep the body in good health is a duty...otherwise we shall not be able to keep our mind strong and clear” (Buddha). Thanks for keeping me healthy and motivated towards lab work and running—I can’t take all of the credit for being able to run that half marathon. To my favourite dry box buddy, Dr. Allison L. Brazeau, we had a really good thing going for us, man. To the rest of the Ragogna group (Jocelyn, Jay, Preeti, Mahboubeh, Tyler, Ryan, Bervo, etc...), we had a lot of great times, thank you! To my e-chem buddy, roommate and great friend, Pierangelo Gobbo, thank you for all of the espressos, Italian food, walking dead marathons, good conversations and great laughs. Evelyn Asiedu, my first and only chemistry baby. I learned more from you than you know. I wish you all the best in your future chemistry and life endeavors, thank you for your contributions to my research.

To Bryan Landschoot, Poly Kyriacou, 7/11 slurpees and Rick McGee—keep leaning back. I would also like to thank the individuals at Chem-Bio stores, Mat Willans (NMR), Doug Hairsine (Mass spectrometry), Paul Boyle and Aneta Borecki (X-ray) and John and Jon (Machine shop). Lastly, to my family and friends, thank you for your encouragement and continued support throughout my time at Western.
Table of Contents

Abstract ..........................................................................................................................ii
Co-Authorship Statement .............................................................................................iii
Acknowledgments ........................................................................................................iv
Table of Contents .........................................................................................................v
List of Tables ................................................................................................................viii
List of Figures ...............................................................................................................xi
List of Schemes .............................................................................................................xii
List of New Compounds Reported ..............................................................................xiv
List of Abbreviations ....................................................................................................xvii

Chapter 1 ......................................................................................................................1

1 Introduction .............................................................................................................1

1.1 Non-Innocent Ligands ........................................................................................1

1.1.1 The Growing World of Non-Innocent Ligands .............................................1

1.1.2 Strategies for Classifying Non-Innocent Ligands ........................................2

1.1.3 Non-Innocent Ligands Affecting the Lewis Acid-Base Properties of the Metal ..............................................................5

1.1.4 Non-Innocent Ligands Acting as Electron-Reservoirs .................................8

1.2 Scope of Thesis ....................................................................................................11

1.3 References ..........................................................................................................12

Chapter 2 ....................................................................................................................15

2 The Syntheses and Electrochemical Studies of a Ferrocene Substituted
Diiminopyridine Ligand and its P, S, Se and Te Complexes ........................................15

2.1 Introduction ........................................................................................................15

2.2 Results and Discussion ....................................................................................18

2.2.1 Synthesis .....................................................................................................18

2.2.2 X-Ray Crystallography ..............................................................................20
List of Tables

Table 2.1: $^1$H NMR Chemical Shifts (ppm) for 2.18, 2.19, 2.20, 2.21 and 2.22. ............ 18

Table 2.2: Selected bond lengths (Å) and angles (°) for 2.19, 2.20, 2.21, 2.22 and their analogues 2.9, 2.10, 2.11 and 2.13................................................................. 22

Table 3.1: $^1$H NMR chemical shifts (ppm) for 2.18, 3.18, 3.19, 3.20 and 3.21 in CD$_2$Cl$_2$. 42

Table 3.2: Bond lengths (Å) and bond angles (°) for 3.18, 3.19, 3.20, 3.21 and their analogues 3.14 and 3.15........................................................................................................ 46

Table 4.1: Selected bond lengths (Å) and bond angles (°) for 4.3, 4.4, 4.5, 4.7, 4.9 and 4.10. ............................................................................................................................................................. 65

Table 5.1: X-ray details for 5.12................................................................................................................. 81
# List of Figures

Figure 1.1: Classic Werner complex containing redox-inactive ligands. .......................... 1

Figure 1.2: Processes involving the forming/breaking of bonds. L=non-innocent ligand, M=metal centre in the +n oxidation state, S/S-X= Substrate. .................................................. 3

Figure 1.3: Redox-active ligands that accept/release electrons. L=non-innocent ligand, M=metal centre in +n oxidation state, S/S'= substrate. ................................................................. 4

Figure 1.4: A multi-redox system composed of transition metals (M) and redox-active ligands (L). ................................................................................................................................. 5

Figure 1.5: Diiminopyridine and 1,3-diaza-1,4-butadiene α-diimine ligands. .................... 10

Figure 2.1: A few known nitrogen-based ligand complexes with ferrocenyl and non-ferrocenyl substituents. .................................................................................................................. 16

Figure 2.2: Solid-state structures of the free ligand (2.18) from two different views. Thermal ellipsoids are drawn to the 50% probability interval and hydrogen atoms are removed for clarity................................................................. 22

Figure 2.3: Solid-state structures of 2.19, 2.20, 2.21 and 2.22 viewed down the ligand basal plane. Thermal ellipsoids are drawn to the 50% probability level. Solvates, anions and hydrogen atoms are removed for clarity. ................................................................. 23

Figure 2.4: Solid-state structures of 2.19, 2.20, 2.21 and 2.22 viewed perpendicular to ligand basal plane. Thermal ellipsoids are drawn to the 50% probability level. Solvates, anions and hydrogen atoms are removed for clarity. “Disorder removed from 2.19. .... 24

Figure 2.5: From top to bottom, CV of 2.18 (A), 2.13 (B) and 2.22 (C) recorded at a Pt electrode in DCM / 0.1 M TBAPF₆ with analyte concentration of 2 mM and at 0.5 Vs⁻¹. Experiment carried out inside of an inert atmosphere glove box at room temperature. 27

Figure 3.1: A few redox-active moieties that have been used to impart redox activity onto substitutionally inert redox-switchable ligands. ........................................................................ 36
Figure 3.2: Nitrogen-based ligands containing redox-active ferrocene substituents........ 37

Figure 3.3: Nitrogen-based ligands containing metallocene (2.18, 3.9-3.12) and non-metallocene (3.13-3.15) substituents. ........................................................................................................ 38

Figure 3.4: $^1$H NMR spectra for compounds 3.17, 3.18, 3.19 from top to bottom in CD$_2$Cl$_2$ on a 400 MHz spectrometer showing an increase in solubility from free ligand (3.17) to Ge (3.18) and Sn (3.19) complexes. Inset: imine protons on 3.19 at $\delta_H$= 7.68. Proton NMR Spectra for 3.19 were obtained on 400 and 600 MHz to confirm the presence of $^{119}$Sn satellites (400 MHz $\delta_H$= 7.64; $^3J_{Sn-H}$= 32.0 Hz)................................................................................ 40

Figure 3.5: Solid-state structures of 3.18 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity........................................................................................................ 44

Figure 3.6: Solid-state structures of 3.19 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity........................................................................................................ 44

Figure 3.7: Solid-state structures of 3.20 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity........................................................................................................ 45

Figure 3.8: Solid-state structures of 3.21 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity........................................................................................................ 45

Figure 3.9: Cyclic voltammograms of 2 mM solutions of 3.16 recorded at a Pt electrode in DCM / 0.1 M TBAPF$_6$ at 5 V s$^{-1}$. .................................................................................................................. 47

Figure 3.10: CV of 3.21 recorded at a GC electrode in MeCN / 0.1 M TBAPF$_6$ with analyte concentration 2 mM and at 0.5 V s$^{-1}$. .................................................................................................................. 48

Figure 3.11: CV of 3.21 recorded at different scan rates at a GC electrode in MeCN / 0.1 M P$_{888}$TB, and with an analyte concentration of 2 mM......................................................... 49
Figure 4.1: Three possible electronic structures of 1,4-diaza-1,3-butadiene ligands. 57

Figure 4.2: Free (4.2, 3.16) 18 electron metallocenes and nitrogen-based ligands containing pendant 18 electron metallocenes (2.18, 3.6, 3.17). 59

Figure 4.3: Solid-state structures of 4.3, 4.4 and 4.5. Thermal ellipsoids are drawn to the 50% probability level. Solvates and hydrogen atoms are removed for clarity. 63

Figure 4.4: Solid-state structures of 4.7, 4.9 and 4.10. Thermal ellipsoids are drawn to the 50% probability level. Solvates and hydrogen atoms are removed for clarity. 64

Figure 4.5: On the left: CV of 3.6 (A, solid line), 4.6 (A, dashed line), 4.8 (B) and 4.10 (C). CV recorded at a GC electrode in MeCN / 0.1 M TBAPF$_6$ with an analyte concentration of 2 mM and at 0.1 Vs$^{-1}$. On the right: CV of 3.6 (D, solid line), 4.6 (D, dashed line), 4.7 (E) and 4.9 (F). CV recorded at a GC electrode in DCM / 0.1 M TBAPF$_6$ with analyte concentration 2 mM and at 0.1 Vs$^{-1}$. Experiments were carried out at room temperature and in an inert atmosphere glove box. 66

Figure 5.1: A generic view of an N-heterocyclic carbene (NHC). 76

Figure 5.2: A few examples of N-Heterocyclic ligands containing ferrocene. 77

Figure 5.3: N-heterocyclic carbene ligands containing redox-active moieties. 77

Figure 5.4: $^1$H NMR spectra for 5.12 and 5.13 in CD$_2$Cl$_2$. 79

Figure 5.5: Solid-state structures of 5.12 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity. 82
List of Schemes

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Depiction of ferrocene as a one-electron redox system.</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>Catalytic activity of a redox-active Kumada cross coupling catalyst.</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Catalytic activity of a redox-active polymerization catalyst.</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>Catalytic activity of a redox-active olefin-metathesis catalyst.</td>
<td>8</td>
</tr>
<tr>
<td>1.5</td>
<td>Representative structural changes from electron transfer to a few potentially redox-active ligands.</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>A ([2+2]) cycloaddition reaction catalyzed by an iron DIMPY complex.</td>
<td>10</td>
</tr>
<tr>
<td>2.1</td>
<td>Synthetic routes to 2.18, 2.19, 2.20, 2.21 and 2.22. (See Appendix (A.1 and A.2) for NMR spectra).</td>
<td>19</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of substitutionally inert, redox-active ligands.</td>
<td>36</td>
</tr>
<tr>
<td>3.2</td>
<td>Synthetic route to 3.17.</td>
<td>39</td>
</tr>
<tr>
<td>3.3</td>
<td>Synthetic route to 3.18 and 3.19.</td>
<td>41</td>
</tr>
<tr>
<td>3.4</td>
<td>Synthetic route to 3.20 and 3.21.</td>
<td>42</td>
</tr>
<tr>
<td>4.1</td>
<td>Reversible catalysis of a diphosphino cobaltocene ligand.</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>Synthetic route to 4.3.</td>
<td>60</td>
</tr>
<tr>
<td>4.3</td>
<td>Synthetic routes to 4.4 and 4.5.</td>
<td>61</td>
</tr>
<tr>
<td>4.4</td>
<td>Synthetic routes to 4.7, 4.8, 4.9 and 4.10.</td>
<td>61</td>
</tr>
<tr>
<td>5.1</td>
<td>Reactivity of 1.4-diaza-1.3-butadiene containing pendant mixed sandwich coblatacne substituents.</td>
<td>78</td>
</tr>
<tr>
<td>5.2</td>
<td>Synthetic Route to 5.12.</td>
<td>79</td>
</tr>
<tr>
<td>5.3</td>
<td>Synthetic Route to 5.13.</td>
<td>80</td>
</tr>
</tbody>
</table>
Scheme 6.1: Proposed synthetic routes to asymmetric metallocene containing β-diketiminate.
## List of New Compounds Reported

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula/Structure</th>
<th>Page # for Characterization Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.18</td>
<td><img src="image1" alt="Structure 1" /> $\text{[OTf]}_2$</td>
<td>29</td>
</tr>
<tr>
<td>2.19</td>
<td><img src="image2" alt="Structure 2" /> $\text{[OTf]}_2$</td>
<td>30</td>
</tr>
<tr>
<td>2.20</td>
<td><img src="image3" alt="Structure 3" /> $\text{[OTf]}_2$</td>
<td>31</td>
</tr>
<tr>
<td>2.21</td>
<td><img src="image4" alt="Structure 4" /> $\text{P}l_3^-$</td>
<td>31</td>
</tr>
<tr>
<td>2.22</td>
<td><img src="image5" alt="Structure 5" /></td>
<td>32</td>
</tr>
<tr>
<td>3.17</td>
<td><img src="image6" alt="Structure 6" /> xiv</td>
<td>51</td>
</tr>
</tbody>
</table>
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Ad</td>
<td>2-adamantyl</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>δΔ</td>
<td>Change in chemical shift</td>
</tr>
<tr>
<td>Σ_v.d.w.</td>
<td>Sum of van der Waals radii</td>
</tr>
<tr>
<td>( {^1H} )</td>
<td>Proton decoupled</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>anti</td>
<td>opposite</td>
</tr>
<tr>
<td>BIAN</td>
<td>bisiminoacenaphthene</td>
</tr>
<tr>
<td>Br</td>
<td>broad</td>
</tr>
<tr>
<td>Calc</td>
<td>Calculated</td>
</tr>
<tr>
<td>cf.</td>
<td>Confer (compare)</td>
</tr>
<tr>
<td>Ch</td>
<td>Chalcogen</td>
</tr>
<tr>
<td>cis</td>
<td>&quot;on the same side [as]&quot; or &quot;on this side [of]&quot;</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl</td>
</tr>
<tr>
<td>DAB</td>
<td>diazabutadiene</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>( D_e )</td>
<td>Calculated density</td>
</tr>
<tr>
<td>DIMPY</td>
<td>diiminopyridine</td>
</tr>
<tr>
<td>Dipp</td>
<td>2,6-diisopropylphenyl</td>
</tr>
<tr>
<td>Dmp</td>
<td>2,6-dimethylphenyl</td>
</tr>
<tr>
<td>D.p.</td>
<td>Decomposition point</td>
</tr>
<tr>
<td>e.g.</td>
<td>Exempli gratia (for example)</td>
</tr>
<tr>
<td>et al.</td>
<td>Et alia (and others)</td>
</tr>
<tr>
<td>Et(_2)O</td>
<td>Diethylether</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FW</td>
<td>Formula weight</td>
</tr>
<tr>
<td>H</td>
<td>hour</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-resolution mass spectrometry</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>'Bu</td>
<td>Iso-butyl</td>
</tr>
<tr>
<td>i.e.</td>
<td>Id est (that is)</td>
</tr>
<tr>
<td>in situ</td>
<td>In its original place</td>
</tr>
<tr>
<td>In vacuo</td>
<td>In a vacuum</td>
</tr>
<tr>
<td>'Pr</td>
<td>Iso-propyl</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>M.p.</td>
<td>Melting point</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>&quot;Bu</td>
<td>Normal-butyl</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OTf</td>
<td>Trifluoromethanesulfonate; triflate; [CF(_3)SO(_3)](^-)</td>
</tr>
<tr>
<td>p</td>
<td>Para</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>p</td>
<td>pentet</td>
</tr>
<tr>
<td>PSsTB</td>
<td>Tetraoctylphosphonium tetrakis(pentafluorophenyl)borate</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>Ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>q</td>
<td>Quartet</td>
</tr>
<tr>
<td>R</td>
<td>Organic substituents</td>
</tr>
<tr>
<td>rt</td>
<td>Room temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>sept</td>
<td>Septet</td>
</tr>
<tr>
<td>Syn</td>
<td>with or together</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TBABr</td>
<td>Tetrabutylammonium bromide</td>
</tr>
<tr>
<td>TBABF4</td>
<td>Tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetrabutylammonium fluoride</td>
</tr>
<tr>
<td>TBAPF6</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>'Bu</td>
<td>Tertiary-butyl</td>
</tr>
<tr>
<td>'BuOK</td>
<td>Potassium tert-butoxide</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>trans</td>
<td>Across</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet-visible</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction

1.1 Non-Innocent Ligands

1.1.1 The Growing World of Non-Innocent Ligands

The development of highly efficient and selective catalysts is a major goal in synthetic chemistry.\(^1\) In an effort towards achieving chemical sustainability, new catalysts are constantly being prepared and modified to improve on reaction specificity and longevity. The properties of a metal complex are the result of the interactions between the metal centre and its surrounding ligands. It is for this reason that there has also been a considerable interest placed on the development of novel ligand classes. In the past, a ligand typically acted as a ‘spectator’ to the reactivity that would take place at the metal centre. Now, ligands are observed to take on more of an active role (i.e. ‘actor’) in the catalytic system, where they can play a more prominent role in the elementary bond activation steps of a catalytic cycle. ‘Actor’ ligands are more commonly referred to as ‘non-innocent’ or ‘redox-active’.\(^1,2\)

The term ‘non-innocent’ has recently appeared frequently in the literature.\(^2,3\) ‘Innocence’ was originally coined in 1966 by Jørgensen who stated, “Ligands are innocent when they allow oxidation states of the central atoms to be defined.”\(^4\) Werner complexes provide classic examples of ligands that are ‘innocent’ (i.e. spectator).\(^5\) In the case of cis-[Co(NH\(_3\))\(_4\)Cl\(_2\)]Cl (Figure 1.1, 1.0) the oxidation state on cobalt can be easily assigned as 3+. That is, the metal oxidation state can be confidently assigned without complications from the redox-activity of the ligands.\(^6\)

![classic werner complex diagram]

**Figure 1.1:** Classic Werner complex containing redox-inactive ligands.
The term ‘non-innocence’ would thus define the case where ambiguity exists in the assignment of oxidation states. This is observed in other cases where the ligands can undergo electron transfer and “ligand oxidation state” changes. Such ligands, e.g. \( \text{O}_2/\text{O}_2^- \) or \( \text{NO}^+/\text{NO}/\text{NO}^- \) were classified by Jørgensen as ‘suspect’ (or ‘non-innocent’). It is believed that complexes containing these types of ligands may offer interesting prospects to unveil new catalytic reactions.

Although some reviewers have made distinctions between the terms ‘non-innocent’ and ‘redox-active’, others do not. For the purpose of this report, these terms will be used synonymously.

1.1.2 Strategies for Classifying Non-Innocent Ligands

Redox-active or non-innocent ligands are terms that describe extremely diverse groups of compounds; however, within these two groups distinctions can be made. Although there are a few discrepancies among scientists in terms of classifying these materials (based on spatial orientation about metal centre vs. chemistry that occurs at ligand vs. chemistry that occurs at metal) de Bruin recently classified non-innocent ligands based on their reactivity in catalysis. By using this method, four subgroups are considered, that is those that: (1) Generate reactive ligand-radicals that actively participate in the making and breaking of chemical bonds during catalysis; (2) Involve the activation or modification of the substrates’ reactivity in cases where the substrates act as a redox non-innocent ligands; (3) Modify the Lewis acidity of the metal inductively by reduction/oxidation of the ligand; and (4) Act as an ‘electron-reservoir’ at the redox-active ligand. In general, strategies 1 and 2 involve the redox-active ligands in the role of forming and breaking chemical bonds of the substrate (Figure 1.2), whereas strategies 3 and 4 involve processes where the redox-active ligands can accept and release electrons (Figure 1.3).

The first two strategies play a more prominent role in the bond-activation processes during the catalytic reaction. This behaviour is important in the catalytic mechanism of several enzymes that proceed via radical-type reactions (i.e. oxidases). In strategy 1, involving ligand radicals participating in the making and breaking of chemical
bonds during catalysis, it is the substrate activation by the non-innocent ligand and the metal that allows for reactions that are otherwise difficult to proceed (Figure 1.2, Strategy 1, A→B).  

Strategy 2 involves the modification of the substrate reactivity in cases where the substrate acts as a redox non-innocent ligand. Electron transfer to or from a redox-active substrate by the ligand imparts radical behaviour. This substrate-centred radical behaviour is useful to future transformations involved in a catalytic cycle (Figure 1.2, Strategy 2, A→B). The radical species in these cases have completely different reactivity than their closed-shell intermediates.  

**Figure 1.2:** Processes involving the forming/breaking of bonds. L=non-innocent ligand, M=metal centre in the +n oxidation state, S/S-X= Substrate.  

Processes in which the redox-active ligands readily accept and release electrons to a metal centre, a substrate, or chemical redox agent, typically involve substitutionally inert ligands. That is, ligands that form strong bonds with a metal and do not become displaced or experience a change in orientation about the metal centre during the catalytic cycle. Strategies 3 and 4 involve this kind of system, as depicted in Figure 1.3. In strategy 3, the catalytic activity of the metal complex is dependent on its change in either Lewis acidity (Figure 1.3, Strategy 3: A→B) or basicity (Figure 1.3, Strategy 3: A→B'). This occurs inductively by reducing or oxidizing the bound ligand, whereby the change in oxidation state of the ligand strongly influences both the incoming substrates affinity as well as the energy profile of subsequent follow-up reactions. In strategy 4, the catalytic activity of the system is based on the redox-active ligand’s ability to act as an electron reservoir, either accepting/releasing electrons from/to the adjacent metal centre.
In this way the metal is able to store electrons in the ligand in the elementary steps, generating excessive electron density (Figure 1.3, Strategy 4: A$\rightarrow$C), as well as accept electron density from the ligands in elementary steps generating deficiencies (Figure 1.3, Strategy 4: A$\rightarrow$C$'$). In all cases, uncommon oxidation states of the metal are avoided.\(^1\)

**Strategy 3: Affecting Lewis Acidity/Basicity on the Metal**

\[
\begin{align*}
&\text{Increased Lewis basicity on metal} \\
&\text{Increased Lewis acidity on metal}
\end{align*}
\]

**Strategy 4: Acting as an "Electron-Reservoir"**

Figure 1.3: Redox-active ligands that accept/release electrons. L= non-innocent ligand, M= metal centre in +n oxidation state, S/S$'$= substrate.

Strategy 4 may also allow for multielectron reactions to take place in low-born metals. Precious metals have been known to catalyze multielectron reactions most efficiently, as they typically undergo ±two-electron oxidation state changes (e.g. Pt(II), Pt(IV); Ir(I), Ir(III), Ir(V)). However, the rising cost of these materials may pose a problem for their continued use and, thus there is a significant desire to move towards the use of low-born metals for these multi-electron transformations. The problem is that such metals often prefer to undergo ±one-electron oxidation state changes (e.g. Co(I), Co(II), Co(III)). Chirik and Wieghardt have proposed that redox-active ligands may be the solution to this problem. By combining a one-electron redox change at a ligand with a one-electron redox change at the metal centre an overall two-electron change is made possible (Figure 1.4).\(^6,7,20\)
Figure 1.4: A multi-redox system composed of transition metals (M) and redox-active ligands (L).

For the purpose of this document, an emphasis will be placed on the latter two classes of ligands (Figure 1.3).

1.1.3 Non-Innocent Ligands Affecting the Lewis Acid-Base Properties of the Metal

One method to modulate reactivity and selectivity of a catalyst is through the redox control of the supporting ligand in a metal complex. In the past, modifications of a ligand’s electronic properties involved laborious syntheses of ligands with different substituents. A simpler approach would involve a reduction or oxidation of a non-innocent ligand that can tune the Lewis acidic properties of the metal in one step. This can be achieved by imparting a redox-active functionality onto an innocent ligand framework. When oxidized or reduced, the redox-active functionality experiences a loss or gain of electrons, inductively affecting the electron density about the ligated metal centre. A variety of substituents have been used in this regard, with ferrocene being of particular interest.

Ferrocene, (FeCp₂, Scheme 1.1; 1.1), is one of the most studied organometallic sandwich molecules. It contains an iron centre bonded to two cyclopentadienyl (Cp= C₅H₅⁻) rings. In addition, it undergoes a well-established reversible one-electron oxidation process. Due to its ability to undergo reversible oxidation to form the ferrocenium complex at low potential, ferrocene has been used as an internal standard for the calibration of redox potentials in non-aqueous electrochemistry (Scheme 1.1). The chemical stability and synthetic versatility of ferrocene has led to its inclusion onto/into a
variety of ligand frameworks. In many cases, an otherwise innocent ligand has the ability to attain novel redox activity.\textsuperscript{21}

\begin{center}
\includegraphics[width=0.5\textwidth]{scheme1.png}
\end{center}

**Scheme 1.1:** Depiction of ferrocene as a one-electron redox system.

Depending on the metal centre, catalysis may be promoted where ancillary ligands are either oxidized or reduced. For example, Bielowski and coworkers have described the synthesis of a nickel complex with ligands containing the redox-active semiquinone moiety and used it in the catalysis of Kumada cross coupling reactions (Scheme 1.2, 1.3).\textsuperscript{22}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme2.png}
\end{center}

**Scheme 1.2:** Catalytic activity of a redox-active Kumada cross coupling catalyst.
The catalytic cycle can be regulated by the addition of cobaltocene (CoCp₂) and ferrocenium tetrafluoroborate ([FeCp₂][BF₄]). The addition of two equivalents of cobaltocene produces semiquinone radical anions on either ligand in the complex. With the resulting increase in electron-richness of the metal, catalysis is arrested. Two equivalents of ferrocenium tetrafluoroborate restores the catalytic activity by oxidizing the nickel complex (Scheme 1.2). In this case, catalysis is promoted by an oxidized ancillary ligand. Another example involving catalytic activity from an electron deficient metal centre was recently reported by Gibson and coworkers.²³ In this case, ferrocene was used as the redox-active substituent to the ligand framework. Lactide polymerization was facilitated upon oxidation of the ferrocene-containing framework by AgOTf (Scheme 1.3, 1.6). This resulting loss of electron density at the metal centre promotes polymerization. Reversible control of the catalysis was aided by the addition of two equivalents of ferrocene to produce the reduce the complex, forming compound 1.5, and thus halting activity (Scheme 1.3).

Scheme 1.3: Catalytic activity of a redox-active polymerization catalyst.
As previously mentioned, some catalytic reactions may require an electron-rich metal to facilitate the rate-determining step of the catalytic cycle. An early example by Plenio demonstrated how the incorporation of ferrocene as a substituent within a Grubbs-type catalyst can facilitate a ring-closing metathesis reaction, where oxidation causes the catalyst to precipitate from the reaction solution, enabling simple physical separation via filtration (Scheme 1.4, 1.7 and 1.8).²⁴

![Scheme 1.4: Catalytic activity of a redox-active olefin-metathesis catalyst.](image)

1.1.4 Non-Innocent Ligands Acting as Electron-Reservoirs

One of the most straightforward applications of non-innocent ligands in catalysis is their ability to function as electron-reservoirs. As previously mentioned, many important transformations in homogeneous catalysis are based on multi-electron processes (e.g. two-electron change involving reductive elimination, oxidative addition, etc.);¹ reactions of this type have been achieved by the use of expensive precious metals.
Low-born and first-row transition metals can be used in this manner if additional electrons can be stored (or released) from a ligand adjacent to the metal centre. This way, the catalyst can perform multi-electron transformations without the metal adopting an unfavourable oxidation state. There are many examples of non-innocent ligands behaving in this way. Scheme 1.5 shows a few such redox-active metal binding systems. Alpha-diimines were among the earliest, but not always clearly recognized, examples.2.20,25,26

Scheme 1.5: Representative structural changes from electron transfer to a few potentially redox-active ligands.

Diiminopyridine pincers were also quickly recognized as redox-active ligands by the Wieghardt group, and have now been extensively explored and harnessed as electron-reservoirs in catalytic applications.27 Chirik and co-workers have developed several iron and cobalt catalysts that illicit multi-electron redox chemistry assisted by the presence of a redox-active ligand based on diiminopyridine (Scheme 1.6).28,29 The diiminopyridine ligands have four accessible oxidation states and participate in redox reactions that enable the metal to mediate multiple electron processes. The Fe(II) complex (Scheme 1.6, 1.7) is reduced under dinitrogen with sodium amalgam to afford the diiminopyridine precatalyst (1.8). This ligand-centred reduction is critical for the iron-catalyzed [2+2] cycloaddition reaction of dienes as the reaction does not proceed in the presence of redox inactive ligands.

Although α-diimines have recently been highlighted for their non-innocent role in catalysis, extensive research into their synthesis and reactivity has been ongoing for decades. Of the variety of α-diimines known, the diiminopyridine and 1,3-diaza-1,4-butadiene classes will be important for the focus of this thesis (Figure 1.5 1.14 and 1.15). These ligands have proven to be excellent for supporting main group, transition metal and rare earth metal centres in a variety of oxidation states (uncommon and common).

Figure 1.5: Diiminopyridine and 1,3-diaza-1,4-butadiene α-diimine ligands.
1.2 Scope of Thesis

The following chapters will focus on the synthesis of nitrogen-based ligands that incorporate redox-active metallocene substituents about their framework. Initially, the incorporation of ferrocene about a diiminopyridine framework will be discussed (Chapter 2). The reactivity of the resulting ligand with phosphorus triiodide and a variety of chalcogen triflates (S, Se and Te) was then examined. The electrochemical properties of the free ferrocene-containing ligand and its complexes are also discussed.

The synthesis of low valent group 15 and 16 complexes with nitrogen-based ligand supports has been an area of interest within the last 10-15 years; however, examples of these systems with elaborate redox-active ligand supports have yet to debut. Chapter 3 focuses on the incorporation of an understudied cobalt-containing mixed sandwich metallocene onto the ligand framework of a diiminopyridine ligand. The electrochemical properties of this moiety unveil the possibility of inducing redox-activity onto an otherwise redox-inactive system. Comparative reactivity studies of this ligand and its redox-active ferrocene analogue with low oxidation state tetrel halides (Ge and Sn) are reported. This chapter also discusses the electrochemical properties of both metallocene ligands and their complexes.

Chapter 4 examines the synthesis of a new 1,4-diaza-1,3-butadiene ligand containing the same redox-active mixed sandwich presented in Chapter 3. Comparative reactivity studies of this ligand and its known ferrocene analogue with main group (Sn) and transition metal (Pt) centres was performed. Full investigations into the electrochemical properties of the ferrocene ligand and its complexes are discussed, where the cobalt-containing compounds were found to be unstable to the electrochemical conditions employed.

Chapter 5 details the synthesis of an N-heterocyclic carbene (NHC) and its silver complex utilizing the cobalt-containing 1,4-diaza-1,3-butadiene ligand introduced in Chapter 4.
From the conclusions of the above studies, steps towards the synthesis of an \(\alpha\)-diimine ligand that is able to harness the redox activity of the understudied mixed sandwich cobaltocene moiety are discussed.

1.3 References

(1) Lyakovskyy, V.; Bruin, Bas de *ACS Catal.*, **2012**, 2, 270-279.


Chapter 2

2 The Syntheses and Electrochemical Studies of a Ferrocene Substituted Diiminopyridine Ligand and its P, S, Se and Te Complexes

2.1 Introduction

In the past decade, there has been an interest in synthesizing monocationic and polycationic main group centred molecules to study the nature of their structure, bonding and reactivity. Although there are a variety of synthetic methods used to produce these species, nitrogen-based ligands have been the dominant support system for the cations.\(^1\)\(^2\) Many reports have focused on producing novel complexes using ligands where the substituents (alkyl or aryl) can be varied within the ligand framework; however, examples of these common supports that feature pendant redox-active (i.e., ferrocene) fragments are relatively rare (Figure 2.1). Transition metal based complexes containing redox-active ligands or ligands substituted with redox-active components have been used in a diverse array of applications including catalysis, optical materials, or in the manufacture of biological sensors.\(^3\)\(^-\)\(^5\) The appeal of ligands with redox-active functional groups stems from their ability to change the electronic properties of the central metal without the need for further synthetic modifications. This occurs by either varying an applied potential or introducing a chemical redox agent into a reaction, whereby an oxidation or reduction at ferrocene has the ability to “turn on” or “turn off” a particular molecule. Imparting redox-active species onto a ligand offers exciting opportunities within homogeneous transition metal catalysts, as the oxidation of the redox-active substituent induces a higher electrophilicity and, therefore, a change in reactivity of a catalytically active transition metal centre.\(^6\) In many cases, these ligands exhibit reversible redox processes, and therefore, enable ‘switchable’ control of the electronic properties of a central metal. The synthesis and reactivity of nitrogen-based ligands containing ferrocene pendant to the ligand framework have been published, but their chemistry largely remains unexplored. Of the few examples reported, studies have been limited to metals of the d-block.
Stephan et al. synthesized ferrocenyl amidinates of Ti or Zr in order to study
these ligands as possible redox tunable olefin polymerization catalysts (Figure 2.1, 2.0 and 2.1). In another report, a bis-ferrocenyl-β-diketiminate was synthesized and used to prepare Zn complexes that revealed unusual ‘non-innocent’ reactivity at the β-diketiminate ligand as opposed to the transition metal centre (Figure 2.1, 2.2 and 2.3). Bildstein et al. has focused their efforts on synthesizing a ferrocene-containing 1,4-diaza-1,3-butadiene ligand for the preparation of Cr, Mo and W complexes, with the intention of producing redox tunable olefin polymerization catalysts (Figure 2.1, 2.4). Gibson et al. has synthesized a diiminopyridine (DIMPY) ligand to complex Fe and Co centres, again with an eye toward effective switchable catalysts for olefin polymerization (Figure 2.1, 2.5). Another example by this group utilizes the bis(iminophenoxide) ligand framework and modifies it in such a way as to contain ferrocene moieties. The resulting Ti complex (Figure 2.1, 1.5) was used to show that activity can indeed be varied by redox switching of the ferrocenyl unit contained within the ligand backbone of a lactide polymerization catalyst by introduction of a chemical redox agent.

Recently, the nitrogen-based ligand set, diiminopyridine (Figure 2.1, 1.14), has been featured prominently in the isolation of cationic main group species. The Ragogna group has utilized the N, N'-aryl substituted versions to stabilize low valent dicaticonic chalcogen (Figure 2.1, 2.9-2.12) or monocationic phosphorus (Figure 2.1, 2.13-2.16) centres; however, there are no reports of utilizing nitrogen-based ligands that feature redox-active substituents in the stabilization of highly novel main group cations.

In this context, we report the synthesis, characterization and electrochemical behavior of a new DIMPY ligand (2.16), containing pendant ferrocenyl fragments on the imine nitrogens (Scheme 2.1, A). We have explored its reactivity with main group metals from groups 15 (P) and 16 (S, Se, Te), and furthermore, the electrochemistries of these compounds have been investigated. The electrochemical studies reveal the possibility of generating the putative tricationic phosphorus-centred species, and under the conditions employed this indicates that the polycation may be isolable. These results represent the first inroads into such redox-active main group compounds.
2.2 Results and Discussion

2.2.1 Synthesis

\( N, N' \)-diferrocenyldiiminopyridine (FcDIMPY; \textbf{2.18}) was prepared by the condensation reaction between aminoferrocene (\textbf{2.17}) and 2,6-pyridinedialdehyde\(^{30}\) in a 2:1 stoichiometry under an ethanol reflux (Scheme 2.1, A). A dark red-purple powder precipitated and was isolated using vacuum filtration. The solids were washed with cold ethanol and dried, and a sample of the bulk powder was redissolved in CDCl\(_3\). The \( ^1\text{H} \) NMR spectrum indicated the presence of six distinct signals: three in the aromatic region, consistent with protons on the DIMPY framework, and three for the monosubstituted ferrocene species that appeared to shift downfield relative to the aminoferrocene starting material (Table 2.1).

A solution of \textbf{2.18} in DCM was stirred with one stoichiometric equivalent of the appropriate chalcogen pseudohalide starting material (S(OTf)\(_2\), [(CyDAB)Se][OTf]\(_2\) and [(Dipp\(_2\)BIAN)Te][OTf]\(_2\)) in the same solvent at room temperature (Scheme 2.1, B). In all cases, colour changes from orange-red to a dark blue-green were immediately observed. Normal pentane and Et\(_2\)O were used to precipitate out the dark blue-green solids, which were then dried \textit{in vacuo}. The resulting \( ^1\text{H} \) NMR spectra of the redissolved solids in CD\(_3\)CN revealed downfield shifts (Table 2.1) for all resonances relative to the free ligand, indicative of coordination of the ligand to an electron deficient chalcogen centre. These compounds were tentatively assigned as the salts \textbf{2.19}, \textbf{2.20} and \textbf{2.21}. X-ray quality crystals of all compounds were grown, and subsequent X-ray diffraction experiments confirmed the identity of the solids, which were isolated in 65-80% yields.

<table>
<thead>
<tr>
<th>Compound</th>
<th>\textbf{2.18}</th>
<th>\textbf{2.19}</th>
<th>\textbf{2.20}</th>
<th>\textbf{2.21}</th>
<th>\textbf{2.22}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_\text{H} ) Imine, 2H</td>
<td>8.81</td>
<td>10.07</td>
<td>10.14</td>
<td>10.32</td>
<td>9.52</td>
</tr>
<tr>
<td>( \delta_\text{H} ) py-\textit{d}, 2H</td>
<td>8.21</td>
<td>9.02</td>
<td>8.94</td>
<td>8.84</td>
<td>8.63</td>
</tr>
<tr>
<td>( \delta_\text{H} ) py-\textit{t}, 1H</td>
<td>7.84</td>
<td>8.84</td>
<td>8.85</td>
<td>8.73</td>
<td>7.12</td>
</tr>
<tr>
<td>( \delta_\text{H} ) H\textit{p}-\textit{m}, 2H</td>
<td>4.71</td>
<td>5.52</td>
<td>5.55</td>
<td>5.55</td>
<td>5.52</td>
</tr>
<tr>
<td>( \delta_\text{H} ) H\textit{p}-\textit{m}, 2H</td>
<td>4.35</td>
<td>5.18</td>
<td>5.15</td>
<td>5.07</td>
<td>4.86</td>
</tr>
<tr>
<td>( \delta_\text{H} ) H\textit{c}-\textit{s}, 10H</td>
<td>4.21</td>
<td>4.53</td>
<td>4.52</td>
<td>4.48</td>
<td>4.57</td>
</tr>
</tbody>
</table>
Scheme 2.1: Synthetic routes to 2.18, 2.19, 2.20, 2.21 and 2.22. (See Appendix (A.1 and A.2) for NMR spectra).

The 1:1 stoichiometric addition of 2.18 with PI₃ underwent a similar colour transformation as was observed in the formation of the chalcogen salts (Scheme 2.1, C). Approximately 10 minutes after the addition of 2.18 to PI₃, the reaction mixture was sampled and analyzed by $^{31}$P{¹H} NMR spectroscopy. The formation of a single phosphorus peak at $\delta_P = 124$ as well as the disappearance of the peak for free PI₃ ($\delta_P = 178$) was noted. This shift is consistent with those that have been observed in other previously characterized P(I) DIMPY complexes. A solid green-black product was precipitated by the addition of a combination of $n$-pentane and Et₂O. The corresponding $^1$H NMR spectrum of the redissolved solids in CD₂Cl₂ showed a diagnostic doublet for
the imine protons ($\delta_{H} = 9.52$; $^3J_{P-H} = 2.8$ Hz), indicative of the successful incorporation of phosphorus into the ligand framework. On the basis of these multinuclear NMR spectroscopic data, the compound was tentatively assigned as being the DIMPY complex of the phosphorus salt 2.22. For further verification, suitable crystals for X-ray diffraction were grown, and subsequent diffraction experiments confirmed the identity of the compound as 2.22.

2.2.2 X-Ray Crystallography

The solid-state structure obtained from X-ray diffraction studies on single crystals of 2.18 confirmed the identity of a diiminopyridine ligand bearing ferrocene groups on the two nitrogen atoms (Figure 2.2). The carbon-nitrogen double bonds (C=N) are indicative of a diimine (C=N; 1.266(6) Å and 1.267(6) Å), and the remaining metrical parameters are consistent with the well-documented diiminopyridine framework. The solid-state structures of the corresponding main group complexes of 2.18 indicate the presence of the cationic phosphorus (2.22) or dicationic chalcogen centres (2.19, 2.20 and 2.21) within the $N, N', N''$ -DIMPY chelate (see Table 2.2 for salient bond lengths and angles, Figure 2.3 and Figure 2.4 for structural views, and Appendix (A.12) for X-ray table). For all species, the bonding within the diiminopyridine framework had little deviation from the previously reported $N, N'$-diisopropylphenyl (Dipp) derivatives (Figure 2.1, 2.9, 2.10, 2.11 and 2.13), demonstrating that the ferrocene groups did not alter the interaction between the ligand to the main group centre. In contrast to the Dipp derivatives that have bulky Aryl groups oriented perpendicular to the diiminopyridine plane, the ferrocene substituents in all species were coplanar with respect to the cyclopentadienyl ring bound at the nitrogen and the diiminopyridine contiguous rings. In all of the structures, the ferrocene groups were oriented anti to one another to minimize steric interactions, and as a result, all of the species have pseudo-$C_2$ symmetry through the E(1)–N(2)–C(4) axis (2.19 and 2.22 are perfectly $C_2$ symmetric). Compound 2.22 is disordered at the phosphorus centre, modeled with a 50% occupancy at both sites. In the case of 2.19, disorder arises from the presence of the other anti configuration of the complex. Compounds 2.19 and 2.22 lack sulfur-oxygen and phosphorus-iodine contacts within the sum of the van der Waals radii to either the triflate (cf. $\Sigma_{c.d.w.}$ S-O= 3.25 Å) or
the triiodide counterion \((cf. \Sigma_{v.d.W.} P-I= 3.88 \text{ Å})\). The closest contacts in 2.20 and 2.21 between the cation and anions lie on the edge of the sum of the van der Waals radii (2.20 Se···O= 3.367 Å \(cf. \Sigma_{v.d.W.} \text{ Se-O= 3.42 Å; } 2.21 \text{ Te···O= 3.068 Å } cf. \Sigma_{v.d.W.} \text{ Te-O= 3.58 Å}\)).\(^{24}\) Despite these distant contacts, all species are viewed as distinct cation–anion pairs, as there is no elongation of the related sulfur–oxygen bond in the triflate anion, indicative of ionic formulations.
Figure 2.2: Solid-state structures of the free ligand (2.18) from two different views. Thermal ellipsoids are drawn to the 50% probability interval and hydrogen atoms are removed for clarity.

Table 2.2: Selected bond lengths (Å) and angles (°) for 2.19, 2.20, 2.21, 2.22 and their analogues 2.9, 2.10, 2.11 and 2.13.

<table>
<thead>
<tr>
<th></th>
<th>2.19</th>
<th>2.9&lt;sup&gt;22&lt;/sup&gt;</th>
<th>2.20</th>
<th>2.10&lt;sup&gt;22&lt;/sup&gt;</th>
<th>2.21</th>
<th>2.11&lt;sup&gt;22&lt;/sup&gt;</th>
<th>2.22</th>
<th>2.13&lt;sup&gt;23&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(1)-N(1)</td>
<td>1.922(5)</td>
<td>1.9068(17)</td>
<td>2.068(2)</td>
<td>2.025(9)</td>
<td>2.230(3)</td>
<td>2.243(4)</td>
<td>2.275(3)</td>
<td>1.877(7)</td>
</tr>
<tr>
<td>E(1)-N(2)</td>
<td>1.709(7)</td>
<td>1.719(3)</td>
<td>1.872(2)</td>
<td>1.872(3)</td>
<td>2.068(3)</td>
<td>2.098(3)</td>
<td>1.724(4)</td>
<td>1.722(6)</td>
</tr>
<tr>
<td>E(1)-N(3)</td>
<td>1.922(5)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.9068(17)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.086(9)</td>
<td>2.025(9)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.208(3)</td>
<td>2.241(4)</td>
<td>1.777(3)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.975(8)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.287(8)</td>
<td>1.280(3)</td>
<td>1.291(3)</td>
<td>1.275(3)</td>
<td>1.285(4)</td>
<td>1.284(6)</td>
<td>1.313(4)</td>
<td>1.303(11)</td>
</tr>
<tr>
<td>C(7)-N(3)</td>
<td>1.287(8)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.280(3)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.284(3)</td>
<td>1.275(3)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.308(4)</td>
<td>1.313(4)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.316(11)</td>
<td></td>
</tr>
<tr>
<td>N(1)-E(1)-N(2)</td>
<td>82.60(17)</td>
<td>82.39(6)</td>
<td>79.22(9)</td>
<td>78.79(6)</td>
<td>73.81(12)</td>
<td>72.77(15)</td>
<td>73.90(11)</td>
<td>81.6(3)</td>
</tr>
<tr>
<td>N(2)-E(1)-N(3)</td>
<td>82.60(17)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>82.39(6)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>78.43(9)</td>
<td>78.79(6)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>74.42(12)</td>
<td>73.35(16)</td>
<td>88.52(14)</td>
<td>81.1(3)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Symmetry arising from the centrosymmetric nature of those marked compounds.
Figure 2.3: Solid-state structures of 2.19, 2.20, 2.21 and 2.22 viewed down the ligand basal plane. Thermal ellipsoids are drawn to the 50% probability level. Solvates, anions and hydrogen atoms are removed for clarity.

"Symmetry arising from the centrosymmetric nature of those marked compounds. "Disorder removed for clarity."
Figure 2.4: Solid-state structures of 2.19, 2.20, 2.21 and 2.22 viewed perpendicular to ligand basal plane. Thermal ellipsoids are drawn to the 50% probability level. Solvates, anions and hydrogen atoms are removed for clarity. a Disorder removed from 2.19.

\[2.19^a\]

\[2.20\]

\[2.21\]

\[2.22\]

\[a\] Symmetry arising from the centrosymmetric nature of those marked compounds. \[b\] Disorder removed for clarity.
2.2.3 Electrochemistry

Compounds 2.18, 2.22, 2.13 and the free Dipp ligand (Figure 2.1, 2.6) were characterized by cyclic voltammetry (CV) using 2 mM solutions in 5 mL of a DCM / 0.1 M TBAPF$_6$ electrolyte solution. The working electrode was a 1 mm platinum disk electrode. The counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl electrode. However, the voltammetric curves were all calibrated to the standard calomel electrode (SCE) using nitrobenzene as the internal standard.

Compound 2.18 (Figure 2.5, A) shows a reversible peak with $E^0$ at 0.73 V related to the two ferrocene moieties. The peak current is indicative of a two-electron process, showing that the two ferrocenes are being oxidized at the same or similar potential, suggesting little or no electronic interaction between them, as expected due to poor conjugation within the molecule. Similar redox behavior has been observed for other $N, N'$-diferrocenyl diazabutadiene type ligands. In the same potential window, compound 2.22 shows three oxidation peaks (Figure 2.5, C): Peak I with $E_{1/2}$ at 0.36 V is quasi-reversible and is a two-electron process. Peak II, appears as a shoulder, overlapping with peak III is a reversible one-electron process. Peak III, with $E^0$ at 0.94 V is a reversible two-electron process. To better understand the electrochemistry of 2.22, an analogous phosphorus complex, containing two Dipp substituents and a triiodide anion, was analyzed under identical experimental conditions (Figure 2.5, 2.13). This complex (Figure 2.5, B) shows two distinct electrochemical processes. The first is a quasi-reversible oxidation with $E_{1/2}$ at 0.36 V and involves two-electrons, and the second is a reversible one-electron peak with $E^0$ at 0.81 V. These two signals appear when nitrogen atoms of the ligand coordinate the phosphorus (see Appendix (A.1)) and are likely related to the loss of two electrons on the P(I) forming a P(III) centre during the first quasi-reversible process and the subsequent reversible oxidation of the ligand induced by complexation to P in the second one-electron reversible process, as these processes are not observed in the free ligand. The complete CV of this compound (See Appendix (A.7)) shows two other irreversible peaks at 2.00 V and 2.54 V due to the oxidation of the two Dipp groups, consistent with the observed electrochemistry for the free ligand (See Appendix (A.7)) where no other redox behavior is observed in the -0.5 to 2.0 V
range. The assignment of the voltammetric peaks I and II (Figure 2.5, C) obtained for the complex 2.22 is supported by comparison with the electrochemical data obtained for the aforementioned derivative (Figure 2.5, 2.13) where the first two oxidations are related to the coordination of the three nitrogens of the ligand to phosphorus. Peak III, the two-electron reversible peak, is absent from the CV of 2.13 and results from the oxidation of the two ferrocene groups present in 2.22. Relative to the free ligand (2.18), this signal is shifted slightly toward more positive potentials due to a loss in electron density from the ligand framework as a result of coordinating to the electron deficient phosphorus centre.

The electrochemistries of complexes 2.19, 2.20 and 2.21 were also investigated by cyclic voltammetry (See Appendix (A.8) for CVs). However, the poor solubility of these complexes and the reactivity of these chalcogen complexes with the electrochemical solvents and electrode materials made analysis more difficult. These compounds were found to be slightly soluble in MeCN / 0.05 M TBABF₄ as an electrolyte solution. Their CVs were recorded saturating the electrolyte solution with analyte. In these cases, the working electrode was a glassy carbon (GC) disk electrode. These CVs (See Appendix (A.8)), show the same general features, although broadened and less resolved as the voltammetric curve obtained for the complex 2.22, namely the quasi-reversible oxidation of the chalcogen-ligand followed by a two-electron oxidation of the ferrocene moieties.
Figure 2.5: From top to bottom, CV of 2.18 (A), 2.13 (B) and 2.22 (C) recorded at a Pt electrode in DCM / 0.1 M TBAPF$_6$ with analyte concentration of 2 mM and at 0.5 Vs$^{-1}$. Experiment carried out inside of an inert atmosphere glove box at room temperature.

2.3 Conclusions

Compounds 2.19, 2.20, 2.21 and 2.22 represent the first examples of group 15 and 16 salts utilizing a redox-active DIMPY ligand (2.18) containing pendant ferrocene functionalities. Cyclic voltammetric studies of the free ligand display a reversible two-electron process with $E^0$ at 0.73 V. A full data collection for the $N$, $N'$, $N''$-chelated chalcogen complexes remains somewhat inconclusive, due to the insolubility of these complexes. An electrochemical investigation of 2.22 was performed, showing three events: a quasi-reversible two-electron process for the production of a P(III) centred
cation with $E_{1/2}^{\text{Ep}}$ at 0.36 V, a second reversible one-electron process from the ligand framework which overlaps with a third two-electron process from the non-communicating ferrocenes ($E^0 = 0.94$ V).

2.4 Experimental

2.4.1 General Procedure

General synthetic, crystallographic and electrochemical experimental details can be found in Appendix 1. The syntheses of S(OTf)$_2$, CyDABSeOTf$_2$, Dipp$_2$BIANTeOTf$_2$, copper phthalimide, $N$-ferrocenyl phthalimide and 2,6-pyridinedialdehyde were prepared via published procedures. Iodoferrocene and 2.17 were prepared using modified published procedures. The electrochemical characterization of compounds 2.18 and 2.22 were carried out in a 5 mL DCM / 0.1 M TBAPF$_6$ (tetrabutylammonium hexafluorophosphate) electrolyte solution containing the appropriate analyte (2 mM) and using the platinum electrode as a working electrode. The electrochemical characterization of compounds 2.19, 2.20 and 2.21 were carried out in a 5 mL MeCN / 0.05 M TBABF$_4$ (tetrabutylammonium tetrafluoroborate) electrolyte solution saturated with the analyte. For these measurements, a glassy carbon working electrode was used.

2.4.2 Synthetic Procedure

**Iodoferrocene:**

A 500 mL Schlenk flask equipped with a large stir bar was charged under a nitrogen atmosphere with ferrocene (8.00 g, 0.043 mol), $t$BuOK (0.48 g, 0.0043 mol) and 300 mL of THF. The orange-yellow solution was cooled to -78 °C; some of the dissolved ferrocene precipitated during this process. Under rigorous stirring, $t$BuLi (25 mL, 0.043 mol) 1.7 M in $n$-hexane, was added drop-wise over 1 hour. The addition was complete after 20 minutes at which time the cold bath was removed and the reaction mixture was allowed to warm to room temperature then stirred for an additional 2 hours. The colour of the reaction mixture changed from opaque orange to red-orange to a dark clear red. The reaction mixture was once again cooled to -78 °C, and under vigorous stirring, I$_2$ (12.00 g, 0.0473 mol) was added in one portion. The cold bath was removed, and the mixture was allowed to warm to room temperature,
stirring continued for 12 hours. The mixture was then first diluted with 200 mL of Et₂O, then washed with portions of saturated aqueous Na₂SO₃ (2 × 100 mL), H₂O (3 × 150 mL), and dried with MgSO₄. The solvent was removed by rotary evaporation to yield the crude product as a yellow-brown oil (8.62 g, 0.026 mol, 60 %), which solidified upon storing in a freezer overnight. Spectroscopic properties were in agreement with published values.³³,³⁴ Unreacted ferrocene was present in the crude product; however, its presence did not affect onward chemistry, and was therefore used without further purification. The relative ¹H signal ratios (ferrocene: iodoferrocene) were examined in order to determine the amount of pure iodoferrocene per gram of crude solid to be used in future transformations.

**Compound 2.17:**

To a 500 mL round bottom Schlenk flask, degassed, anhydrous ethanol (100 mL) was added to a slurry of N-ferrocenyl phthalimide²⁹ (5.99 g, 0.018 mol) and hydrazine monohydrate (0.873 mL, 0.018 mol). The clear yellow solution was refluxed under N₂ for 2.5 hours. The mixture was then cooled to room temperature. Degassed H₂O was added (200 mL) and the product was extracted with Et₂O. The yellow organic layer was dried over MgSO₄, the supernatant transferred to a Schlenk tube, and evaporated *in vacuo* to dryness, yielding a bright yellow-orange powder (2.57 g, 0.012 mol, 68 %). Impurities were removed by sublimation under a dynamic vacuum at 60 °C (cold finger at -15 °C). The product was stored under an inert atmosphere of N₂. Aminoferrocene prepared according to the above procedure showed spectroscopic properties consistent with those previously published.³⁵

**Compound 2.18:**

Mixtures of 2.17 (1.91 g, 9.48 mol), degassed ethanol (50 mL) and 2,6-pyridinedialdehyde³⁰ (0.636 g, 4.72 mmol) were refluxed under an inert atmosphere for 12 hours with constant stirring. The product was collected by filtration, washed with cold ethanol (2 × 50 mL), and dried *in vacuo* to give a fine dark red-purple powder.
Yield: 89 % (2.10g, 4.20 mmol);
M.p.: 223-230 °C;
$^1$H NMR (CDCl$_3$, δ): 8.81 (s, 2 H), 8.21 (d, 2 H, $^3$J$_{H-H}$= 7.6 Hz), 7.84 (t, 1 H, $^3$J$_{H-H}$= 7.6 Hz), 4.71 (m, 4 H), 4.35 (m, 4 H), 4.21 (s, 10 H);
$^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 156.37, 154.11, 136.10, 120.66, 102.27, 68.77, 67.02, 62.62;
UV/Vis (DCM): $\lambda_{max}$ = 319.9 nm;
FT-IR (cm$^{-1}$ (ranked intensity)): 1579(13), 1561(4), 1462(6), 1348(14), 1232(11), 1106(3), 1040(15), 1001(7), 962(8), 927(5), 804(1), 738(12), 523(10), 491(2), 456(9);
FT-Raman (cm$^{-1}$ (ranked intensity)): 1616(1), 1580(2), 1458(4), 1376(12), 1273(5), 1229(3), 1110(8), 990(6), 670(11), 642(14), 585(13), 334(10), 283(9), 162(15);
Elemental analysis: Calc for C$_{27}$H$_{23}$N$_3$Fe$_2$: 64.71 % C, 4.63 % H, 8.38 % N; Found: 64.47 % C, 4.67 % H, 8.34 % N.

Compound 2.19:

A solution of 2.18 (150.0 g, 0.299 mmol) in DCM (3 mL) was added dropwise to a solution of S(OTf)$_2$ (0.076 g, 0.229 mmol) in DCM (3 mL) at room temperature. The product was precipitated by the addition of n-pentane (3 × 10 mL) and Et$_2$O (3 × 10 mL) and dried in vacuo to give a dark blue-green fine powder. Single crystals were obtained via vapour diffusion of Et$_2$O in MeCN.

Yield: 70 % (0.133 g, 0.160 mmol);
D.p.: 120-130 °C;
$^1$H NMR (CD$_3$CN, δ): 10.07 (s, 2 H), 9.02 (d, 2 H, $^3$J$_{H-H}$= 7.8 Hz), 8.85 (t, 1 H, $^3$J$_{H-H}$= 7.8 Hz), 5.52 (m, 4 H), 5.18 (m, 4 H), 4.53 (s, 10 H);
UV/Vis (MeCN): $\lambda_{max}$ = 260.0 nm;
FT-IR (cm$^{-1}$ (ranked intensity)): 3071(10), 1617(9), 1573(15), 1553(11), 1515(4), 1403(7), 1266(1), 1227(14), 1179(5), 1027(2), 817(8), 636(3), 574(12), 518(13), 484(6);
FT- Raman (cm$^{-1}$ (ranked intensity)): 1614(9), 1547(3), 1511(1), 1499(11), 1400(2), 1294(13), 1231(5), 1090(8), 1064(15), 1043(14), 628(4), 493(7), 296(3), 332(10), 120(12);
HRMS: C_{29}H_{23}N_{3}Fe_{2}Se_{1}O_{6}S_{2}F_{6} Calc (Found): 681.9832 (681.9846).

**Compound 2.20:**

A solution of 2.18 (0.227 g, 0.453 mmol) in DCM (3 mL) was added dropwise to a solution of CyDABSeOTf_{2}^{26} (0.266 g, 0.453 mmol). The product was then precipitated by the addition of n-pentane (3 × 10 mL) and Et_{2}O (3 × 10 mL) and dried in vacuo to give a dark green-blue powder. Single crystals were obtained via vapour diffusion of Et_{2}O in MeCN.

**Yield:** 68 % (0.270 g, 0.308 mmol);

**D.p.:** 205-212 °C;

**^{1}H NMR (CD_{3}CN, δ):** 10.14 (s, 2H), 8.94 (d, 2H, 3J_{H-H}= 7.8 Hz), 8.85 (t, 1H, 3J_{H-H}= 7.8 Hz), 5.55 (m, 4 H), 5.15 (m, 4 H), 4.52 (s, 10 H);

**UV/Vis (MeCN):** λ_{max}= 314.9 nm;

**FT-IR (cm^{-1} (ranked intensity)):** 3058(13), 1607(10), 1573(12), 1549(9), 1512(3), 1407(7), 1267(1), 1221(15), 1169(6), 1028(4), 820(11), 635(2), 571(14), 513(8), 484(5);

**FT-Raman (cm^{-1} (ranked intensity)):** 2005(15), 1608(10), 1549(2), 1512(1), 1407(3), 1241(4), 1222(6), 1085(13), 1035(12), 629(5), 495(9), 394(14), 324(11), 295(8), 285(7);

**Elemental analysis:** Calc for C_{29}H_{23}N_{3}Fe_{2}Se_{1}O_{6}S_{2}F_{6}: C 39.66, H 2.49, N 4.78, S 7.30; Found: C 38.97 H 2.49, N 4.76, S 6.84.

**Compound 2.21:**

2.18 (0.079 g, 0.157 mmol) in DCM (3 mL) was added dropwise to a solution of Dipp_{2}BIANTeOTf_{2}^{27} (0.145 g, 0.157 mmol) in DCM (3mL). The product was then immediately precipitated and washed by the addition of n-pentane (3 × 10 mL) and Et_{2}O (3 × 10 mL), and dried in vacuo to give a dark blue-green fine powder. Single crystals were obtained via vapour diffusion of Et_{2}O in MeCN.
Yield: 65 % (0.095 g, 0.102 mmol);
D.p.: 115-121 °C;
$^1$H NMR (CD$_3$CN, δ): 10.32 (s, 2 H), 8.84 (d, 2 H, $^3$J$_{H-H}$= 7.8 Hz), 8.73 (t, 1 H, $^3$J$_{H-H}$= 7.8 Hz), 5.55 (m, 4 H), 5.07 (m, 4 H), 4.48 (s, 10 H);
UV/Vis (MeCN): $\lambda_{\text{max}}$ = 255.0 nm;
FT-IR (cm$^{-1}$ (ranked intensity)): 3052(13), 1606(9), 1572(7), 1544(11), 1506(4), 1436(15), 1410(5), 1268(1), 1225(10), 1029(2), 797(6), 636(3), 572(8), 517(14), 484(12);
FT-Raman: (cm$^{-1}$ (ranked intensity)): 2137(13), 2000(14), 1571(15), 1543(2), 1508(1), 1409(3), 1241(4), 1220(5), 1067(12), 1029(8), 630(6), 497(10), 321(11), 296(7), 284(9);
HRMS: C$_{28}$H$_{23}$N$_3$Fe$_2$Te$_1$O$_3$S$_1$F$_3$ Calc (Found): 779.91737 (779.91706);
Elemental analysis: Calc for C$_{29}$H$_{23}$N$_3$Fe$_2$Te$_1$O$_6$S$_2$F$_6$: 37.58 % C, 2.50 % H, 4.53 % N, 6.92 % S; Found: 37.08 % C, 2.19 % H, 4.54 % N, 6.31 % S.

Compound 2.22:

A mixture of 2.18 (0.150 g, 0.299 mmol) in DCM (3 mL) was added dropwise to a solution of PI$_3$ (0.123 g, 0.299 mmol) in DCM (3 mL) at room temperature and was allowed to stir for 10 minutes. The product was precipitated by the addition of n-pentane (3 × 10 mL) and Et$_2$O (3 × 10 mL) and dried in vacuo to give a dark green-black fine powder.

Yield: 80 % (0.218 g, 0.239 mmol);
D.p.: 228-233 °C;
$^1$H NMR (CD$_3$CN, δ): 9.52 (d, 2H), 8.63 (d, 2H, $^3$J$_{H-H}$= 7.8 Hz), 8.12 (t, 1H, $^3$J$_{H-H}$= 7.8 Hz), 5.52 (m, 4H), 4.86 (m, 4H), 4.57 (s, 10H);
$^{31}$P NMR (CD$_3$CN, δ): 123.99;
UV/Vis (DCM): $\lambda_{\text{max}}$ = 285.1 nm;
FT-IR (cm$^{-1}$ (ranked intensity)): 3081(7), 1628(14), 1459(15), 1407(8), 1375(10), 1335(4), 1242(11), 1104(6), 1025(3), 1001(13), 934(12), 820(2), 769(5), 708(9), 499(1);
FT-Raman (cm\(^{-1}\) (ranked intensity)): 3101(10), 1627(6), 1572(2), 1497(9), 1451(5), 1373(7), 1239(4), 1105(12), 1055(11), 831(15), 641(3), 478(13), 298(8), 163(14), 110(1);

**HRMS:** C\(_{27}\)H\(_{23}\)N\(_3\)Fe\(_2\)P\(_1\) Calc (Found): 532.03290 (532.03176);

**Elemental analysis:** Calc for C\(_{27}\)H\(_{23}\)N\(_3\)Fe\(_2\)P\(_1\): 35.52 % C, 2.54 % H, 4.60 % N; Found: 35.55 % C, 2.43 % H, 4.78 % N.

**2.5 References**


Chapter 3

3 A Novel Diiminopyridine Ligand Containing Redox-Active Co(III) Mixed Sandwiches

3.1 Introduction

Tunable catalysis by way of redox-active ligands is a vast area with many different approaches for achieving control over a catalytic process. 1-6 Substitutionally inert redox-switchable ligands (or redox switches) are a category of ligand sets that form strong inert bonds to a given transition metal and are resistant to ligand exchange, as well as undergo controlled redox process(es) suitable for metal centred reactivity. These systems have recently shown promise as redox switches, where changes in the oxidation state of the ligand affect the reactivity of the metal by altering its electronic nature without changing its formal oxidation state (Scheme 3.1). 6

Scheme 3.1: Schematic of substitutionally inert, redox-active ligands.

The redox activity originates from the incorporation of a functional group that can be readily oxidized/reduced reversibly either chemically or electrochemically and can include organic (e.g., hydroquinone (3.0), 7 naphthoquinone (3.1), 8 quinoxaline (3.2), 9 nicotinamide (3.3) 10-11) as well as organometallic substituents (e.g. ferrocene(1.1)) onto an otherwise redox-inert ligand framework (Figure 3.1).

Figure 3.1: A few redox-active moieties that have been used to impart redox activity onto substitutionally inert redox-switchable ligands.
Ferrocene is often utilized as the redox-active component because of its very well established electrochemical characteristics and for the stability of the sandwich complex in the oxidized and reduced states (Fe(II)/Fe(III)). Useful ligand frameworks that include ferrocene as an appendage are often nitrogen-based (Figure 3.2, 3.4-3.8), where a few of these systems have proven to be useful for their ability to turn catalytically active complexes either ‘on’ or ‘off’ depending on the oxidation state of the ferrocene unit.12-16

**Figure 3.2:** Nitrogen-based ligands containing redox-active ferrocene substituents.

A variety of other metalloccenes have also been incorporated into redox-active ligands to support transition metals, where the metalloccene framework is affixed with pendant donor atoms. Aside from ferrocene, cobaltocene has been successfully employed as the redox-active component (Figure 3.3, 3.9-3.12).17 Wrighton et al. synthesized a redox-active 1,1’-bis(diphenylphosphino)cobaltocene ligand (Figure 3.3, 3.12) capable of reversibly controlling the Rh(I)-catalyzed reduction and isomerization of ketones and alkenes by a ligand centred oxidation or reduction.18,19

The cobaltocene/cobaltocenium ligands (3.9-3.12) are found to be either formally neutral, containing 19 electrons, or cationic 18 electron complexes. The 19 electron cobaltocenes are highly reactive and readily oxidize to take on a more stable electronic configuration; however, the resulting 18 electron salts generally have poor solubility. These are complicating factors when attempting to both synthesize the cobalt-containing ligands themselves as well as utilizing such fragments in subsequent chemistry.
Therefore, to employ Co in such applications it would seem more favourable to construct a neutral, 18 electron complex, which would enhance solubility and overall stability of the ligands. In this context, we now describe the synthesis of a novel diiminopyridine ligand containing two mixed sandwich cobaltocene functionalities, unveil its reactivity with the tetrels (M= Ge, Sn), and comparatively discuss the electrochemistries of the free ligand and its $N, N', N''$-$M$(II) chelates to their ferrocene analogues (Figure 3.3 for free ligand, 2.18).

3.2 Results and Discussion

3.2.1 Synthesis

Compound 3.16 was treated with 2,6-pyridinedialdehyde in a 1:2 stoichiometry at reflux in THF for 1.5 hours, over which time the clear dark orange solution became opaque, bright orange. The slurry was then cooled to room temperature, centrifuged, and the resulting orange precipitate was washed. The volatiles were removed in vacuo
yielding a bright orange solid that was sparingly soluble in most common organic solvents. A portion of the bulk solid was suspended in CDCl₃, and a ¹H NMR spectrum was acquired. The insolubility of the compound made it difficult to assign peaks associated with the DIMPY framework; however, a diagnostic downfield shift from cyclopentadienyl (Cp) protons (δ_H = 4.94 and 4.75 ppm) relative to the starting material (3.16) (δ_H = 4.38 and 4.12 ppm) was apparent (Figure 3.4, top). High-resolution mass spectrometry was performed to further identify the product with an m/z = 1090.2972 corresponding to the expected m/z of a protonated DIMPY ligand containing pendant mixed sandwich cobaltocene functionalities (cf. calculated 1090.2976). These results as well as those from the ¹H NMR spectrum led to the temporary assignment of the product as 3.17 (Scheme 3.2).

**Scheme 3.2**: Synthetic route to 3.17.

Compound 3.17 was then reacted with GeCl₂•dioxane at room temperature in a 1:2 stoichiometric ratio. The orange slurry immediately gave rise to a dark green-blue solution. After 1 hour, the solvent was removed in vacuo and the crude product was washed by adding a minimal amount of MeCN and precipitating a green-black solid upon the addition of Et₂O. An aliquot of the precipitate was redissolved in CD₂Cl₂ and the ¹H NMR spectrum displayed downfield shifts for all protons relative to the free ligand, and was consistent with findings for compound 3.17 binding to a metal centre (Scheme 3.3, 3.28; Table 3.1 for chemical shifts). A welcome improvement in the solubility of this product relative to the sparingly soluble starting material was noted (Figure 3.4, middle). The cyclopentadienyl signals appear broad in comparison to the resonances of related systems and are likely a result of steric restrictions introduced by the formation of the N, N’, N”-chelated cationic Ge(II) centre, and an attenuation of the free rotation of the CbCoCp fragment. This is especially pronounced for Cp protons.
located on carbons β to the imine-nitrogen atoms, where the signal at 5.33 ppm appears as a broad doublet (Figure 3.4, middle).

Figure 3.4: $^1$H NMR spectra for compounds 3.17, 3.18, 3.19 from top to bottom in CD$_2$Cl$_2$ on a 400 MHz spectrometer showing an increase in solubility from free ligand (3.17) to Ge (3.18) and Sn (3.19) complexes. Inset: imine protons on 3.19 at $\delta_H = 7.68$. Proton NMR Spectra for 3.19 were obtained on 400 and 600 MHz to confirm the presence of $^{119}$Sn satellites (400 MHz $\delta_H = 7.64$; $^3J_{Sn-H} = 32.0$ Hz).

Compound 3.17 was also treated with SnCl$_2$ at room temperature in a 1:2 stoichiometric ratio. After 12 hours the resulting dark brown-black slurry was centrifuged, the eluent was decanted and dried in vacuo to yield a dark blue-black solid. A portion of the solid was redissolved in CD$_2$Cl$_2$, with a drastic improvement in solubility once again noted. The resulting $^1$H NMR spectrum revealed diagnostic tin coupling for imine protons ($\delta_H = 7.68$; $^3J_{Sn-H} = 32.0$ Hz; Figure 3.4, bottom).
Cyclopentadienyl protons $\beta$ to imine nitrogens once again appear broad relative to those in similar systems. These findings, which agree with published studies involving similar systems, led to the tentative assignment of the $N, N', N''$-chelating cationic Sn(II) complex (Scheme 3.3, 3.19; Table 3.1 for chemical shifts).

Scheme 3.3: Synthetic route to 3.18 and 3.19.

In order to conduct a comparative electrochemical study on these unique cobaltocene containing compounds, analogues of the group 14 complexes with the previously reported $N, N'$-diferrocenyl diiminopyridine ligand (Scheme 3.4, 2.18) were prepared. The ligand (2.18) was treated separately with either GeCl$_2$$\cdot$dioxane or SnCl$_2$ in a 1:2 stoichiometric ratio in THF at room temperature. After 5 minutes the initially red solutions turned dark green-blue. The solvent was removed in vacuo to yield a lustrous green or blue solid for Ge and Sn, respectively. Both compounds were redissolved in CD$_3$CN and the $^1$H NMR spectra displayed downfield shifts for all protons relative to the free ligand (Table 3.1). In both cases, signals associated with protons para- to the nitrogen on the pyridine ring shift downfield relative to protons at the meta- position. A room temperature solution-state $^{119}$Sn$\{^1$H$\}$ NMR spectrum was also obtained for 3.21, consisting of two singlets ($\delta= -262.56$ and $-482.42$), which are consistent with a cationic {SnCl} and an anionic {SnCl$_3$} fragment, respectively. These combined data led to the tentative assignment of the given solids as 3.20 and 3.21 (Scheme 3.4, See Appendix (A.3) for NMR spectra of compounds 2.18, 3.21 and 3.22).
Scheme 3.4: Synthetic route to 3.20 and 3.21.

Table 3.1: $^1$H NMR chemical shifts (ppm) for 2.18, 3.18, 3.19, 3.20 and 3.21 in CD$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2.18</th>
<th>3.18</th>
<th>3.19</th>
<th>3.20</th>
<th>3.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_H$ Imine, 2H</td>
<td>8.81</td>
<td>7.56</td>
<td>7.64</td>
<td>9.13</td>
<td>9.18</td>
</tr>
<tr>
<td>$\delta_H$ py- d, 2H</td>
<td>8.21</td>
<td>7.80</td>
<td>7.72</td>
<td>8.21</td>
<td>8.17</td>
</tr>
<tr>
<td>$\delta_H$ py- t, 1H</td>
<td>7.84</td>
<td>8.64</td>
<td>8.59</td>
<td>8.56</td>
<td>8.52</td>
</tr>
<tr>
<td>$\delta_H$ H$_a$- m, 2H</td>
<td>4.71</td>
<td>5.10</td>
<td>5.26</td>
<td>5.21</td>
<td>5.13</td>
</tr>
<tr>
<td>$\delta_H$ H$_b$- m, 2H</td>
<td>4.35</td>
<td>3.33</td>
<td>4.99</td>
<td>4.83</td>
<td>4.79</td>
</tr>
<tr>
<td>$\delta_H$ H$_c$- s, 10H</td>
<td>4.21</td>
<td>--</td>
<td>--</td>
<td>4.39</td>
<td>4.42</td>
</tr>
<tr>
<td>$\delta_H$ PhH- m, 16H</td>
<td>--</td>
<td>7.33</td>
<td>7.32</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\delta_H$ PhH- m, 8H</td>
<td>--</td>
<td>7.18</td>
<td>7.19</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\delta_H$ PhH- m, 16H</td>
<td>--</td>
<td>7.12</td>
<td>7.12</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

3.2.2 X-Ray Crystallography

Suitable single crystals of 3.18, 3.19, 3.20 and 3.21 were obtained by vapour diffusion of DCM into hexane at 243 K (See Figures 3.5-Figure 3.8 for structural views, and Appendix (A.13) for X-ray table). Attempts to crystallize 3.17 by conventional techniques have thus far been met with failure due to the sparingly soluble nature of this compound. However from the solid-state structures of 3.18 and 3.19, any doubt of the identity of 3.17 is obviated. The molecular structures of all compounds reveal one cation consisting of a metal centre (Sn or Ge) supported by a tridentate diiminopyridine ligand and one chlorine atom. The nature of the ligand for 3.18 and 3.19 successfully revealed the anticipated diiminopyridine framework containing pendant, neutral, mixed sandwich cobaltocenes. Imine bond lengths were consistent with those previously reported for diiminopyridine based frameworks (1.275(6), 1.276(6) for 3.18 and 1.274(3), 1.280(3) for 3.19, cf. 1.26-1.29). The cation of all compounds adopted a distorted square pyramidal geometry. The deviation from planarity was more prominent in the Sn
complexes (3.19 and 3.21), where the metal centre prefers to lie below the ligand plane (-0.1577 Å for 3.18, -0.5275 Å for 3.19, -0.1577 Å for 3.20, and -0.3284 Å for 3.21). Even with this deviation, pyridyl nitrogens (N(2)) interact more strongly with main group centres than other imine nitrogens in the chelate (N(1) and N(3)). In all cases, the bound chlorine atom was oriented perpendicular to the ligand framework. Each cation is paired with a trigonal pyramidal MCl$_3^-$ anion (M= Ge or Sn). The bonding arrangements of these compounds show little deviation from those previously reported by Roesky and co-workers who initially investigated the formation of such complexes utilizing a 2,6-diacetylpyridinebis(2,6-diisopropylaniline) ligand support (See Figure 3.3. 3.13-3.15 for structural views, and Table 3.4 for salient bond lengths and angles for comparison). Other than 3.19, all metallocene substituents prefer to rest syn relative to the diiminopyridine framework. This can be explained upon examining the N-M(1)-Cl(1) bond angles. In the case of 3.19, the N(1)-Ge(1)-Cl(1) is much less than in the other compounds, causing the Cl(1) atom to lean slightly towards the N(1) side of the molecule, resulting in the mixed sandwich on N(1) to lie anti to the ligand plane. In addition, the Ge-Cl bond length is shorter than that of the Sn-Cl bond thus allowing the Cl atom to fit under the phenyl groups present on the Cb ring more easily. It is interesting to note that the Cp rings bound directly to imine nitrogens are found out of plane with respect to the ligand basal plane. This is unusual, as past examples depict the Cp rings lying preferentially in a conjugated linear plane along side of the diiminopyridine framework, but can be explained by the addition steric restrictions posed by the Cl(1) atom.
**Figure 3.5:** Solid-state structures of 3.18 from two different views. Thermal ellipsoids are drawn to the 50 % probability interval. Solvates, anions and hydrogen atoms are removed for clarity.

**Figure 3.6:** Solid-state structures of 3.19 from two different views. Thermal ellipsoids are drawn to the 50 % probability interval. Solvates, anions and hydrogen atoms are removed for clarity.
Figure 3.7: Solid-state structures of 3.20 from two different views. Thermal ellipsoids are drawn to the 50 % probability interval. Solvates, anions and hydrogen atoms are removed for clarity.

Figure 3.8: Solid-state structures of 3.21 from two different views. Thermal ellipsoids are drawn to the 50 % probability interval. Solvates, anions and hydrogen atoms are removed for clarity.
Table 3.2: Bond lengths (Å) and bond angles (°) for 3.18, 3.19, 3.20, 3.21 and their analogues 3.14 and 3.15.

<table>
<thead>
<tr>
<th></th>
<th>3.14(^{22})</th>
<th>3.15(^{22})</th>
<th>3.18</th>
<th>3.19</th>
<th>3.20</th>
<th>3.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)-N(1)</td>
<td>2.255(2)</td>
<td>2.403(2)</td>
<td>2.271(4)</td>
<td>2.451(4)</td>
<td>2.297(4)</td>
<td>2.495(2)</td>
</tr>
<tr>
<td>M(1)-N(2)</td>
<td>2.071(2)</td>
<td>2.286(2)</td>
<td>2.052(4)</td>
<td>2.295(4)</td>
<td>2.064(4)</td>
<td>2.271(2)</td>
</tr>
<tr>
<td>M(1)-N(3)</td>
<td>2.267(2)</td>
<td>2.411(2)</td>
<td>2.251(4)</td>
<td>2.422(4)</td>
<td>2.316(4)</td>
<td>2.408(2)</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.275(2)</td>
<td>1.274(3)</td>
<td>1.294(6)</td>
<td>1.299(6)</td>
<td>1.275(6)</td>
<td>1.283(3)</td>
</tr>
<tr>
<td>C(7)-N(3)</td>
<td>1.277(2)</td>
<td>1.280(3)</td>
<td>1.284(6)</td>
<td>1.294(6)</td>
<td>1.276(6)</td>
<td>1.281(3)</td>
</tr>
<tr>
<td>M(2)-Cl(2)</td>
<td>2.3100(8)</td>
<td>2.4801(8)</td>
<td>2.2998(18)</td>
<td>2.482(1)</td>
<td>2.258(2)</td>
<td>2.4621(10)</td>
</tr>
<tr>
<td>M(2)-Cl(3)</td>
<td>2.3246(9)</td>
<td>2.5190(9)</td>
<td>2.3116(19)</td>
<td>2.501(1)</td>
<td>2.330(2)</td>
<td>2.446(6)</td>
</tr>
<tr>
<td>M(2)-Cl(4)</td>
<td>2.3128(9)</td>
<td>2.4870(8)</td>
<td>2.2911(17)</td>
<td>2.522(1)</td>
<td>2.305(2)</td>
<td>2.479(10)</td>
</tr>
<tr>
<td>N(1)-M(1)-Cl(1)</td>
<td>87.18(5)</td>
<td>86.18(6)</td>
<td>89.45(11)</td>
<td>86.50(10)</td>
<td>84.30(11)</td>
<td>86.62(5)</td>
</tr>
<tr>
<td>N(2)-M(1)-Cl(1)</td>
<td>94.25(6)</td>
<td>88.31(6)</td>
<td>96.50(13)</td>
<td>92.28(11)</td>
<td>94.68(11)</td>
<td>97.35(6)</td>
</tr>
<tr>
<td>N(3)-M(1)-Cl(1)</td>
<td>88.09(5)</td>
<td>85.59(6)</td>
<td>88.65(12)</td>
<td>85.53(10)</td>
<td>90.24(10)</td>
<td>83.56(6)</td>
</tr>
<tr>
<td>N(1)-M(1)-N(2)</td>
<td>73.52(7)</td>
<td>68.71(7)</td>
<td>73.59(16)</td>
<td>68.81(14)</td>
<td>73.78(15)</td>
<td>67.72(7)</td>
</tr>
<tr>
<td>N(2)-M(1)-N(3)</td>
<td>73.28(7)</td>
<td>68.79(7)</td>
<td>73.99(16)</td>
<td>68.82(14)</td>
<td>73.63(15)</td>
<td>69.17(7)</td>
</tr>
<tr>
<td>N(1)-M(1)-N(3)</td>
<td>145.99(7)</td>
<td>136.87(7)</td>
<td>147.08(16)</td>
<td>136.44(14)</td>
<td>146.35(14)</td>
<td>133.97(7)</td>
</tr>
</tbody>
</table>
3.2.3 Electrochemistry

It was not possible to characterize compounds 3.17, 3.18 and 3.19 because of either their extremely poor solubility in MeCN, or their electrochemical instability in DCM leading to irreproducible results from electrode fouling. It was possible to characterize the ligand precursor, 3.16. The CV was recorded in DCM / 0.1 M TBAPF₆ and using a Pt disk electrode as the working electrode (Figure 3.9). From examining the CV, a chemically reversible two-electron oxidation peak was observed at 0.98 V and with $E^0= 0.87$ V; the signal was chemically reversible at scan rates higher than 1 V s⁻¹, while at lower scan rates it was irreversible. In cases where the potential vertex was more positive than 1.45 V additional unresolved oxidations occurred and then it was no longer possible to observe the corresponding reduction of the reversible reduction peak at 0.75 V in the reverse scan; compound 3.16 decomposed at potentials higher than 1.45 V.

![Cyclic voltammograms of 2 mM solutions of 3.16 recorded at a Pt electrode in DCM / 0.1 M TBAPF₆ at 5 V/s.](image)

Figure 3.9: Cyclic voltammograms of 2 mM solutions of 3.16 recorded at a Pt electrode in DCM / 0.1 M TBAPF₆ at 5 V/s.
Compound 3.21 was characterized by cyclic voltammetry (CV). The electrochemical experiment was carried out in 5 mL of MeCN / 0.1 M TBAPF$_6$ electrolyte solution. In this case, the working electrode was a GC disk and the reference was a quasi-reference Ag/AgCl electrode (for more details see experimental session). The CV of 3.21 recorded at 0.5 V s$^{-1}$ of scan rate (Figure 3.10) shows a one-electron chemically reversible peak at -0.46 V with a standard potential of $E^0 = -0.43$ V, which is most likely related to a reduction about the cationic metal centre. The same CV also shows an apparent two-electron chemically reversible peak in the oxidation at 1.03 V, which is related to the consecutive oxidation of the two ferrocenes belonging to the DIMPY ligand at very similar oxidation potentials. By changing the electrolyte from TBAPF$_6$ to tetraoctylphosphonium tetrakis(pentafluorophenyl)borate (P$_{8888}$TB) allows us to better distinguish the two overlapping oxidation peaks of the two ferrocene moieties (Figure 3.11).

![Figure 3.10: CV of 3.21 recorded at a GC electrode in MeCN / 0.1 M TBAPF$_6$ with analyte concentration 2 mM and at 0.5 V s$^{-1}$.](image)

Figure 3.11 shows the CVs recorded at different scan rates for the oxidation of the ferrocenes in P$_{8888}$TB as the electrolyte, and more clearly shows two overlapping
consecutive one-electron oxidations of the two ferrocene moieties with oxidation peaks at 0.88 V and 0.96 V at 0.1 Vs$^{-1}$, respectively. This is in line with what was previously observed with other low valent main group complexes supported by a $N, N'$-differocenyl diiminopyridine framework.$^{21}$ The CV characterization of the other FcDIMPY complexes was not possible. The complexes had very poor solubility in suitable solvents and/or lead to poor resolved and irreproducible voltammograms due to electrogenerated decomposition at the electrode surface.

![Graph](image.png)

**Figure 3.11:** CV of 3.21 recorded at different scan rates at a GC electrode in MeCN / 0.1 M $P_{888}$TB, and with an analyte concentration of 2 mM.

### 3.3 Conclusions

A bulky diiminopyridine ligand containing mixed sandwich cobaltocenes (3.17) was prepared. Reactivity of 3.17 with two equivalents of SnCl$_2$ and GeCl$_2$•dioxane lead to the formation of the respective low valent cation-anion pair (3.19 and 3.19) in good yields. The cation is supported by the $N, N', N''$-DIMPY chelate as well as one chlorine atom, and takes on a distorted square pyramidal geometry. The anion adopts a *pseudo* trigonal pyramidal geometry with three chlorine atoms oriented about the main group centre. The structural analogues utilizing the $N, N'$-differocenyl diiminopyridine ligand were also synthesized (3.20 and 3.21). Although the majority of the compounds displayed instability to the electrochemical conditions employed, the amine precursor of
3.17 (Scheme 3.2, 3.16) and 3.21 were studied. Investigations of 3.21 in MeCN / 0.1 M TBAPF$_6$ shows two events: a one-electron chemically reversible peak at -0.46 V with a standard potential of $E^0 = -0.43$ V, and a two-electron chemically reversible peak in the oxidation at 1.03 V due to the consecutive oxidation of the two ferrocenyl moieties at similar potentials. Changing the electrolyte from TBAPF$_6$ to tetraoctylphosphonium tetrakis(pentafluorophenyl) borate (P$_{8888}$TB) allows us to better distinguish the two overlapping peaks of the ferrocenes. Compound 3.16 shows a reversible two-electron oxidation peak at 0.98 V and with $E^0 = 0.87$ V. This result supports the possibility for harnessing the redox activity from this moiety under suitable structural and electrochemical conditions for the generation of a future novel redox-active ligand.

3.4 Experimental

3.4.1 General Procedure

General synthetic, crystallographic and electrochemical experimental details can be found in Appendix 1. The syntheses of 2.18, 21 3.16$^{20e}$ and 2,6-pyridinedialdehyde$^{23}$ were prepared via published procedures. The dark composition of the solids made decomposition events difficult to assign by the traditional Gallenkamp Variable Heater method. Thermal degradation was instead determined using Thermal Gravimetric Analysis (TGA) on a Q600 SDT TA instrument: a sample of 5-15 mg was placed in an alumina cup and heated at a rate of 10°C / minute from room temperature to 800 °C under nitrogen atmosphere (100 mL / minute). In all cases, two onsets of decomposition are reported; an initial temperature that occurs at mass losses between 2-10 %, and then an additional decomposition that occurs with a much higher mass loss percentage. The electrochemical characterization of 3.21 was carried out in a 5 mL MeCN / 0.1 M TBAPF$_6$ electrolyte solution, and in MeCN / 0.1 M tetraoctylphosphonium tetrakis(pentafluorophenyl)borate (P$_{8888}$TB). The analyte was present inside the electrolyte solution at a concentration of 2 mM. The electrochemical characterization of the complex 3.16 was carried out in the same way but in DCM / 0.1 M TBAPF$_6$, using a 1 mm platinum disk working electrode, and nitrobenzene as an internal standard.
3.4.2 Synthetic Procedure

**Compound 3.17:** Mixtures of 3.16 (0.152 g, 0.307 mmol) and 2,6-pyridinedialdehyde (0.021 g, 0.155 mmol) in 75 mL of THF were refluxed under an inert atmosphere for 1.5 hours with constant stirring. The product precipitated out of solution during this time. The reaction mixture was then centrifuged, washed with THF (3 × 10 mL), DCM (3 × 10 mL), and dried in vacuo to give a fine light orange-red powder. **Yield:** 80 % (0.135 g, 0.124 mmol); **D.p.:** Initial 131.5 °C (90.88 %) final 378.41 °C (32.09 %); **UV/Vis (DCM):** λ= 290 nm (4.00 × 10⁻⁴ M⁻¹ cm⁻¹), 319 nm (2.99 × 10⁻³ M⁻¹ cm⁻¹), 374 nm (2.02 × 10⁻⁴ M⁻¹ cm⁻¹), 441 nm (1.41 × 10⁻⁴ M⁻¹ cm⁻¹); **FT-IR (cm⁻¹ (ranked intensity)):** 3056(13), 1616(1), 1601(5), 1583(6), 1534(12), 1498(10), 1460(2), 1368(14), 1344(8), 1278(7), 1241(3), 997(4), 692(15), 588(9), 101(11); **FT-Raman (cm⁻¹ (ranked intensity)):** 3851(14), 3056(11), 1596(6), 1565(15), 1498(2), 1444(10), 1067(5), 1026(12), 815(9), 781(4), 700(7), 745(3), 589(8), 567(3), 544(13); **HRMS:** C₇₃H₅₄N₃Co₂ Calc (Found): 1090.29715 (1090.29763);

**Compound 3.18:** A mixture of 3.17 (0.120 g, 0.110 mmol) in THF (3 mL) was added dropwise to a solution of GeCl₂.dioxane (0.051 g, 0.220 mmol) in THF (3 mL) at room temperature and was allowed to stir for 1 hour. The solvent of the resulting dark green-black solution was then removed in vacuo. A minimal amount of MeCN was added to the solid, and Et₂O (3 × 10 mL) was added to precipitate the product. Residual solvent was once again removed in vacuo, to give a dark blue-green-black powder. Single crystals were obtained via vapour diffusion of DCM in hexane.
Yield: 83 % (0.126 g, 0.091 mmol);
D.p: Initial 120.09 °C (98.60 %) final 298.60 °C (32.09 %);

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, δ): 8.64 (t, 1 H, $^3$J$_{H-H}$= 8.0 Hz), 7.80 (d, 2 H, $^3$J$_{H-H}$= 8.0 Hz), 7.56 (s, 2 H), 7.33 (m, 16 H), 7.18 (m, 8 H), 7.12 (m, 16 H), 5.33 (broad d, 4 H), 5.10 (m, 4 H);

$^{13}$C$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, δ): 149.74, 146.93, 144.98, 134.42, 129.22, 128.81, 127.46, 104.99, 85.68, 80.10, 79.04, 69.05;

UV/Vis (DCM): $\lambda$= 289 nm (2.79 × 10$^{-4}$ M$^{-1}$cm$^{-1}$), 310 nm (2.13 × 10$^{-4}$ M$^{-1}$cm$^{-1}$), 414 nm (9.27 × 10$^{-3}$ M$^{-1}$cm$^{-1}$), 709 nm (5.66 × 10$^{-3}$ M$^{-1}$cm$^{-1}$);

FT-IR (cm$^{-1}$ (ranked intensity)): 1603(5), 1571(2), 1540(1), 1499(15), 1430(3), 1350(7), 1238(4), 1207(9), 1062(13), 1022(6), 999(10), 656(12), 588(8), 325(11), 219(14);

FT-Raman (cm$^{-1}$ (ranked intensity)): 3057(13), 1596(7), 1543(4), 1498(2), 1440(10), 1355(15), 1283(9), 1171(5), 1068(11), 808(14), 781(12), 739(6), 695(1), 587(8), 565(3);

HRMS: C$_{73}$H$_{53}$Cl$_1$N$_3$Co$_2$Ge$_1$ Calc (Found): 1198.18359(1198.18201).

**Compound 3.19:**

A mixture of 3.17 (0.080 g, 0.073 mmol) in THF (3 mL) was added dropwise to a solution of SnCl$_2$ (0.028 g, 0.147 mmol) in THF (3 mL) at room temperature and was stirred for 12 hours. During this time the orange slurry turned dark brown in colour. The slurry was centrifuged, and the eluent was decanted into a vial, where the solvent was removed in vacuo. A minimal amount of MeCN was added to the solid, and Et$_2$O (3 × 5 mL) was added to precipitate the product. Residual solvent was once again removed in vacuo, to give a dark blue-black powder. Single crystals were obtained via vapour diffusion of DCM in hexane.

Yield: 30 % (0.032 g, 0.022 mmol);
D.p.: Initial 134.93 °C (98.49 %) final 372.78 °C (15.89 %);

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, δ): 8.59 (t, 1 H, $^3$J$_{H-H}$= 8.0 Hz), 7.72 (d, 2 H, $^3$J$_{H-H}$= 8.0 Hz), 7.64 (s, 1 H, $^3$J$_{Sn-H}$= 32.0 Hz), 7.32 (m, 16 H), 7.19 (m, 8 H), 7.12 (m, 16 H),
5.26 (m, 4 H), 4.99 (m, 4 H); 
\(^{13}\)C\(^{1\,\text{H}}\) NMR (400 MHz, CD\(_2\)Cl\(_2\), 25 °C, \(\delta\)): 199.30, 150.35, 144.73, 134.49, 130.45, 129.28, 128.88, 127.48, 105.92, 85.45, 78.92, 40.34; 
UV/Vis (DCM): \(\lambda\) = 285 nm (2.52 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 310 nm (1.66 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 407 nm (6.25 \times 10^{-3} \text{ M}^{-1} \text{cm}^{-1}), 694 nm (3.65 \times 10^{-3} \text{ M}^{-1} \text{cm}^{-1}); 
FT-IR (cm\(^{-1}\) (ranked intensity)): 199.30, 150.35, 144.73, 134.49, 130.45, 129.28, 128.88, 127.48, 105.92, 85.45, 78.92, 40.34; 
UV/Vis (DCM): \(\lambda\) = 285 nm (2.52 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 310 nm (1.66 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 407 nm (6.25 \times 10^{-3} \text{ M}^{-1} \text{cm}^{-1}), 694 nm (3.65 \times 10^{-3} \text{ M}^{-1} \text{cm}^{-1}); 
FT-IR (cm\(^{-1}\) (ranked intensity)): 1600(3), 1569(4), 1538(1), 1498(15), 1432(2), 1352(8), 1235(5), 1203(7), 1057(14), 1017(6), 999(11), 637(12), 588(9), 115(10); 
FT-Raman (cm\(^{-1}\) (ranked intensity)): 3851(15), 3455(14), 2961(11), 1595(9), 1538(7), 1497(4), 1437(13), 1280(12), 1262(6), 1024(2), 804(3), 740(8), 694(1), 587(10), 564(5); 
HRMS: C\(_7\)H\(_{53}\)Cl\(_1\)N\(_3\)Co\(_2\)Sn\(_1\) Calc (Found): 1244.16225 (1244.16251). 

**Compound 3.20:**

A solution of 2.18 (0.100 g, 0.200 mmol) in THF (3 mL) was added dropwise to a solution of GeCl\(_2\) (0.092 g, 0.399 mmol) in DCM (3 mL) at room temperature and was allowed to stir for 1 hour. The product was precipitated by the addition of \(n\)-pentane (3 \times 10 mL) and Et\(_2\)O (3 \times 10 mL) and dried in vacuo to give a fine dark shiny green solid. Single crystals were obtained via vapour diffusion of DCM in hexane.

**Yield:** 45 % (0.71 g, 0.090 mmol); 
**D.p.:** Initial 241.92 °C (95.35 %) final 370.07 °C (66.26 %); 
\(^1\)H NMR (600 MHz, CD\(_3\)CN, 25 °C, \(\delta\)): 9.13 (s, 2 H), 8.56 (t, 1 H, \(3J_{H-H}= 6.0 \text{ Hz}\)), 8.21 (d, 2 H, \(3J_{H-H}= 6.0 \text{ Hz}\)), 5.21 (m, 2 H), 4.83 (m, 2 H), 4.39 (s, 10 H); 
UV/Vis (DCM): \(\lambda\) = 263 nm (2.69 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 337 nm (2.37 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 381 nm (2.15 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 439 nm (1.46 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}), 739 nm (1.06 \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1}); 
FT-IR (cm\(^{-1}\) (ranked intensity)): 3094(14), 1604(5), 1570(10), 1537(1), 1481(11), 1428(2), 1284(3), 1236(12), 1168(6), 1108(9), 1039(8), 935(7), 822(13), 801(2), 541(15), 504(4); 
FT-Raman (cm\(^{-1}\) (ranked intensity)): 1601(9), 1588(15), 1569(2), 1535(1), 1427(3), 1235(4), 1204(8), 1059(12), 1020(6), 656(10), 639(5), 591(11), 487(14), 307(7), 85(13);
HRMS: C\textsubscript{27}H\textsubscript{23}Cl\textsubscript{1}N\textsubscript{3}Fe\textsubscript{2}Ge\textsubscript{1} Calc (Found): 609.9500(609.9494);

Elemental analysis: Calc for C\textsubscript{27}H\textsubscript{23}Cl\textsubscript{4}N\textsubscript{3}Fe\textsubscript{2}Ge\textsubscript{2}: 41.14 % C, 2.94 % H, 5.33 % N; Found: 41.68 % C, 2.81 % H, 5.31 % N.

**Compound 3.21:**

A solution of 2.18 (0.085 g, 0.170 mmol) in THF (3 mL) was added dropwise to a solution of GeCl\textsubscript{2} (0.064 g, 0.339 mmol) in THF (3 mL) at room temperature and was allowed to stir for 1 hour. The product was precipitated by the addition of \textit{n}-pentane, centrifuged, washed with additional \textit{n}-pentane (3 \times 10 mL) and finally dried \textit{in vacuo} to give a fine dark shiny blue solid. Single crystals were obtained \textit{via} vapour diffusion of DCM in hexane.

**Yield:** 63 % (0.094 g, 0.107 mmol);

**D.p.:** Initial 222.78 °C (98.19 %) final 447.58 °C (73.80 %);

\textsuperscript{1}H NMR (600 MHz, CD\textsubscript{3}CN, 25 °C, δ): 9.18 (s, 2 H, \textit{J}\textsubscript{Sn-H}= 36.0 Hz), 8.52 (t, 1 H, \textit{J}\textsubscript{H-H}= 6.0 Hz), 8.17 (d, 2 H, \textit{J}\textsubscript{H-H}= 6.0 Hz), 5.13 (broad s, 4 H), 4.79 (m, 4 H), 4.42 (s, 10 H);

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (400 MHz, CD\textsubscript{3}CN, 25 °C, δ): 152.16, 151.69, 146.03, 129.86, 72.52, 72.22, 69.99, 37.46;

\textsuperscript{119}Sn\{\textsuperscript{1}H\} NMR (400 MHz, CD\textsubscript{3}CN, 25 °C, δ): 262.56, 482.42;

UV/Vis (DCM): \textlambda\textsubscript{max} = 255 nm (2.72 \times 10\textsuperscript{-4} M\textsuperscript{-1}cm\textsuperscript{-1}), 337 nm (1.92 \times 10\textsuperscript{-4} M\textsuperscript{-1}cm\textsuperscript{-1}), 430 nm (1.21 \times 10\textsuperscript{-4} M\textsuperscript{-1}cm\textsuperscript{-1}), 692 nm (8.85 \times 10\textsuperscript{-3} M\textsuperscript{-1}cm\textsuperscript{-1});

FT-IR (cm\textsuperscript{-1} (ranked intensity)): 3090(13), 1603(5), 1544(1), 1475(11), 1432(6), 1365(15), 1282(4), 1168(8), 1107(9), 1036(7), 1002(14), 937(10), 805(3), 539(12), 499(2);

FT-Raman (cm\textsuperscript{-1} (ranked intensity)): 3098(10), 1601(4), 1574(3), 1544(1), 1433(2), 1236(5), 1217(12), 1201(8), 1059(13), 1019(6), 659(11), 640(7), 592(14), 305(9);

HRMS: C\textsubscript{27}H\textsubscript{23}Cl\textsubscript{1}N\textsubscript{3}Fe\textsubscript{2}Sn\textsubscript{1} Calc (Found): 655.92903(655.93014).
3.5 References


Chapter 4

4 The Synthesis and Reactivity of Metallocene-Substituted 1,4-Diaza-1,3-Butadiene Ligands

4.1 Introduction

The use of non-innocent (i.e. redox-active) ligands in metal complexes has been an area of interest over the last decade.\(^1\)-\(^8\) The incorporation of these types of ligands allows for the possibility of modifying the electronic environment and therefore the reactivity of the associated metal centre without extensive synthetic modifications. The 1,4-diaza-1,3-butadiene (DAB) ligands are one class that is important in this regard, as the steric and electronic effects they can exert upon the metal in their resulting complexes can be easily varied. These α-diimine ligands have proven to be useful in the synthesis of both early\(^9\) and late\(^10\) transition metals, f-block\(^11\) metals, and s-\(^12\) and p-block\(^12\) complexes.\(^13\) It is within the α-diimine backbone that a one- or two-electron reduction can occur, producing either a π-radical monoanion (Figure 4.1, DAB\(^{1-}\)) with longer C-N bond distances and shorter C-C bond distances relative to the neutral DAB or an enediamide dianion (Figure 4.1, DAB\(^{2-}\)) containing even longer C-N bonds, and a shorter C-C bond relative to the radical DAB\(^1-\), respectively.\(^14\)-\(^17\)

\[
\begin{align*}
\text{R'–N} & \quad \text{R} \quad \text{N–R'} \\
\text{1,4-diaza-1,3-butadiene (DAB)} & \quad \text{R'–N} \quad \text{N–R'} \\
\end{align*}
\]

\[
\begin{align*}
\text{R'–N} & \quad \text{R} \quad \text{N–R'} \\
\text{DAB}^{1-} & \quad \text{R'–N} \quad \text{N–R'} \\
\end{align*}
\]

\[
\begin{align*}
\text{R'–N} & \quad \text{R} \quad \text{N–R'} \\
\text{DAB}^{2-} & \quad \text{R'–N} \quad \text{N–R'} \\
\end{align*}
\]

**Figure 4.1:** Three possible electronic structures of 1,4-diaza-1,3-butadiene ligands.

The synthesis of transition metal complexes with strongly bound redox-active ligands have targeted tunable catalysis, where the change in oxidation state of the ligand inductively affects the electronic state of the coordinated metal centre, either turning ‘on’ or ‘off’ the active catalyst. The category of substitutionally inert redox-active (noninnocent) ligands has taken new leads with the use of α-diimines in this way. Although the majority of α-diimine ligands are known to undergo some redox processes,
a controlled reversible redox activity can be imparted by functionalizing the ligand framework. Several types of moieties with this controlled redox ability have appeared in the literature.\textsuperscript{18-24} Ferrocene has played a significant role as a backbone substituent in such redox-active ligands, as its steric, electronic and redox behaviour is well documented.\textsuperscript{25} A variety of other metallocenes have also been studied as redox-active ligands to support transition metals. Cobalt-based metallocenes have been of particular interest in this regard. Wrighton \textit{et al}. synthesized a 1,1'-bis(diphenylphosphino) cobaltocene ligand, which demonstrated the ability to control the electron density, and thus reactivity of the ligated metals \textit{via} oxidation state changes. These redox events could be used to modulate the Rh(I)-catalyzed hydrogenation of cyclohexene to cyclohexane. When the cobaltocene moiety is in a neutral state (Co(II), containing 19 electrons; Scheme 4.1, \textbf{4.0}) the catalytic activity is possible; however, the oxidation by [Fe(\eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}]PF\textsubscript{6} yields an insoluble 18 electron Co(III) complex that arrests catalytic activity (Scheme 4.1, \textbf{4.1}). The catalytic activity can be reversibly restored with the introduction of CoCp\textsubscript{2} (Scheme 4.1).\textsuperscript{26,27}

\begin{center}
\includegraphics[width=\textwidth]{scheme4.1.png}
\end{center}

\textbf{Scheme 4.1:} Reversible catalysis of a diphosphino cobaltocene ligand.

Although the above example depicts a 19 electron system that reversibly activates and arrests the hydrogenation reaction of cyclohexene, the 19 electron cobaltocene complex underscores the high reactivity of the system, as it looks to take on a more stable electronic configuration (18 electrons). Ligand systems that utilize the more stable cationic 18 electron cobaltocium salt often suffer from solubility issues. Therefore, the use of a neutral 18 electron cobalt complex is appealing as it would be isoelectronic with ferrocene, and have a good solubility in organic solvents. Richards and co-workers have extensively studied the reactivity and synthesis of neutral bulky 18 electron mixed
sandwich cobaltocene containing both $\eta^4$-cyclobutadiene and $\eta^5$-cyclopentadienyl fragments (Figure 4.2, 4.2).\textsuperscript{28a-f} A few other groups have also investigated derivations of this organometallic complex as a ligand for use in catalysis.\textsuperscript{28g-j} Although the redox properties of these stable metallocenes have yet to be extensively studied, there is precedent for their use in the synthesis and preparation of redox-active ligands.

\textbf{Figure 4.2:} Free (4.2, 3.16) 18 electron metallocenes and nitrogen-based ligands containing pendant 18 electron metallocenes (2.18, 3.6, 3.17).

The Ragogna group has recently reported a diiminopyridine (DIMPY) ligand containing pendant 18 electron mixed sandwich cobaltocenes (Figure 4.2, 3.17).\textsuperscript{29} They have explored the reactivity of these ligands with Sn and Ge centres, and investigated the electrochemistry of these systems relative to their ferrocene analogues (Figure 4.2, 3.20 and 3.21). The CV of the ligand precursor (Figure 4.2, 3.16) unveiled the possibility of harnessing a reversible two-electron oxidation process. Electrochemical studies of the cobalt-containing DIMPY ligand or its complexes were unstable to the electrochemical conditions employed. Thus, there is a desire to expand the ligand scaffold and incorporate this redox-active moiety onto a framework that will be more stable to the electrochemical conditions. In this context, we report the synthesis and electrochemical studies of a novel bulky 1,4-diaza-1,3-butadiene ligand containing pendant mixed...
sandwich cobaltocenes (Scheme 4.2, 4.3) and comparatively discuss its reactivity and electrochemistry with a known ferrocene analogue (Figure 4.2, 3.6).

4.2 Results and Discussion

4.2.1 Synthesis

Compound 4.3 was prepared by the condensation reaction between 3.16 and glyoxal in a 2:1 stoichiometry (Scheme 4.2). The suspension was centrifuged under an inert atmosphere and the resulting orange-red precipitate was washed with cold aliquots of THF, dried and a sample of the bulk powder was redissolved in CDCl₃.

![Scheme 4.2: Synthetic route to 4.3.](image)

The \(^1\)H NMR spectrum of 4.3 displayed slight downfield shifts for all protons relative to the starting material (for cyclopentadienyl protons \(\Delta\delta = 0.65\) and 0.46) as well as a of amine protons at \(\delta = 2.15\). In addition to the \(^1\)H NMR data, high-resolution mass spectrometry revealed a m/z peak consistent to the molecular weight of the desired ligand (1013.27271 (cf. 1013.27163)).

A solution of 4.3 in DCM was stirred with a stoichiometric equivalent of SnCl₄ at room temperature for 10 minutes. A colour change from orange-red to dark blue-green was observed during this time. The addition of \(n\)-pentane precipitated a blue-green solid from the solution, which was further washed with \(n\)-pentane, Et₂O, and dried \(\textit{in vacuo}\) to yield a fine dark blue-green powder. A sample of the bulk solid was redissolved in CDCl₃ and the \(^1\)H NMR spectrum revealed diagnostic downfield shifts for all protons, consistent with the inclusion of a Sn centre within the DAB chelate (Scheme 4.3, 4.4).
Compound 4.3 was also reacted in a 2:1 stoichiometric ratio with Pt$_2$(SMe)$_2$Me$_4$ in DCM at room temperature. After several minutes, a dark precipitate formed and the solution changed from orange-red to purple-black in colour. Diethyl ether was added to further precipitate the dark solid from solution. It was then washed with n-hexane, dried in vacuo, and a sample of the solid was taken up in CDCl$_3$ for $^1$H NMR spectroscopy, which displayed diagnostic downfield shifts for all proton resonances relative to 4.3. A new signal at $\delta_H = 1.55$ revealed the presence of platinum satellites ($^2J_{Pt-H} = 83.9$ Hz), with $J$-values consistent with a methyl group on platinum.$^{31}$ The downfield shift and presence of platinum satellites led to the tentative assignment of 4.5 (Scheme 4.3; See Appendix (A.4) for NMR spectra of compounds 4.3, 4.4 and 4.5).

To better understand the future electrochemical studies that would be performed, in particular the redox behaviour of the mixed sandwich cobaltocenes relative to ferrocene, ferrocene analogues of 4.3, 4.4 and 4.5 were synthesized (Scheme 4.4) using similar methodologies. For further insight into the redox activity of the central metal, analogues of the aforementioned cobaltocene compounds, containing non-redox-active fragments (cyclohexyl) on the imine nitrogens, were also prepared (Scheme 4.4) by these methods (See Appendix (A.5 and A.6) for NMR spectra of 4.7, 4.8, 4.9 and 4.10).
4.2.2 X-Ray Crystallography

Suitable crystals for X-ray crystallography were grown for all compounds by vapour diffusion. The solid-state structure of 4.3 confirmed the identity of the anticipated 1,4-diaza-1,3-butadiene bearing mixed sandwich cobaltocene groups on both imine nitrogens. The carbon-nitrogen double bonds are indicative of an diimine (C=N; 1.272(9) and 1.277(8)), and the remaining metrical parameters are consistent with the well-documented 1,4-diaza-1,3-butadiene (DAB) framework. With respect to the ligands carbon-nitrogen plane, the mixed sandwich cobaltocenes lie anti to one another, to relieve the steric demands imposed by the cobaltocenyl unit.

The solid-state structures of the corresponding metal complexes of 4.3, 3.6 and 4.6, indicate the presence of the N, N'-DAB chelate (see Figure 4.3 and Figure 4.4 for structures, Table 4.1 for salient bond lengths and angles, and Appendix (A.14) for X-ray table). Compounds 4.4, 4.7 and 4.9 all have a distorted six-coordinate octahedral geometry about the Sn centre. In the case of 4.7, mixed sandwich substituents lie 90° to one another, whereas for 4.9, ferrocenyl substituents retain their ability to lie anti to one another with respect to the 1,4-diaza-1,3-butadiene framework. The cyclohexyl groups of 4.7 take on a boat-shaped conformation and lie perpendicular to the ligand framework. Complexes of 4.5 and 4.10 both contain four-coordinate Pt(II) centres with pseudo square planar geometry about the metal centre. As was observed for 4.4, the 4.5 complex contains mixed sandwich cobaltocenes lying 90° with respect to one another. In the case of 4.10, steric interactions between methyl groups and ferrocenyl substituents are avoided with the ferrocenyl substituents lying syn to one another with respect to the ligand framework. The methyl platinum lies slightly above the plane at the furthest point away from the large metallocene substituents. With the exception of 4.10 all remaining species have pseudo-C2 symmetry through the E(1)-N(2)-C(13) axis, where 4.7 and 4.5 are both perfectly C2 symmetric.
Figure 4.3: Solid-state structures of 4.3, 4.4 and 4.5. Thermal ellipsoids are drawn to the 50% probability level. Solvates and hydrogen atoms are removed for clarity.
**Figure 4.4:** Solid-state structures of 4.7, 4.9 and 4.10. Thermal ellipsoids are drawn to the 50% probability level. Solvates and hydrogen atoms are removed for clarity.
Table 4.1: Selected bond lengths (Å) and bond angles (°) for 4.3, 4.4, 4.5, 4.7, 4.9 and 4.10.

<table>
<thead>
<tr>
<th></th>
<th>4.3</th>
<th>4.4</th>
<th>4.5</th>
<th>4.7</th>
<th>4.9</th>
<th>4.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(1)-N(1)</td>
<td>--------</td>
<td>2.299(3)</td>
<td>2.1190(5)</td>
<td>2.242(5)</td>
<td>2.258(6)</td>
<td>2.125(7)</td>
</tr>
<tr>
<td>E(1)-N(2)</td>
<td>--------</td>
<td>2.299(3)</td>
<td>2.1190(5)</td>
<td>2.242(5)</td>
<td>2.319(6)</td>
<td>2.141(8)</td>
</tr>
<tr>
<td>C(3)-N(1)</td>
<td>1.272(9)</td>
<td>1.281(5)</td>
<td>1.282(8)</td>
<td>1.284(10)</td>
<td>1.303(9)</td>
<td>1.346(11)</td>
</tr>
<tr>
<td>C(13)-N(2)</td>
<td>1.277(8)</td>
<td>1.281(5)(^a)</td>
<td>1.282(8)(^a)</td>
<td>1.284(10)(^a)</td>
<td>1.291(9)</td>
<td>1.339(12)</td>
</tr>
<tr>
<td>N(1)-E(1)-N(2)</td>
<td>--------</td>
<td>72.88(1)</td>
<td>76.35(30)</td>
<td>74.31(31)</td>
<td>74.69(22)</td>
<td>77.59(33)</td>
</tr>
</tbody>
</table>

\(^a\) Symmetry arising from the centrosymmetric nature of those marked compounds
4.2.3 Electrochemistry

Compounds 4.10, 4.8, 3.6 and 4.6 were characterized by cyclic voltammetry (CV). The electrochemical experiments were carried out using 2 mM of analyte in 5 mL of MeCN / 0.1 M TBAPF$_6$. The working electrode was a 3mm GC disk electrode, the counter electrode was a platinum wire, and the reference electrode was a stabilized Ag/AgCl quasi-reference electrode.

Figure 4.5: On the left: CV of 3.6 (A, solid line), 4.6 (A, dashed line), 4.8 (B) and 4.10 (C). CV recorded at a GC electrode in MeCN / 0.1 M TBAPF$_6$ with an analyte concentration of 2 mM and at 0.1 Vs$^{-1}$. On the right: CV of 3.6 (D, solid line), 4.6 (D, dashed line), 4.7 (E) and 4.9 (F). CV recorded at a GC electrode in DCM / 0.1 M TBAPF$_6$ with analyte concentration 2 mM and at 0.1 Vs$^{-1}$. Experiments were carried out at room temperature and in an inert atmosphere glove box.

The CV for the free ligand 3.6 shows the presence of two one-electron reversible peaks due to consecutive oxidation of each of the two ferrocenes, the first one with $E^\circ=$
0.60 V and the second with $E^0 = 0.79$ V (see Figure 4.5, CV A). For comparison, a similar ligand, with the electroactive ferrocene groups replaced with the electrochemically inactive cyclohexyl groups (4.6 ligand) is also shown; its CV shows just the background current (Figure 4.5, CV A, dashed voltammetric curve). The CV of complex 4.8 therefore shows voltammetric peaks related only to the reduction and oxidation of the platinum centre (Figure 4.5, CV B). In particular at -1.25 V it is possible to distinguish the reversible reduction of Pt(IV) to Pt(II), involving a double electron transfer, and at 0.90 V the irreversible oxidation of Pt(IV). The peak data are consistent with the results previously obtained by Kaim and co-workers on the same molecular system.\textsuperscript{31} The CV of the 4.10 complex (Figure 4.5, CV C) shows a reversible reduction peak at -0.82 V is consistent with the reduction of the Pt(IV) to Pt(II) and was shifted to more positive potentials because of the effect of the ferrocenyl groups, and three overlapping yet distinguishable oxidation peaks at 0.61 V, 0.68 V, and 0.83 V, respectively. In comparison to the model compound (4.8), the more positive oxidation peak is due to the oxidation of the metal centre and the two less positive oxidations are due to the consecutive oxidations of the two ferrocenyl groups.

The same methodology was applied to characterize complex 4.9 by cyclic voltammetry using 2 mM solution in 5 mL of DCM / 0.1 M TBAPF$_6$ electrolyte. DCM was used as the solvent because of the low solubility of 4.9 in MeCN. The CV of the free ligand 3.6 in DCM (Figure 4.5, CV D, solid voltammetric curve) shows a weaker communication between the two ferrocenes than in MeCN as solvent, resulting in a single broader voltammetric peak with an apparent $E^0 = 0.76$ V, and with current intensity indicating a two-electron process. By comparison the free ligand (4.6) shows, as expected, no electrochemical activity also in DCM as solvent (Figure 4.5, CV D, dashed voltammetric curve). Analysis of the model complex 4.7 under the same experimental conditions shows only a single two-electron reversible oxidation peak with $E^0 = -0.27$ V that therefore can be due only to the reduction of the Sn(IV) to Sn(II) (Figure 4.5, CV E). Finally, the CV of 4.9 (Figure 4.5, CV F) clearly shows a reversible peak with $E^0 = 0.05$ V, whose current intensity indicates a two-electron process, and is consistent with the reversible reduction of the Sn metal centre. On the positive potential scan there are two
overlapping reversible peaks with $E^0 = 1.00$ V and $1.16$ V, respectively, most likely due to the two ferrocene functionalities that because of the presence of the metal centre are now distinguishable.

### 4.3 Conclusions

Compounds 3.6, 4.9, 4.10, 4.3, 4.4 and 4.5 represent the first examples of group 10 and 14 complexes utilizing redox-active 1,4-diaza-1,3-butadiene ligands (3.6 or 4.3) containing pendant ferrocene or mixed sandwich cobaltocenes functionalities. Cyclic voltammetric studies of 3.6 in MeCN display two overlapping reversible peaks for the two ferrocenes, the first one with $E^0 = 0.60$ V and the second with $E^0 = 0.79$ V, whereas studies in DCM reveal a single reversible two-electron process with $E^0 = 0.76$ V. A full data collection for 4.3 and its respective complexes remains somewhat inconclusive due to the complex nature of the cyclic voltammograms obtained. Full electrochemical investigation of 4.10 reveals four events: a reversible two-electron process from platinum (Pt(IV)-Pt(II)) at $E^0 = -0.82$ V, two reversible single electron overlapping peaks from the ferrocenes at $E^0 = 0.61$ V and $0.68$ V, and an additional irreversible oxidation of Pt(IV) at $E^0 = 0.83$ V. Studies with 4.9 reveals three peaks: a reversible two-electron process from tin (Sn(IV)-Sn(II)) at $E^0 = 0.05$V and two overlapping reversible peaks due to the two ferrocene functionalities at $E^0 = 1.00$ V and $1.16$ V.

### 4.4 Experimental

#### 4.4.1 General Procedure

General synthetic, crystallographic and electrochemical experimental details can be found in Appendix 1. The syntheses of 3.16, 3.6, 4.6, and Pt$_2$Me$_4$(SMe$_3$)$_4$ were prepared via published procedures. The electrochemical characterization of 4.7 and 4.9 were carried out in a 5 mL DCM / 0.1 M TBAPF$_6$ electrolyte solution, while complexes 4.8 and 4.10 were carried out in a 5 mL MeCN / 0.1 M TBABF$_4$ electrolyte solution. The analytes were present inside the electrolyte solution at a concentration of $2$ mM.
4.4.2 Synthetic Procedure

**Compound 4.3:**

Mixtures of 3.16 (1.44 g, 2.91 mmol), degassed glyoxal (166.3 µL, 1.46 mmol) and 100 mL of THF were refluxed under an inert atmosphere for 12 hours with constant stirring. The product was precipitated by the addition of cold THF (3 × 10 mL), and dried in vacuo to give a fine light orange-red powder. Single crystals were obtained via vapour diffusion of n-hexane in DCM.

**Yield:** 87 % (1.29 g, 1.27 mmol);  
**D.p.:** 223-230 °C;  
**¹H NMR (CDCl₃, δ):** 7.36 (m, 17 H), 7.16 (m, 25 H), 4.03 (m, 4 H), 4.77 (m, 4 H);  
**UV/Vis (DCM):** λ = 529 nm (5.14 × 10⁻³ M⁻¹ cm⁻¹), 454 nm (1.08 × 10⁻⁴ M⁻¹ cm⁻¹), 294 nm (3.47 × 10⁻⁴ M⁻¹ cm⁻¹);  
**FT-IR (cm⁻¹ (ranked intensity)):** 3057(14), 1597(6), 1500(1), 1445(13), 1260(11), 1177(10), 1067(3), 1026(5), 925(15), 813(9), 782(8), 745(7), 696(2), 589(12), 566(4);  
**FT-Raman (cm⁻¹ (ranked intensity)):** 1588(1), 1453(2), 1370(4), 1236(6), 1222(7), 1159(3), 999(5);  
**HRMS:** C₆₈H₅₁N₂Co₂ Calc (Found): 1013.27271 (1013.27163).

**Compound 4.4:**

A solution of 4.3 (0.081 g, 0.080 mmol) in DCM (3 mL) was added dropwise to a solution of SnCl₄ (9.3 µL, 0.080 mmol) in DCM (3 mL) and was allowed to stir for 10 minutes. The product was then precipitated and washed by the addition of n-pentane (3 × 10 mL) and Et₂O (3 × 10 mL), and dried in vacuo to give a dark blue-green fine powder. Single crystals were obtained via vapour diffusion of n-hexane in DCM.

**Yield:** 100 % (0.101 g, 0.080 mmol);  
**D.p.:** 187-238 °C;  
**¹H NMR (CDCl₃, δ):** 7.30 (m, 42 H), 5.28 (m, 4 H), 4.90 (m, 4 H);
UV/Vis (DCM): $\lambda = 702$ nm $(6.29 \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1})$, 429 nm $(3.58 \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1})$, 322 nm $(1.86 \times 10^{-4} \text{ M}^{-1}\text{cm}^{-1})$, 292 nm $(3.88 \times 10^{-4} \text{ M}^{-1}\text{cm}^{-1})$;

FT-IR (cm$^{-1}$ (ranked intensity)): 3054(14), 1593(8), 1498(2), 1443(10), 1358(9), 1168(15), 1026(4), 962(11), 817(7), 743(5), 703(1), 585(3), 563(6), 545(12).

**Compound 4.5:**

A solution of **4.3** (0.100 g, 0.099 mmol) in DCM (3 mL) was added dropwise to a solution of Pt$_2$Me$_4$(SMe)$_2$$_4$ (0.034 g, 0.049 mmol) in DCM (3 mL) at room temperature. The product was precipitated by the addition of Et$_2$O (3 × 10 mL) and n-hexane (3 × 10 mL) and dried *in vacuo* to give a dark purple-black fine powder. Single crystals were obtained *via* vapour diffusion of n-hexane in DCM.

**Yield:** 78% (0.095 g, 0.077 mmol);  
**D.p.:** 123-135 °C;

$^1$H NMR (CDCl$_3$, $\delta$): 7.34 (m, 17 H), 7.23 (m, 25 H), 4.97 (m, 4 H), 4.76 (m, 4 H), 1.55 (s, 6 H, $^3$J$_{Pr-H}$ = 83.9 Hz);

UV/Vis (DCM): $\lambda = 679$ nm $(2.70 \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1})$, 396 nm $(8.87 \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1})$, 316 nm $(3.44 \times 10^{-4} \text{ M}^{-1}\text{cm}^{-1})$, 288 nm $(5.50 \times 10^{-4} \text{ M}^{-1}\text{cm}^{-1})$;

FT-IR (cm$^{-1}$ (ranked intensity)): 3049(10), 1595(6), 1498(2), 1442(9), 1268(13), 1067(11), 1024(5), 967(15), 817(12), 778(8), 765(14), 738(4), 693(1), 587(7), 562(3);

HRMS: C$_{70}$H$_{56}$N$_2$Co$_2$Pt$_1$Na$_1$ Calc (Found): 1260.25991 (1260.26581).

**Compound 4.7:**

A mixture of **4.6** (0.110 g, 0.499 mmol) in DCM (3 mL) was added dropwise to a solution of SnCl$_4$ (58.43 µL, 0.499 mmol) in DCM (3 mL) at room temperature and was allowed to stir for 10 minutes. The product was precipitated by the addition of $n$-pentane (3 × 10 mL) and Et$_2$O (3 × 10 mL) and dried *in vacuo* to give a white fine powder. Single crystals were grown by vapour diffusion of Et$_2$O into MeCN.

**Yield:** 94% (0.226 g, 0.469 mmol);  
**D.p.:** 238-250 °C;
$^1$H NMR (CD$_3$CN, δ): 8.45 (s, 2 H, $^3$J$_{Sn-H}$= 34.6), 4.48 (p, 2 H, $^3$J$_{H-H}$= 4.0), 2.20 (m), 2.12 (m), 1.85 (m), 1.73 (m), 1.53 (m), 1.44 (m);

FT-IR (cm$^{-1}$ (ranked intensity)): 3033(9), 2946(1), 2853(11), 1597(14), 1451(2), 1410(10), 1321(6), 1265(13), 1146(15), 1068(3), 1001(8), 884(5), 849(12), 673(7), 487(4);

FT-Raman (cm$^{-1}$ (ranked intensity)): 2948(1), 2853(6), 1598(3), 1453(12), 1349(15), 1265(14), 1147(11), 946(9), 792(10), 327(2), 301(5), 259(7), 222(13), 154(4), 126(8).

HRMS: C$_{14}$H$_{24}$N$_2$Fe$_2$SnCl$_4$Na Calc (Found): 502.95917 (502.96093);

Elemental Analysis: Calc for C$_{14}$H$_{24}$N$_2$Fe$_2$SnCl$_4$: 34.97 % C, 5.03 % H, 5.83 % N; Found: 34.91 % C, 5.13 % H, 5.49 % N.

Compound 4.9:

3.6 (0.090 g, 0.212 mmol) in DCM (3 mL) was added dropwise to a solution of SnCl$_4$ (24.83 µL, 0.212 mmol) in DCM (3mL). After 10 minutes the product was precipitated and washed by the addition of n-pentane (3 × 10 mL) and Et$_2$O (3 × 10 mL), and dried in vacuo to give a bright green-yellow fine powder. Single crystals were obtained via vapour diffusion of n-hexane in DCM.

Yield: 88 % (0.128 g, 0.187 mmol);

D.p.: 178-200 °C;

$^1$H NMR (CDCl$_3$, δ): 8.35 (s, 2 H, $^3$J$_{Sn-H}$= 35.2 Hz), 5.39 (m, 4 H), 5.02 (m, 4 H), 4.61 (s, 10 H);

UV/Vis (DCM): λ = 453 nm (1.06 × 10$^{-4}$ M$^{-1}$cm$^{-1}$);

FT-IR (cm$^{-1}$ (ranked intensity)): 3423(11), 2924(3), 2676(2), 2345(15), 2256(5), 2108(14), 1935(4), 1847(7), 1752(13), 1719(6), 1702(1), 1686(8), 1543(12), 1039(9), 902(10);

HRMS: C$_{22}$H$_{20}$N$_2$Fe$_2$SnCl$_4$ Calc (Found): 683.80792 (683.80987);

Elemental Analysis: Calc for C$_{22}$H$_{20}$N$_2$Fe$_2$SnCl$_4$: 38.60 % C, 2.94 % H, 4.09 % N; Found: 39.07 % C, 3.10 % H, 3.90 % N.
Compound 4.10:

A cold solution of 3.6 (0.100 g, 0.236 mmol) in DCM (3 mL) was added dropwise to a cold solution of Pt$_2$Me$_4$(SMe$_2$)$_4$ (0.082 g, 0.118 mmol). The product was immediately precipitated by the addition of Et$_2$O (3 × 10 mL) and n-hexane (3 × 10 mL) and dried in vacuo to give a dark green-blue powder. Single crystals were obtained via vapour diffusion of n-hexane in DCM.

**Yield:** 70 % (0.107 g, 0.165 mmol);

**D.p.:** 180-189 °C;

$^1$H NMR (CDCl$_3$, δ): 9.71 (s, 2 H, $^3$J$_{Pt-H}$ = 82.9 Hz), 4.83 (m, 4 H), 4.46 (m, 4 H), 4.25 (s, 10 H), 1.81 (s, 6 H);

$^{13}$C{$^1$H} NMR (CDCl$_3$, δ): 159.88, 106.94, 70.93, 68.29, 67.27, -13.90;

**UV/Vis (DCM):** ϵ = 661 nm (5.28 × 10$^{-4}$ M$^{-1}$cm$^{-1}$), 456 nm (2.72 × 10$^{-3}$ M$^{-1}$cm$^{-1}$), 414 nm (7.52 × 10$^{-3}$ M$^{-1}$cm$^{-1}$);

**FT-IR (cm$^{-1}$ ranked intensity):** 3089(10), 2868(4), 2801(15), 1408(11), 1365(6), 1261(5), 1105(3), 1020(7), 964(9), 819(1), 653(14), 573(8), 532(12), 514(13), 498(2);

**FT-Raman (cm$^{-1}$ ranked intensity):** 3263(2), 2157(12), 2061(15), 1480(3), 1441(1), 1376(6), 1324(8), 1245(11), 1068(5), 929(13), 653(9), 638(4), 314(7), 242(14), 113(10);

**HRMS:** C$_{24}$H$_{26}$N$_2$Fe$_2$Pt$_1$I$_1$ Calc (Found): 775.9479 (775.9491).

### 4.5 References


Chapter 5

5 Progress Towards an N-Heterocyclic Carbene Containing Bulky Mixed-Sandwich Cobaltocenes

5.1 Introduction

Following Wanzlic’s 1961 report of the first N-heterocyclic carbene (NHC) came several reports from Öfele and Lappert in the 1970s.1-7 Early work by Lappert showed promising results; however, due to the synthetic difficulty of preparing these compounds advancements in this field were set back. In 1991 Arduengo et al. discovered the first example of a stable (i.e. without tendency to dimerize) crystalline carbene.8 Since its discovery, NHCs have received significant attention as ligands for catalytic systems (Figure 5.1, 5.0).9-18

![Figure 5.1: A generic view of an N-heterocyclic carbene (NHC).](image)

These compounds were hailed for having a σ-donating ability greater than the popular and commercially available tertiary phosphines, as well as a strong nucleophilic character and a weak π back-donating ability.19 Now, more than 20 years later, the scope of NHC ligands has been extensively studied. Their popularity arose from endless accounts of topological modifications, where each carbene was easily tuned to provide improved performance for an array of applications.20-22 Varying substituents on the nitrogen atoms and imparting functionality to backbone carbons has recently been of interest to such fields as tunable catalysis. Metal-containing substituents are no exception, where a redox-active functionality can be tethered onto the 5 membered N-heterocyclic ring, which leads to interesting properties in the resulting metal complexes (See Chapter 1 Redox-Active Ligands).23 Although there are many reports of NHCs, which include a redox-active ferrocene onto the ligand framework (Figure 5.2), only a
few have extensively studied the viability of these systems for use in tunable catalysis. 24,25

**Figure 5.2:** A few examples of N-Heterocyclic ligands containing ferrocene.

Recent reports of NHCs bearing a naphthoquinone (Figure 5.3, 5.9), 26 a nicotinamide (Figure 5.3, 5.10), 27 or a quinoxaline (Figure 5.3, 5.11) 28 moiety have also appeared in the literature. While ligands 5.10 and 5.11 allow the catalysis of proton-coupled electron-transfer processes, 5.9 was found to be useful in assisting in Ni(II)-catalyzed Kumada cross-coupling reactions between PhMgCl and bromoarenes. Depending on the oxidation state of the quinone moiety, the catalysis was controllably turned ‘on’ or ‘off’ by the addition of ferrocenium or cobaltocene, respectively.

**Figure 5.3:** N-heterocyclic carbene ligands containing redox-active moieties.
Synthesis of related NHC systems containing 18 electron metallocenes other than ferrocene are not known. Chapter 4 described the synthesis of 1,4-diaza-1,3-butadiene ligand containing pendant mixed sandwich cobaltocene substituents. Despite the incredible steric bulk from the metallocenes, we were able to demonstrate that electrophilic main group (Sn) and transition metal (Pt) complexes could be isolated (Scheme 5.1).

Scheme 5.1: Reactivity of 1,4-diaza-1,3-butadiene containing pendant mixed sandwich cobalatocene substituents.

Previous studies from the Ragogna group have revealed the possibility of a reversible two-electron oxidation from the ligands metallocene precursor (Scheme 5.1, 3.17). Incorporating this substituent about a robust NHC framework may allow for the possibility of using the resulting NHC for tunable catalysis.

In this chapter, the synthesis, characterization and electrochemical study of an N-heterocyclic carbene-silver compound containing bulky mixed sandwich cobaltocenes will be discussed.

5.2 Results and Discussion

5.2.1 Synthesis

In a 5-hour THF reflux, compound 4.3 was treated with para-formaldehyde and TMSCl in a 1:1:1.04 stoichiometric ratio. The initially opaque orange solution turned transparent dark yellow-brown during this time. The solvent was then removed in vacuo and the product purified precipitating a grey-black solid upon the addition of n-hexane to a saturated DCM solution. A sample of the bulk solid was redissolved in CD$_2$Cl$_2$ and the $^1$H NMR spectrum was acquired. The disappearance of amine protons at $\delta_{H}=2.15$ ppm
and the presence of broad singlets at $\delta_{H}= 10.67$ (when the baseline is strongly enhanced), 5.93 and 5.41 were immediately observed. In accordance with previous reports, the furthest downfield peak at $\delta_{H}= 10.67$ likely corresponds to a single proton resonance from an imidazolium proton. The peak at $\delta_{H}= 5.93$, which integrates to two protons, can be assigned to those present on the imidazolium alkene backbone. The most upfield broad singlet, which accounts for 4 protons, is consistent with the cyclopentadienyl protons on carbons $\beta$ to nitrogens (Figure 5.3, top).

**Scheme 5.2**: Synthetic Route to 5.12.

**Figure 5.4**: $^1$H NMR spectra for 5.12 and 5.13 in CD$_2$Cl$_2$. 
The broadening of these protons can be explained by steric restrictions introduced from the formation of the 5-membered heterocycle and an attenuation of the free rotation of the CbCoCp fragment. High-resolution mass spectrometry was performed to further identify the product with an m/z = 1025.2703 corresponding to the expected m/z of an imidazolium cation containing pendant mixed sandwich cobaltocene functionalities (cf. calculated 1025.2716). These results as well as those from the $^1$H NMR spectrum and X-ray crystallographic studies of 5.12 led to the temporary assignment of the product as the imidazolium chloride (Scheme 5.2).

Compound 5.12 was reacted with an excess amount of Ag$_2$O in DCM at room temperature. After 24 hours of stirring, no apparent colour change was observed. The solution was then filtered, and the solvent was removed in vacuo to give a dark brown-black solid. The product was purified precipitating a dark orange solid with the addition of n-hexane to a saturated DCM solution. A sample of the bulk solid was redissolved in CD$_2$Cl$_2$ and the $^1$H NMR spectrum acquired. The imidazolium proton at $\delta_H = 10.67$ was no longer observed and the ethylene backbone protons on the heterocyclic ring appear as a doublet, consistent with $^4J_{H-Ag}$ coupling from Ag ($^4J_{H-Ag} = 1.6$ Hz; Figure 5.3 bottom). These results led to the tentative assignment of this compound as the silver chloride complex (Scheme 5.3, 5.13).

![Scheme 5.3: Synthetic Route to 5.13.](image)

### 5.2.2 X-Ray Crystallography

Suitable single crystals of 5.12 were obtained by cooling a saturated solution of CHCl$_3$ to -30°C (See Table 5.1 for X-ray data and Figure 5.5 for structural views). From the solid-state structure it was apparent that a 5-membered heterocyclic ring was present. To confirm the nature of the 5-membered ring, bond lengths were examined. Carbon-
nitrogen bond lengths increase in distance with respect to those observed in the diimine starting material (C=N 1.269(7) Å for 4.5; C-N 1.382(5) Å and 1.384(5) Å for 5.12), whereas the carbon-carbon backbone distance decreased relative to those of the precursor’s (C-C 1.456(10) Å for 4.5; C-C 1.344(6) Å for 5.12). Due to resonance and the formation of a double bond between a nitrogen and the newly added carbon apex, bond lengths between nitrogen and carbon were observed to have an intermediate single/double bond character (C-N 1.343(6) Å 1.340(6) Å. These results confirmed the heterocycle was an imidazolium ion, while the presence of a single chloride anion further supported this finding. The imidazole ring exists in the same plane as the pendant cp rings of the mixed sandwich cobaltocene substituents. For steric reasons, these groups preferentially lie anti with respect to the imidazolium basal plane.

Table 5.1: X-ray details for 5.12.

<table>
<thead>
<tr>
<th>Compound</th>
<th>5.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{71}$H$</em>{53}$Cl$_7$Co$_2$N$_2$</td>
</tr>
<tr>
<td>FW (g/mol)</td>
<td>1300.16</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2(1)$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>10.218(5)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>21.098(11)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>13.987(8)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90.000</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>97.416(8)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90.000</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>2990(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>$D_c$ (mg m$^{-3}$)</td>
<td>1.444</td>
</tr>
<tr>
<td>Radiation, $\lambda$ (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>temp (K)</td>
<td>113(2)</td>
</tr>
<tr>
<td>R1([I&gt;2\sigma(I)])$^a$</td>
<td>0.0474</td>
</tr>
<tr>
<td>$wR2(F^2)$</td>
<td>0.0830</td>
</tr>
<tr>
<td>GOF(S)$^a$</td>
<td>1.029</td>
</tr>
</tbody>
</table>

$^a$ R1(F[I > 2(1)]) = $\sum||F_o| - |F_c||/\sum|F_o|$; $wR2(F^2$ [all data]) = $[w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and $a$ and $b$ are constants suggested by the refinement program.
Figure 5.5: Solid-state structures of 5.12 from two different views. Thermal ellipsoids are drawn to the 50% probability interval. Solvates, anions and hydrogen atoms are removed for clarity.
5.3 Conclusions

Novel imidazolium chloride and N-heterocyclic carbene compounds containing bulky pendant mixed sandwich coblatacenes were prepared and characterized. Future electrochemical studies of these complexes and their metal complexes may reveal ligand centred redox-activity. These compounds represent the first examples of N-heterocyclic carbenes containing cobalt mixed sandwich metallocene functionalities.

5.4 Experimental

5.4.1 General Procedure

General synthetic, crystallographic and electrochemical experimental details can be found in Appendix 1. The synthesis of 4.5 was prepared via published procedures. 29

5.4.2 Synthetic Procedure

**Compound 5.12:**

To a 50 mL round bottom Schlenk flask equipped with a magnetic stirbar, THF solutions of 4.6 (0.090 g, 0.089 mmol), p-formaldehyde (0.002 g, 0.089 mmol) and TMSCl (11.70 µL, 0.092 mmol) were added. The slurry was then refluxed for 5 hours, over which time a colour change from opaque orange to clear dark yellow-brown occurred. After cooling to room temperature, the solvent was removed in vacuo, and the resulting dark brown-black solid was taken up in a minimal amount of DCM (1 mL). The product was precipitated and washed with the addition of n-hexane (3 × 10 mL). Residual solvent was removed in vacuo. A saturated solution of CHCl₃ at -30 °C yielded amber coloured crystals suitable for structural analysis.

**Yield:** 71 % (0.067 g, 0.063 mmol);

**D.p.:** 196.5-208.5 °C;

**¹H NMR (400 MHz, CD₂Cl₂, 25 °C, δ):** 10.67 (broad s, 1 H), 7.32 (m, 40 H), 5.93 (broad s, 2 H), 5.41 (broad s, 4 H), 4.75 (m, 4 H);
\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \degree \text{C}, \delta): 134.55, 130.26, 129.63, 128.60, 127.36, 99.90, 92.24, 83.40, 81.57, 77.62;\]

\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \degree \text{C}, \delta): 134.55, 130.26, 129.63, 128.60, 127.36, 99.90, 92.24, 83.40, 81.57, 77.62;\]

\[\text{FT-IR (cm}^{-1} \text{ ranked intensity): } 3055(7), 1944(15), 1596(9), 1571(13), 1498(4), 1443(12), 1262(11), 1096(2), 804(5), 741(10), 694(1), 588(6), 563(3), 545(14), 468(8);\]

\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \degree \text{C}, \delta): 134.55, 130.26, 129.63, 128.60, 127.36, 99.90, 92.24, 83.40, 81.57, 77.62;\]

\[\text{FT-IR (cm}^{-1} \text{ ranked intensity): } 3055(7), 1944(15), 1596(9), 1571(13), 1498(4), 1443(12), 1262(11), 1096(2), 804(5), 741(10), 694(1), 588(6), 563(3), 545(14), 468(8);\]

\[^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \degree \text{C}, \delta): 7.33 (m, 8 H), 7.22 (m, 32 H), 6.03 (d, 2 H, }^4J_{\text{H-Ag}}= 1.6 \text{ Hz), 5.20 (m, 4 H), 4.64 (m, 4 H);\]

\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \degree \text{C}, \delta): 134.98, 128.66, 128.19, 126.79, 120.03, 105.80, 82.43, 77.41, 76.57;\]

\[\text{FT-IR (cm}^{-1} \text{ ranked intensity): } 3055(10), 2962(7), 2923(14), 1596(6), 1573(15), 1498(1), 1443(13), 1261(4), 1024(2), 910(12), 869(8), 803(5), 740(9), 694(3), 618(11);\]

\section{5.5 References}


Chapter 6

6 Conclusions and Future Work

6.1 Conclusions

This thesis describes: (i) the syntheses of a series of primarily nitrogen-based $\alpha$-diimine ligands containing novel redox-active metalloence substituents, (ii) their reactivity towards main group and transition metal centres (iii) and the electrochemical properties of the ligands and their respective complexes.

Initially, the focus was to synthesize a diiminopyridine ligand containing the known redox-active metalloence, ferrocene, for supporting low valent chalcogen ($S^{2+}$, $Se^{2+}$ and $Te^{2+}$) and pnictogen ($P^{+}$) centres. Electrochemical studies of the phosphorus centred species reveal the possibility of generating the putative tricationic phosphorus complex, and under the conditions employed this indicates that the polycation may be isolable. This work represents the first examples of supporting main group centres (cationic and dicationic) within redox-active ligands containing ferrocenyl substituents.

In order to pioneer this work even further, a focus was placed on modifying the redox-active metalloence substituent. A novel 18 electron mixed sandwich Co(III) complex became of synthetic interest. Electrochemical investigations unveiled a possible two-electron reversible oxidation process from the Co(III) amine (3.16) that would be used in further transformations for the synthesis of nitrogen-based ligands. Never before has such a complex moiety been used in such a manner.

From the early success of the diiminopyridine ligand containing pendant-ferrocene functionalities came the synthesis of a diiminopyridine ligand containing the mixed sandwich cobaltocene moiety. Once again the ligand was capable of supporting main group centres, producing cationic tetrel chelate complexes of Sn and Ge. Analogues ferrocenyl derivatives were also synthesized for further electrochemical comparison. Unfortunately, the Co(III) containing compounds were unstable to the electrochemical conditions employed.
Another attempt of harnessing the electrochemical properties of the mixed sandwich cobaltocene moiety was through its incorporation about a 1,4-diaza-1,3-butadiene framework (4.3). To produce species that may have controlled redox properties, our attention turned to chelating PtMe$_2$ and SnCl$_4$. Previous reports have investigated the redox properties of a dimethyl platinum chelate composed of a $N, N'$-cyclohexyl DAB support, and it was believed that synthesizing a less reactive, neutral, main group complex may simplifying the resulting CVs of the complexes produced. Analogous reactivity of a known $N, N'$-diferrocenyl analogue to tin and platinum was performed for comparative future electrochemical studies. Unfortunately, a full electrochemical investigation was only possible for both complexes using the $N, N'$-diferrocenyl DAB support, as compounds containing mixed sandwich metalloccenes showed complicated cyclic voltammograms.

Instead of utilizing another ligand scaffold supporting the mixed sandwich cobaltocene moiety, 4.3 was used towards the synthesis of an N-heterocyclic carbene complex. Although the electrochemical properties of this system were once again complex, future studies may find utility with the ligands bulky nature.

In all cases, incorporating metalloccene substituents about nitrogen-based ligand frameworks represents innovative supports for both main group (neutral, cationic and dicationic) and transition metal (Pt) centres.

6.2 Future Work

The electrochemical studies of the presented nitrogen-based ligands (and their complexes) containing mixed sandwich cobaltocene substituents were unstable to the electrochemical conditions employed, or produced CVs that were difficult to assign. In the journey to understanding the electronics of symmetric $\alpha$-diimine ligands containing the mixed sandwich cobaltocene or ferrocene moieties, we observed that the redox events of these systems occurred at different potentials. Synthesis of a diimine system containing both moieties sufficiently distant to one another may allow for access of two redox events, from the mixed sandwich cobaltocene and ferrocene, respectively. This type of scaffold should be possible from the $\beta$-diketiminate ligand class, for which the
synthesis of symmetric and asymmetric proligands is well understood in the literature.\textsuperscript{1,2}
Numerous studies have been described targeting the development and stabilization of reactive transition metal and main group systems. There are a number of examples that have been reported where these ligands act in an ancillary manner to stabilize unusually reactive metal fragments or provide species capable of catalyzing various processes.\textsuperscript{3-7}
On the other hand, there are a number of reports in which the β-diketiminate ligands are not innocent observers of the chemistry at the metal, but rather undergo reactions on the ligand backbone.\textsuperscript{8-14} Ligand-centred reactivity (in the framework) could make these compounds more stable towards electrochemical conditions or redox-active agents introduced to the system. This should prevent degradation at the metallocene moiety. Scheme 6.1 describes two proposed routes to asymmetric β-diketimimates that are either neutral or ionic.

**Scheme 6.1:** Proposed synthetic routes to asymmetric metallocene containing β-diketimimates.
In addition to the β-diketimate syntheses, further investigations into the reactivity and properties (e.g. donor ability and electrochemistry) of 5.13 will need to be examined. The reactivity of Rh₂(CO)₂Cl₂ with 5.13 should allow for the synthesis of a Rh complex that is capable of gauging the donor ability of the NHC ligand (via examination of carbonyl IR stretching frequencies).\textsuperscript{15} Other metal complexes may also be synthesized for further electrochemical studies involving this NHC support.

6.3 References


Appendix 1

General Experimental Details

All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Labmaster double station glovebox or using standard Schlenk techniques unless stated otherwise. Reagents were obtained from commercial sources. All solvents were dried using an MBraun controlled atmosphere solvent purification system and stored in Straus flasks under an N₂ atmosphere or over 4 Å molecular sieves in the glovebox. Chloroform-d was dried over calcium hydride, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. Acetonitrile-d₃ and CD₂Cl₂ were purchased from Cambridge Isotope Laboratories and stored in the glovebox over 3 Å or 4 Å molecular sieves, respectively. Proton and $^{13}$C{¹H}, $^{19}$F{¹H}, $^{31}$P{¹H} and $^{119}$Sn{¹H} NMR spectroscopic data were collected on a 400 MHz Varian Inova spectrometer (399.762 MHz for $^1$H; 100.52 MHz for $^{13}$C; 376.15 for $^{19}$F; 161.825 MHz for $^{31}$P; 149.163 MHz for $^{119}$Sn). NMR spectra were recorded at room temperature, unless otherwise indicated, in CDCl₃, CD₃CN, or CD₂Cl₂ and were referenced using the residual protons of the deuterated solvents (CHCl₃, δ_H = 7.26; MeCN, δ_H = 1.94; DCM, δ_H = 5.30), coupling constants are listed in Hz. Carbon-13 NMR spectra were referenced using carbon signals from the respective solvent (CHCl₃, δ_C = 77.16(3); MeCN, δ_C = 1.32(7), 118.26(1); DCM, δ_C = 54.00(5)). Phosphorus-31{¹H}, $^{19}$F{¹H} and $^{119}$Sn{¹H} NMR spectra were recorded unlocked relative to an external standard (³¹P{¹H}, 85% H₃PO₄, δ_p = 0.00; $^{19}$F{¹H}, CF₃C₆H₅, δ_F = -63.9; $^{119}$Sn{¹H}, Me₄Sn 90% in C₆D₆, δ.Sn = 0.00). Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD or a Bruker Apex II-CCD area detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under Paratone-N oil, mounted on MiTeGen micromounts or nylon loops then immediately placed in a cold stream of N₂. Structures were solved and refined using SHELXXTL. UV/Vis absorption spectra were recorded over a range of 235-800 nm using a Varian Cary 300 spectrometer in either DCM (for 2.18, 2.22, 3.17, 3.18, 3.19, 3.20, 3.21, 4.3, 4.4, 4.5, 4.7, 4.8, 4.9, 4.10) or MeCN (for 2.19, 2.20 and 2.21). 2.22 was measured at a concentration of $2.5 \times 10^{-5}$ M; 2.19, 2.20, 2.21, 3.6 and 4.9 were measured at a concentration of $2.0 \times 10^{-5}$ M; 3.21, 4.3, 4.4, 4.5 and 4.10 were measured at a concentration of $1 \times 10^{-5}$ M; and
3.17, 3.18, 3.19, 3.20 were measured at a concentration of $5 \times 10^{-6}$ M. The electrochemical instrumentation employed for Cyclic Voltammetry (CV) was an Autolab30 electrochemical workstation equipped with GPES 4.9 software. The working electrodes involved in the experiments were either a glassy carbon (GC) electrode built from a Tokai GC-20 glassy carbon rod (3 mm diameter) or a platinum electrode built from a platinum wire (1 mm diameter), a Premion product purchased from Alfa Aesar. The disk electrode surface was prepared by polishing on silicon carbide papers (500, 1200, 2400 and 4000) and successively over diamond pastes (1 and 0.25 µm) from Struers. The working electrodes were stored in ethanol and, before using, were polished with diamond paste (1 µm), rinsed with dry ethanol, sonicated in dry ethanol for 5 minutes, and dried. The previous sequence with ethanol was then repeated using 0.25 µm diamond paste. Electrochemical activation of the disk electrode surfaces was carried out before each measurement by multicycling between 0.0 V and 0.5 V at 0.1 Vs$^{-1}$ in the background solution until stabilization of the capacitive current. The reference electrode was a stabilized Ag/AgCl quasi-reference electrode, built by filling a glass tube closed at an extremity with a junction, with an MeCN / 0.1 M TBAPF$_6$ solution. A silver wire was then immersed inside of a glass tube containing the solution, where it was left to stabilize its potential for a week prior to use. Data for 2.13, 2.18, 2.22, are reported verses the standard calomel electrode (SCE). At the end of the electrochemical experiments the CVs were calibrated using either nitrobenzene or ferrocene as an internal standard. The potentials of the reversible voltammetric peak due to the reduction of nitrobenzene to its radical anion (for compounds containing a ferrocene) or the oxidation of ferrocene to ferrocenium (for compounds containing a mixed sandwich cobaltocene) were used to make sure that the CV recorded in different experiment were all correctly calibrated towards the reference electrode. In addition, the reversible reduction of nitrobenzene to its radical anion or the reversible oxidation of ferrocene to ferrocenium involve single electron transfers, therefore the intensity of the voltammetric peak was used to gauge the number of electrons exchanged in the electrochemical processes of the studied compounds. The counter electrode was either a platinum flag or wire. All electrochemical measurements were carried out using the same set of electrodes.
The electrochemical measurements of all compounds were conducted in a home-built glass cell at room temperature. Due to the sensitivity of the compounds to moisture and air, the experiments were performed inside an MBraun Labmaster double station glovebox. For all measurements, feedback correction was employed to minimize the ohmic drop between reference and working electrode. The corresponding background curves were then subtracted from the CVs in order to eliminate the capacitive current contribution.

**Additional Figures**

![NMR spectra for 2.18 and 2.22, respectively, in CD$_2$Cl$_2$.](image)

**A.1:** NMR spectra for 2.18 and 2.22, respectively, in CD$_2$Cl$_2$. 
A.2: NMR spectra for 2.19, 2.20 and 2.21, respectively, in CD$_3$CN.
A.3: NMR spectra for 2.18, 3.20 and 3.21, respectively, in CD$_2$Cl$_2$. 
A.4: NMR spectra for 4.3, 4.4 and 4.5, respectively, in CD$_2$Cl$_2$. 
A.5: NMR spectra for 4.6, 4.7 and 4.8, respectively, in CD$_3$CN.
A.6: NMR spectra for 3.6, 4.9 and 4.10, respectively, in CDCl₃.
A.7: CVs of 2.6 (A) and 2.13 (B) recorded at a Pt electrode in DCM / 0.1 M TBPF₆ with an analyte concentration of 2 mM and at 0.5 V s⁻¹. Experiment done inside an inert atmosphere glove box at room temperature.
A.8: CVs of 2.19 (A), 2.20 (B) and 2.21 (C) recorded at a GC electrode in MeCN / 0.05 M TBABF$_4$ saturated with analyte at 0.1 V s$^{-1}$. Experiment done inside an inert atmosphere glove box at room temperature.
A.9: Compounds 3.17 (DCM), 3.18 (DCM), 3.19 (DCM), 2.18 (DCM), 3.20 (MeCN) and 3.20 (MeCN). For NMR spectra of 3.17, 3.18 and 3.19 see Chapter 3, Figure 3.4.

A.10: Compounds 4.3, 4.4, 4.5, 3.6, 4.9, 4.10, 4.6, 4.7 and 4.8 in DCM.
A.11: Copyright approval for use of Chapter 2 in this document.
A.12: X-ray details for 2.18, 2.19, 2.20, 2.21 and 2.22.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2.18</th>
<th>2.19</th>
<th>2.20</th>
<th>2.21</th>
<th>2.22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₃₁H₳₳Fe₂N₳</td>
<td>C₂₉H₂₳N₳O₶ S₃F₆Fe₂</td>
<td>C₂₉H₂₳N₳O₶ S₂Se₁F₆Fe₂</td>
<td>C₂₉H₂₳F₆Fe₂N₳O₶ S₂Te₁</td>
<td>C₂₇H₂₳N₳P₁Fe₂</td>
</tr>
<tr>
<td>FW (g/mol)</td>
<td>573.29</td>
<td>831.38</td>
<td>878.28</td>
<td>926.92</td>
<td>912.00</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>C2/c</td>
<td>P-1</td>
<td>P-1</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.2926(16)</td>
<td>12.970(2)</td>
<td>10.7138(9)</td>
<td>10.732(3)</td>
<td>12.0077(10)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.6402(17)</td>
<td>18.528(3)</td>
<td>11.5291(9)</td>
<td>11.537(3)</td>
<td>17.2096(14)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>68.139(3)</td>
<td>90.000</td>
<td>104.007(2)</td>
<td>103.487(6)</td>
<td>90.000</td>
</tr>
<tr>
<td>β (deg)</td>
<td>72.717(3)</td>
<td>109.608(4)</td>
<td>94.864(3)</td>
<td>94.198(7)</td>
<td>99.153(2)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>61.101(3)</td>
<td>90.000</td>
<td>107.862(2)</td>
<td>106.741(6)</td>
<td>90.000</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1286.9(3)</td>
<td>3050.8(8)</td>
<td>1530.0(2)</td>
<td>1557.2(7)</td>
<td>2832.12</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Dₐ (mg m⁻³)</td>
<td>1.157</td>
<td>1.810</td>
<td>1.906</td>
<td>1.977</td>
<td>2.143</td>
</tr>
<tr>
<td>radiation, λ (Å)</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
</tr>
<tr>
<td>temp (K)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>R1[I&gt;2σ(I)]</td>
<td>0.0602</td>
<td>0.0706</td>
<td>0.0325</td>
<td>0.0407</td>
<td>0.0343</td>
</tr>
<tr>
<td>wR2(F²)</td>
<td>0.1712</td>
<td>0.1586</td>
<td>0.0790</td>
<td>0.0882</td>
<td>0.0634</td>
</tr>
<tr>
<td>GOF(S)</td>
<td>1.018</td>
<td>1.102</td>
<td>1.039</td>
<td>1.054</td>
<td>1.090</td>
</tr>
</tbody>
</table>

* R1(F[I > 2(I)]) = \sum |F_o| - |F_c|/\sum |F_o|; wR2(F² [all data]) = [w(F_o² - F_c²)²]^{1/2}; S(all data) = [w(F_o² - F_c²)²/(n - p)]^{1/2} (n = no. of data; p = no. of parameters varied; w = 1/[\{F_o² + (aP)^2 + bP\}] where P = (F_o² + 2F_c²)/3 and a and b are constants suggested by the refinement program.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.18</th>
<th>3.19</th>
<th>3.20</th>
<th>3.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{27}H_{23}Cl_{4}Fe_{2}Ge_{2}N_{3}</td>
<td>C_{27}H_{23}Cl_{4}Fe_{2}N_{3}Sn_{2}</td>
<td>C_{77}H_{61}Cl_{4}Co_{2}Ge_{2}N_{3}O</td>
<td>C_{77}H_{65}Co_{2}N_{3}Sn_{2}</td>
</tr>
<tr>
<td>FW (g/mol)</td>
<td>788.16</td>
<td>880.36</td>
<td>1449.13</td>
<td>1554.25</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/c</td>
<td>P2(1)/n</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.791(7)</td>
<td>13.383(5)</td>
<td>10.980(5)</td>
<td>13.035(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>28.663(16)</td>
<td>7.448(3)</td>
<td>14.830(7)</td>
<td>15.667(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.870(4)</td>
<td>29.974(11)</td>
<td>22.891(10)</td>
<td>16.661(5)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>107.17(2)</td>
<td>74.260(12)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>104.54(1)</td>
<td>96.220(4)</td>
<td>91.04(1)</td>
<td>78.500(8)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90.00</td>
<td>90.00</td>
<td>108.93(1)</td>
<td>77.023(15)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2793(3)</td>
<td>2970(2)</td>
<td>3342(3)</td>
<td>3156.5(13)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>D_c (mg m⁻³)</td>
<td>1.875</td>
<td>1.969</td>
<td>1.440</td>
<td>1.637</td>
</tr>
<tr>
<td>radiation, λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>temp (K)</td>
<td>110(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>112(2)</td>
</tr>
<tr>
<td>R1[I&gt;2σ(I)]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wR2(F²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GOF(S)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0442</td>
<td>0.0380</td>
<td>0.0637</td>
<td>0.0494</td>
<td></td>
</tr>
<tr>
<td>0.0982</td>
<td>0.0927</td>
<td>0.1523</td>
<td>0.1475</td>
<td></td>
</tr>
<tr>
<td>1.002</td>
<td>1.027</td>
<td>1.065</td>
<td>1.081</td>
<td></td>
</tr>
</tbody>
</table>

---

\[ R1(F[I > 2(I)]) = \frac{\sum \sqrt{|F_o^2| - |F_c^2|}}{\sum |F_o^2|}; \]

\[ wR2(F^2) \text{ [all data]} = \left[ \frac{w(F_o^2 - F_c^2)^2}{\sum (w(F_o^2 - F_c^2)^2)} \right]^{1/2}; \]

\[ S(\text{all data}) = \left[ \frac{w(F_o^2 - F_c^2)^2}{\sum (w(F_o^2 - F_c^2)^2)(n - p)} \right]^{1/2} (n = \text{no. of data}; p = \text{no. of parameters varied}; w = 1/[\sum (F_o^2) + (aP)^2 + bP] \text{ where } P = (F_o^2 + 2F_c^2)/3 \text{ and } a \text{ and } b \text{ are constants suggested by the refinement program.} \]
A.14: X-ray details for 4.3, 4.4, 4.5, 4.7, 4.8, 4.9 and 4.10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>4.3</th>
<th>4.4</th>
<th>4.5</th>
<th>4.7</th>
<th>4.9</th>
<th>4.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW (g/mol)</td>
<td>Triclinic</td>
<td>P-I</td>
<td>C2/c</td>
<td>C2/c</td>
<td>P-1</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.450(2)</td>
<td>20.824(4)</td>
<td>20.811(4)</td>
<td>20.687(4)</td>
<td>22.472(5)</td>
<td>19.450(4)</td>
<td>17.690(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.904(3)</td>
<td>20.943(4)</td>
<td>10.489(2)</td>
<td>22.472(5)</td>
<td>16.457(3)</td>
<td>16.392(3)</td>
<td>84.46(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>18.275(4)</td>
<td>15.698(3)</td>
<td>28.669(5)</td>
<td>7.9288(16)</td>
<td>19.450(4)</td>
<td>17.690(3)</td>
<td>88.99(3)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>97.88(3)</td>
<td>90.00(0)</td>
<td>90.00(0)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>88.48(3)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>106.17(3)</td>
<td>121.68(3)</td>
<td>109.59(3)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>88.48(3)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>106.09(3)</td>
<td>90.00(0)</td>
<td>90.00(0)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>88.48(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2799.1(1)</td>
<td>5826.05</td>
<td>5896.10</td>
<td>3685.9(13)</td>
<td>2348.8(7)</td>
<td>3240.51</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>D (mg m⁻³)</td>
<td>1.304</td>
<td>1.641</td>
<td>1.590</td>
<td>1.740</td>
<td>1.942</td>
<td>2.015</td>
<td></td>
</tr>
<tr>
<td>Radiation, λ</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td>.71073</td>
<td></td>
</tr>
<tr>
<td>temp (K)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td></td>
</tr>
<tr>
<td>R1(I&gt;2σI)</td>
<td>0.1049</td>
<td>0.0429</td>
<td>0.0581</td>
<td>0.0453</td>
<td>0.0467</td>
<td>0.0521</td>
<td></td>
</tr>
<tr>
<td>wR2(F²)</td>
<td>0.3047</td>
<td>0.1509</td>
<td>0.2033</td>
<td>0.1240</td>
<td>0.1029</td>
<td>0.1615</td>
<td></td>
</tr>
<tr>
<td>GOF(S)</td>
<td>1.746</td>
<td>1.186</td>
<td>1.046</td>
<td>1.081</td>
<td>1.067</td>
<td>1.023</td>
<td></td>
</tr>
</tbody>
</table>


\[ R_1(F[I>2(I)]) = \frac{\sum |F_o| - |F_c| \sqrt{\sum |F_o|} }{ \sum |F_o| } ; \]
\[ wR_2(F^2) = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \]
\[ S(\text{all data}) = [\frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)}]^{1/2} \]

\( n = \) no. of data; \( p = \) no. of parameters varied; \( w = \frac{1}{[\sum (F_o^2 + aP^2 + bP)]} \)

where \( P = \frac{(F_o^2 + 2F_c)^2}{3} \) and \( a \) and \( b \) are constants suggested by the refinement program.
Curriculum Vitae

Name: Eleanor Magdzinski

Post-secondary Education and Degrees:
- University of Western Ontario, London, Ontario, Canada
- The University of Western Ontario, London, Ontario, Canada
  2006-2011 B.Sc.
  2011-2013 M.Sc.

Honours and Awards:
- Western Graduate Research Scholarship (WGRS), 2011-2013

Related Work Experience:
- Teaching Assistant, The University of Western Ontario, 2011-2013

Publications:


Research Presentations:


Note: Presenter Underlined.