4,5-Diazafluorenyl Derivatives as Binucleating Ligands for the Syntheses of Heterobimetallic Complexes

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Chemistry
University of Toronto

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Abstract

This thesis explores 4,5-diazafluorenyl derivatives as binucleating ligands for the syntheses of heterobimetallic complexes. The 4,5-diazafluorenylide (L⁻) ligand contains two coordination sites: a Cp moiety and two N-donors. L⁻ was used to construct Pt^{II}-Cu^{I} and Pt^{II}-Ru^{II} heterobimetallic complexes. Various modifications have been made to the L⁻ framework to alter the regioselectivity. A pendent phosphine was arm attached to the methylene linker to form 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorenylide (Lₚ⁻) and provides a P,C-chelate to anchor metals to the C-donor on the L⁻ backbone. Lₚ⁻ was used to synthesize Pt^{II}-Cu^{I} complexes and dinuclear Ru^{II} complexes. Bulky mesityl groups were installed ortho- to the N-donors to form 3,6-dimesityl-4,5-diazafluorenylide (L_{Mes}⁻). The L_{Mes}⁻ derivative provides steric protection that prevents bulky metal fragments from binding to the N-donors. L_{Mes}⁻ was used to construct a series of Ru^{II}-M complexes (M = Fe^{II}, Co^{II}, Pt^{II}, Cu^{I}) where the metals span from group 8 to 11.
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List of Abbreviations

LH  4,5-diazafluorene

L^- 4,5-diazafluorenide

L_pH 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorene

L_p^- 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorenide

L_MesH 3,6-dimesityl-4,5-diazafluorene

L_Mes^- 3,6-dimesityl-4,5-diazafluorenide

IPr  N,N'-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene

IMes  N,N'-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene

Cp  Cyclopentadienyl

Cp*  1,2,3,4,5-pentamethylcyclopentadienyl

NHC  N-heterocyclic carbene

1  PtPh_2(LH)

2  [PtPh_2L][Na(DME)_3]

3  Cu(IPr)L

4  Cu(IPr)LPtPh_2

5  RuCp*L

6  RuCp*LPtPh_2

7  [RuCp*(L_pH)]_2Cl_2

8  [RuCp*L_p]_2
9a \([\text{Cu(IPr)}L_p]_2\)

9a’ \(\text{Cu(IPr)}L_p\)

9b \([\text{Cu(IMes)}L_p]_2\)

9b’ \(\text{Cu(IMes)}L_p\)

10a \(\text{PtPh}_2L_p\text{Cu(IPr)}\)

10b \(\text{PtPh}_2L_p\text{Cu(IMes)}\)

11 \(\text{PtPh}_2(L_{\text{Mes}H})\)

12 \([\text{PtPh}_2L_{\text{Mes}}][\text{K(DME)}]_2\)

13 \(\text{Cp(NMe}_2)\text{Zr(µ-NMe}_2)_2\text{PtPh}_2\)

14 \(\text{RuCp}^*L_{\text{Mes}}\)

15 \(\text{RuCp}^*L_{\text{Mes}}\text{PtPh}_2\)

16 \(\text{RuCp}^*L_{\text{Mes}}\text{FeCl}_2\)

17 \(\text{RuCp}^*L_{\text{Mes}}\text{CoCl}_2\)

18 \(\text{RuCp}^*L_{\text{Mes}}\text{CuCl}\)

DME 1,2-dimethoxyethane

THF tetrahydrofuran

DMSO dimethyl sulfoxide

DCM dichloromethane

d deuterated protons

° degrees
°C  degrees Celsius
Å  Angstroms
mg  milligrams
mL  milliliters
µmol micromoles
h  hour(s)
NMR nuclear magnetic resonance
δ  chemical shift
ppm parts per million
MHz megahertz
%  percent
s  singlet
d  doublet
sept septet
dd doublet of doublets
m multiplet
J coupling constant
Anal. elemental analysis
Calcd calculated
1 Introduction

1.1 A Source of Inspiration

Nature is a constant and reliable source of inspiration. Metalloenzymes provided the initial spark of inspiration that lead to the field of heteromultimetallic chemistry. The active sites of these proteins spread the workload over a number of different metals to overcome the difficulties of a variety of redox reactions.\(^1\),\(^2\),\(^3\),\(^4\),\(^5\),\(^6\),\(^7\),\(^8\),\(^9\) Hydrogenase uses an Fe-Ni active site to catalyze the reversible two electron oxidation of H\(_2\) (Scheme 1A).\(^1\),\(^2\),\(^3\),\(^4\) Cytochrome c oxidase uses a tris-histidine-ligated copper ion and a high-spin iron heme to mediate the four electron reduction of O\(_2\) to H\(_2\)O (Scheme 1B).\(^5\),\(^6\) Nitrogenase uses seven Fe centres and a Mo centre in the Fe-Mo cofactor to mediate the catalytic six electron reduction of N\(_2\) to ammonia (Scheme 1C).\(^7\),\(^8\),\(^9\)

\begin{center}
\begin{tabular}{c}
\textbf{A)} \hspace{2cm} \textbf{B)} \hspace{2cm} \textbf{C)}
\end{tabular}
\end{center}


Chemists have been using this heteromultimetallic approach in the development of multimetallic catalysts for synthetic chemical purposes.\(^10\),\(^11\) The potential metal-metal cooperativity attainable by heteromultimetallic complexes, unseen by their monometallic or homomultimetallic derivatives, has made this a recent topic of interest.\(^11\)
1.2 The Synthetic Challenge

Amongst all the excitement, the synthesis of heteromultimetallic compounds has proven not to be a trivial process. The ability to synthesize homomultimetallic complexes in a controlled manner requires a lot of effort, let alone the selective synthesis of heteromultinuclear complexes. A variety of strategies have been employed to construct heterobimetallic complexes. The use of metal-metal bonds to assemble these complexes is one viable strategy. Ligands have been used to support these metal-metal interactions by bridging two metals into close proximity (Scheme 2A),\(^{12, 13}\) however there have also been cases with ligand unsupported metal-metal bonds (Scheme 2B).\(^{14, 15, 16, 17, 18}\) One possible strategy is the use of bridging ligands to link different metals. A simple oxo-bridge can be used to synthesize a series of heterobimetallic complexes ranging from all corners of the periodic table (Scheme 2C).\(^{19}\) Cyanide has also been used as a bridging ligand to construct multinuclear metal clusters (Scheme 2D).\(^{20}\) These synthetic strategies maybe simple and hold the metal centres in close proximity, however the chemist loses control over the relative spatial arrangement of the metal centres.

![Scheme 2. A) Ligand supported metal-metal bond. B) Ligand unsupported metal-metal bond. C) Oxo-bridge between zirconium and titanium. D) Cyanide bridge between copper and platinum.](image)

Through careful ligand design multidentate binucleating ligands offer more control when constructing multimetallic complexes.\(^{21}\) With multiple coordination sites residing on a ligand controlling the regioselectivity is crucial to obtain the desired product instead of a statistical mixture. The stepwise metallation of the ligand is one possible strategy to control the regioselectivity. Akita and coworkers observed a proton-induced reversible metal migration with a 3-diphenylphosphinomethyl-5-pyridylpyrazolate ligand. The addition of a base to the monometallic Ir species deprotonated the pyrazolyl moiety allowing migration of the [Ir(cod)]\(^+\) fragment to the P,N-chelate. This isomerization leads to the syntheses of Ir-Rh and Ir-Pd
heterobimetallic isomers where the selectivity depends on the protonation state of the ligand (Scheme 3). \(^{22}\)

**Scheme 3. Synthetic routes to Ir-Pd and Ir-Rh heterobimetallic complexes where the selectivity is determined by the protonation state of the ligand.**

One strategy to govern the regioselectivity is to take advantage of the hard and soft acid-base properties of the binding sites and the metals. Tilley and coworkers used Kumada’s ferrocene based bisphosphine-diamine ligand to construct a variety of heterobimetallic complexes. \(^{23}\) When the ligand was reacted with a Pd\(^{II}\) starting material an equilibrium was seen where the Pd\(^{II}\) centre coordinated to the P,P-chelate and the P,N-chelate. With the addition of a Cu\(^{I}\) starting material the equilibrium was pushed so that the Pd\(^{II}\) was coordinated solely to the P,N-chelate and the Cu\(^{I}\) centre occupied the second phosphine coordination site (Scheme 4). Selective coordination to the harder N,N-chelate was observed when the ligand was first reacted with a hard Mg\(^{2+}\) ion leaving the soft Pd\(^{II}\) centre to coordinated solely to the softer P,P-chelate. The isomerization equilibrium observed with Pd\(^{II}\) was not observed with Pt\(^{II}\). The soft Pt\(^{II}\) centre selectively coordinated to the soft P,P-chelate leaving the N,N-chelate vacant for the addition of a second metal. \(^{23}\)
Scheme 4. The stepwise metallation of Kumada’s ferrocene based biphosphine-diamine ligand with Pd$^{II}$ and Cu$^{I}$.

These stepwise approaches can require the tedious isolation and purification of the mononuclear intermediates. McElwee-White reported a two-step one-pot synthesis of a Rh-Pd heterobimetallic complex where the isolation of a mononuclear species was not required. The ligand was first coordinated to a Rh$^{I}$ centre followed by coordination to the Pd$^{II}$ centre. The bipyridine moiety of the dipicolylamine-bipyridine ligand coordinates solely to the Rh$^{I}$ centre and the dipicolylamine moiety coordinates solely to the Pd$^{II}$ centre (Scheme 5). The selectivity is governed by the geometric preferences of the individual metals to the dipicolylamine-bipyridine ligand.

Scheme 5. Two-step one-pot synthesis of a Rh-Pd heterobimetallic complex.

Previously Hahn and coworkers reported the synthesis of multinuclear Rh$^{III}$ and Ir$^{III}$ complexes using a symmetric 1,3,5-tricarbene ligand where the metals coordinate to one NHC arm and orthometallated into the C-H bond of the central phenyl ring (Scheme 6A). A dinuclear Pt$^{II}$ complex can be synthesized using a symmetric 1,2,4,5-tetracarbene ligand where two adjacent NHC arms coordinate to Pt$^{II}$ in a chelating fashion, and no orthometallation was observed (Scheme 6B). An asymmetric 1,4,5-tricarbene ligand was designed to contain both types of coordination sites: a bis-NHC chelate and an NHC-aryl chelate. When the asymmetric tricarbene was added to Pd(OAc)$_2$ and [MCp*Cl$_2$]$_2$ (M = Rh or Ir) simultaneously the desired Pd-Rh and
Pd-Ir heterobimetallic complexes were formed where the coordination chemistry of the metals governed the regioselectivity (Scheme 6C).  

Scheme 6. A) The coordination chemistry of the 1,3,5-poly NHC ligand. B) The coordination chemistry of the 1,2,4,5-poly NHC ligand. C) The coordination chemistry of the asymmetric poly NHC ligand.

1.3 Ligand Synthesis and Background

1.3.1 4,5-Diazafluorene

Recently our group has taken an interest in 4,5-diazafluorene (LH). LH is made up of two pyridyl moieties connected by a methylene linker. To synthesize LH, 1,10-phenanthroline undergoes an oxidative ring contraction to 4,5-diazafluorenone using KMnO₄ in aqueous base. A Wolff-Kishner reduction of the resulting ketone using hydrazine monohydrate at 180 °C for 6 hours yields LH. Once LH is deprotonated, monoanionic 4,5-diazafluorenide (L⁻) is formed (Scheme 7).

Our group has explored the coordination chemistry of LH and L⁻. Some complexes have shown some very interesting reactivity towards a variety of small molecules. It was found that a few Rh⁻ complexes could catalyze the hydrogenation of a variety of olefins. LH is air stable, however the aerobic oxidation of the sp³ hybridized carbon in the 9-position of LH was observed when coordinated to a [Ru(PPh₃)₂Cl₂] unit. Metal-ligand cooperativity was observed when a Ru⁺ complex engaged in long-range heterolytic cleavage of H₂, where the H⁺ fragment coordinated to the carbanion at the 9-position of L⁻ and the H⁻ fragment coordinated to the Ru⁺.
The same Ru$^{II}$ complex and an isoelectronic Rh$^{III}$ complex have been able to reversibly trap and release CO$_2$ within the C-H bond at the 9-position of the ligand framework.$^{33,34}$ The formal insertion of CO$_2$ into the C-H bond results in the formation of COOH- at the 9-position.$^{33,34}$ The more electron rich Cu$^I$ and Rh$^I$ species trap CO$_2$ through the formation of dinuclear carboxylate complexes.$^{34}$

**Scheme 7. Synthesis of LH and L$^-$.**

L$^-$ is a potential binucleating ligand with two electronically distinct coordination sites: a soft Cp moiety and a hard N,N-chelate. The majority of the metals seem to coordinate to the N,N-chelate and leave the Cp moiety vacant.$^{29,30,31,32,33,34}$ However there have been a few notable exceptions. The addition of NaL to Pd(PPh$_3$_)$_2$Cl$_2$ results in a head-to-tail dimer, where the Pd$^{II}$ centre is coordinated to a single N-donor of one L$^-$ and the carbanion at the 9-position of a second L$^-$ in an $\eta^1(\sigma)$-fashion. More recently the coordination chemistry of a [RuCp*]$^+$ fragment has been explored using L$^-$. Depending on the ligand salt used (i.e. KL or NaL) different linkage isomers were observed. The addition of 4 equiv. of KL to a [RuCp*(μ$_3$-Cl)]$_4$ resulted in the formation of a highly insoluble tetramer [RuCp*L]$_4$. The addition of NaL to 0.25 equiv. of [RuCp*(μ$_3$-Cl)]$_4$ while stirring yielded a ruthenocene type complex RuCp*L (5) in a 43% yield where the [RuCp*]$^+$ fragment is coordinated in an $\eta^5$-fashion to the Cp moiety. It was proposed that the remaining 57% of the [RuCp*]$^+$ fragment was filtered off in the form of the insoluble tetramer (Scheme 8).$^{35}$
Scheme 8. Synthetic routes to RuCp*L (5) and [RuCp*L]₄.

1.3.2 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorene

Modifications made to the L⁻ framework may provide regioselective control during the syntheses of heterobimetallic complexes. The addition of a pendent phosphine arm to the 9-position of LH to form 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorene (LₚH) may compete with the N,N-chelate. LₚH can be prepared from LH by first cyclopropanation of L⁻ to form a spiro compound. The spiro compound then undergoes a nucleophilic attack by LiPPh₂ to form LiLₚ. Because of purification difficulties, the anionic species is protonated to yield LₚH. LₚH can then be deprotonated to yield 9-(2-(diphenylphosphino)ethyl)-4,5-diazafluorene (Lₚ⁻) (Scheme 9).
L$_p$H and L$_p^-$ are both potential binucleating ligands. L$_p$H contains a phosphine donor site and an N,N-chelate, however no binuclear species containing L$_p$H have been reported. The only reported species containing neutral L$_p$H was a Au$^+$ species, where a [AuCl] unit is coordinated to the phosphine donors of two L$_p$H ligands. L$_p^-$ contains two electronically distinct chelate sites: a soft P,Cp-chelate and a hard N,N-chelate. The addition of KL$_p$ to the [Rh]$^+$-Cl and [Au]$^+$-Cl starting materials yielded head-to-tail dimers, however these complexes were difficult to purify as there was not an easy way to remove the product from the resulting KCl precipitate.

L$_p^-$ was used to synthesize [Cu(4-IPr)L$_p$]$_2$ (9a), a dynamic complex that existed as a head-to-tail dimer in the solid state and at cold temperatures in solution, and a monomer in solution at room temperature. In solution the monomeric form of the copper complex (9a$^-$) contains a dangling phosphine arm that could be occupied by a second metal. When 9a was add to [Rh]$^+$-Cl and [Au]$^+$-Cl starting materials the transfer of L$_p^-$ to the Rh$^+$ or Au$^+$ metal centres was observed resulting in the formation of the same Rh$^+$ and Au$^+$ macrocycles and reformation of Cu(4-IPr)Cl (Scheme 10). KL$_p$ is poorly soluble in non-polar organic solvents resulting in long reaction times to form the macrocycles due to the low concentration of L$_p^-$ in solution. The use of 9a$^-$ as an L$_p^-$ ligand transfer reagent not only shortened the reaction times, but also greatly simplified the purification of the macrocycles. Complexes 9a$^-$ and Cu(4-IPr)Cl are soluble in non-polar organic solvents while the resulting macrocycles are poorly soluble. This results in a high
concentration of $L_p^{-}$ in solution and the simple isolation of pure macrocycles by filtration (Scheme 10).\textsuperscript{36}

Scheme 10. Synthetic routes to Rh\textsuperscript{1} and Au\textsuperscript{1} macrocycles.

1.3.3 3,6-dimesityl-4,5-diazafluorene

A second modification of $L^{-}$ is the addition of bulky mesityl groups ortho- to the N-donors. The synthetic route to form $L_{\text{Mes}}H$ from 1,10-phenanthroline is seven steps long. The N-donors of 1,10-phenanthroline have to first be protected with 1,3-dibromopropane and then the carbons ortho- to the N-donors are oxidized, and then chlorinated. Unlike 1,10-phenanthroline, 2,9-dichloro-1,10-phenanthroline could not undergo the oxidative ring contraction due to its insolubility in H\textsubscript{2}O. The synthesis of 2,9-dichloro-1,10-phenanthroline-5,6-dione is required before the oxidative ring contraction can take place. Suzuki coupling was then used to install the mesityl groups ortho- to the N-donors. Finally the bulky ketone could undergo a Wolff-Kishner reduction using hydrazine monohydrate at 180 °C for 24 hours to yield 3,6-dimesityl-4,5-diazafluorene ($L_{\text{Mes}}H$) (Scheme 11).\textsuperscript{35}
Scheme 11. Synthesis of $L_{\text{Mes}}^-$ and $L_{\text{Mes}}^\text{H}$.

This bulky monoanionic ligand 3,6-dimesityl-4,5-diazafluroenide ($L_{\text{Mes}}^\text{H}$) is analogous to the $\beta$-diketiminate AKA nacnac.\textsuperscript{37,38,39,40,41} The coordination chemistry of $L_{\text{Mes}}^\text{H}$ and $L_{\text{Mes}}^-$ was explored using [RuCp*(μ$_3$-Cl)]$_4$ as a [RuCp*]$^+$ fragment.\textsuperscript{35} It was found that the bulky mesityl groups ortho- to the N-donors prevented the bulky [RuCp*]$^+$ fragment from binding to the N-donors. A variety of linkage isomers were constructed depending on the protonation state of the ligand. If $K_{\text{L-Mes}}$ was added to the Ru$^{II}$ tetramer an organo ruthenium sandwich complex, RuCp*$L_{\text{Mes}}$ (14), was formed selectively (Scheme 12). This selectivity was not observed with $L^-$, where either the ruthenocene complex 5, or the tetramer [RuCp*$L$]$_4$ formed (Scheme 8). The bulky mesityl groups prevented the [RuCp*]$^+$ fragment from coordinating to the N-donors.\textsuperscript{35} If the 0.25 equiv. of [RuCp*(μ$_3$-Cl)]$_4$ are added to $L_{\text{Mes}}^\text{H}$ an arene salt [RuCp*(L$_{\text{Mes}}^\text{H}$)]Cl is formed where the [RuCp*]$^+$ fragment is coordinated in an η$^6$-fashion to one of the mesityl substituents. If the arene salt is deprotonated a zwitterionic complex, RuCp*$L_{\text{Mes}}^-$, is formed where the [RuCp*]$^+$ fragment remains coordinated in an η$^6$-fashion to one of the mesityl substituents.\textsuperscript{35}
11. Scheme 12. Syntheses of Ru\textsuperscript{II} linkage isomers using L\textsubscript{Me}H and L\textsubscript{Mes}\textsuperscript{2−}.

Similar to both L\textsuperscript{−} and L\textsubscript{p}\textsuperscript{−}, L\textsubscript{Mes}\textsuperscript{2−} is a potential binucleating ligand with a soft Cp moiety and a hard N,N-chelate site. Compound 14 provides the first complex reported from our group where a metal fragment selectively binds to the Cp site in an \(\eta^5\)-fashion leaving the N,N-chelate vacant for the coordination of less bulky metal starting materials.

1.4 Organo Ruthenium Coordination

Organo Ru fragments have found a niche in the past decade within the field supramolecular coordination complexes. These fragments have been used as building blocks in the construction of complex architectures including squares, triangles, and other 2D or 3D metallacycles and metallacages utilizing coordination-driven self-assembly.\textsuperscript{42, 43, 44, 45, 46, 47, 48} The [RuCp\textsuperscript{+}]\textsuperscript{+} fragment has shown to be an arenophile and favors coordination to π systems,\textsuperscript{49} as a result it has been used to construct a variety of heterobimetallic complexes where it coordinates to π systems in an \(\eta^5\)- or \(\eta^6\)-fashion.\textsuperscript{50, 51, 52, 53, 54, 55, 56}

The syntheses of mononuclear organo ruthenium sandwich complexes using monoanionic ligands have been reported.\textsuperscript{57, 58, 59} Bildstein and White have reported the synthesis of
mononuclear RuCp* complexes using monoanionic N,N-chelate ligands known as aminofulvene aldimate ligands. The synthesis of heteromultimetallic complexes using a variety of pincer type ligands as well as functionalized pentafulvene ligands has been achieved (Scheme 13). These pincer type ligands provide a conjugated π system for the metals to communicate and the [RuCp*]⁺ fragment coordinated to the ligand has been shown to affect the electronics of the metal coordinated in a σ-fashion.

Scheme 13. A variety of Ru-M heteromultimetallic complexes using pincer ligands (A) and (C) and aminofulvene aldimate ligands (B).

The heteromultimetallic complexes reported show the [RuCp*]⁺ fragment coordinating in an η⁵- or η⁶-fashion, similar to what was seen when using LMesH and LMes⁻. Both LMes⁻ and the aminofulvene aldimate are monoanionic nitrogen chelate ligands with a central Cp moiety, the [RuCp*]⁺ fragment coordinates to the central C₅ ring resulting in sandwich complexes with a vacant N,N-chelate site.

1.5 Scope of this Thesis

The major focus of this thesis was to explore 4,5-diazafluorenyl derivatives as binucleating ligands for the synthesis of heterobimetallic complexes. This work is expected to lead to the design of heterobimetallic complexes where the metal combinations and ligand derivatives are specifically selected for the desired reactivity or catalytic application. Separate chapters have been designated to discuss the respective coordination chemistry observed for each 4,5-diazafluorenyl derivative. The Pt⁻II-Zr⁺IV heterobimetallic complex reported is excluded from the manuscript in preparation as additional reactivity is being explored.

Chapter 2 is an accumulation of all the experimental data for the compounds presented in this thesis. Chapter 3 discusses the coordination chemistry of LH and L⁻. The stepwise and one-pot
syntheses of a Pt$^{II}$-Cu$^{I}$ heterobimetallic complex are reported, along with the synthetic routes to a Ru$^{II}$-Pt$^{II}$ heterobimetallic complex. Chapter 4 explores the coordination chemistry of L$_p$H and L$_p^-$. The syntheses of homodinuclear Ru$^{II}$ species, and the stepwise and one-pot syntheses of the Pt$^{II}$-Cu$^{I}$ heterobimetallic complexes are discussed. The syntheses of Ru$^{II}$-M (M = Fe, Co, Pt, Cu) heterobimetallic complexes using L$_{Mes}^-$ are reported in Chapter 5. Chapter 6 summarizes the results presented in this work and explores some of the future directions available for this project.

With the exception of elemental analysis and X-ray experiments the synthetic work and characterizations were performed by the author. Complex 3 and mononuclear ruthenium sandwich complexes 5 and 14 were synthesized and characterized by Vincent T. Annibale. Frederick S. N. Chiu performed the synthesis and characterization of 9a, and the stepwise synthesis and characterization of 10a. Crystals of 4 were obtained by Jung-Eun U. Huh. Datong Song solved the crystal structure for complexes 11 and 16. Vincent T. Annibale solved all other structures. At the time of submission of this thesis, several structures require further refinement and will be completed for publication purposes.

At the time this thesis was being prepared portions of each chapter have been published, or drafted for publication:


**Chapter 5:** Batcup, R.; Annibale, V. T.; Song, D. “Heterobimetallic complexes using 4,5-diazafluorenyl derivatives displaying $\eta^5$, $\kappa^2$ coordination modes”. *Manuscript in preparation.*
2 Experimental

2.1 General Considerations

Unless otherwise noted, all reactions and manipulations were performed in an MBraun glovebox under a dinitrogen atmosphere. All air- or moisture sensitive operations performed out of the glovebox used standard Schlenk/vacuum-line techniques under a dinitrogen atmosphere. All solvents were dried and degassed using standard procedures and stored in the glovebox over 4Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Compounds LH, LpH, LpH, LMesH, Cu(IPr)Cl, Cu(IMes)Cl, Cu(IMes)Cl, [PtPh₂(µ-SMe₂)]ₙ, [RuCp*(µ₃-Cl)]₄, [RuCp*(µ₃-Cl)]₄, 3, 5, 9a, and 14 were synthesized according to literature procedures. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Varian 300 MHz, Varian 400 MHz, Varian 500 MHz, and an Agilent DD2 600 spectrometer. Chemical shifts were referenced relative to the solvents’ residual signals. Elemental analyses were performed on a PE 2400 C/H/N/S analyser at the ANALEST facility of our Chemistry Department.

2.2 Synthesis of PtPh₂(LH) (1)

In air, a solution of LH (6.13 mg, 36.46 µmol) in 2 mL of DCM was layered on top of 1 unit equiv. of [PtPh₂(µ-SMe₂)]ₙ (15 mg, 36.36 µmol) dissolved in 8 mL of DCM. Toluene was layered on top of the resulting yellow solution. The solution was left to sit undisturbed overnight. Yellow crystals of 1 were obtained, washed with hexanes, and dried under vacuum (18 mg, 95% yield). The poor solubility of 1 hindered the collection of ¹³C NMR data. ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ 8.35 (dd, ³J = 4.8 Hz, ⁴J = 0.8 Hz, 2H), 8.11 (dd, ³J = 7.6 Hz, ⁴J = 0.8 Hz, 2H), 7.52-7.49 (m, 4H), 7.44 (dd, ³J = 7.6 Hz, ³J = 5.2 Hz, 4H), 7.07-7.01 (m, 4H), 6.97-6.93 (m, 2H). Anal. Caled for C₂₃H₁₈N₂Pt: C, 53.38; H, 3.51; N, 5.41. Found: C, 53.24; H, 3.58; N, 5.45.

2.3 Synthesis of [PtPh₂L][Na(DME)₃] (2)

NaH (60 wt% in oil, 42 mg, 1.0 mmol) and LH (35 mg, 208 µmol) were suspended in 3 mL of THF. The resulting pink solution was stirred for 5 hours. The pink solution-suspension was then filtered into a vial containing 1 unit equiv. of [PtPh₂(µ-SMe₂)]ₙ (85.6 mg, 208 µmol). A colour change was observed from pink to purple, and the solution was stirred for 6 hours. A yellow
precipitate was removed by filtration and the solvent was removed from the filtrate under vacuum to give a pink residue. The yellow precipitate was determined to be PtPh₂(LH) by independent synthesis and NMR spectroscopy. The pink residue was washed with hexanes, and re-dissolved in a 5:1 DME-THF solution. The solvent was evaporated and purple microcrystals of 2 were obtained (152 mg, 187 µmol, 90% yield). X-ray diffraction quality crystals of 2 were obtained by vapour diffusing hexanes into a DME solution. If the compound was placed under vacuum overnight 1 molecule of DME was lost. Free DME is seen in an NMR sample with DMSO-d₆, while coordinated DME was observed in the C₆D₆ sample. ¹H NMR (DMSO-d₆, 400 MHz, 25 °C): δ 7.90 (dd, 3J = 8.0 Hz, 4J = 0.8 Hz, 2H), 7.46-7.42 (m, 3H), 7.36 (dd, 3J = 4.8 Hz, 4J = 1.2 Hz, 2H), 7.00 (dd, 3J = 4.8 Hz, 3J = 8.4 Hz, 2H), 6.86-6.80 (m, 5H), 6.75-6.68 (m, 2H), 6.15 (s, 1H). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 8.06 (dd, 3J = 8.0 Hz, 4J = 0.8 Hz, 2H), 7.95 (dd, 3J = 8.0 Hz, 4J = 1.6 Hz, 3H), 7.81 (dd, 3J = 4.8 Hz, 4J = 1.2 Hz, 2H), 7.20-7.14 (m, 5H), 7.09-7.03 (m, 2H), 6.90 (dd, 3J = 8.0 Hz, 4J = 4.4 Hz, 2H), 6.87 (s, 1H), 2.94 (s, 12H, DME), 2.81 (s, 18H, DME). ¹³C NMR (DMSO-d₆, 100 MHz, 25 °C): δ 143.4, 141.3, 139.0, 131.5, 125.6, 125.4, 120.2, 116.8, 79.2. Anal. Calcd for C₂₃H₁₇N₂NaPt₂DME: C, 51.73; H, 5.18; N, 3.89. Found: C, 51.37; H, 5.72; N, 3.59.

2.4 Synthesis of [(IPr)CuLPtPh₂] (4)

2.4.1 Method 1

To the solid 2 (90 mg, 111 µmol) a solution of Cu(IPr)Cl (54 mg, 111 µmol) dissolved in 3.5 mL of toluene was added. The resulting brown solution was left to sit for 30 minutes at room temperature. A yellow precipitate was observed. The solution was then filtered and pentane was left to diffuse into the filtrate at -33 °C for four days. Yellow crystals were obtained (18 mg, 18.6 µmol, 17% crystalline yield).

2.4.2 Method 2

A suspension of 3 (60 mg, 96.9 µmol) in 6 mL of hexanes was added to a suspension of 1 unit equiv. of [PtPh₂(µ-SMe₂)]ₙ (39.9 mg, 96.9 µmol) in 1 mL of toluene. The suspension was stirred for 11 hours. The resulting yellow precipitate of complex 4 was collected by filtration (74 mg, 76.4 µmol, 79% yield). Complex 4 was stored in the -33 °C freezer. X-ray quality crystals of 4·
(C₇H₈) were obtained by diffusing pentanes into a toluene solution at -33 °C for four days (18.1 mg, 18.7 µmol, 19% crystalline yield).

2.4.3 One-pot synthesis

LH (10 mg, 59.4 µmol) was added to a suspension of NaH (60 wt% in oil, 12 mg, 297.3 µmol) in 1 mL of THF. After 1.5 hours the pink solution-suspension was filtered into a vial containing Cu(IPr)Cl (29 mg, 59.4 µmol) and 1 unit equiv. of [PtPh₂(μ-SMe₂)]ₙ (24.4 mg, 59.4 µmol). The filter was rinsed with an additional 2 mL of THF. The reaction mixture initially turned purple, and after 30 minutes the solution was brown and a yellow precipitate was observed. The addition of 17 mL of hexanes caused the rest of the yellow precipitate to form, and the yellow precipitate was collected on a filter. The yellow precipitate was re-dissolved in 8 mL of toluene and 50 mL of hexanes was added to the bright yellow solution, producing the precipitate of 4. The solution was placed in the freezer overnight and a bright yellow precipitate was collected on a filter. Complex 4 was removed from the filter in a slurry of hexanes and dried under vacuum (30 mg, 30.97 µmol, 52% yield). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 8.30 (br, 4H), 8.13 (br, 2H), 7.40 (br, 5H), 7.30-7.18 (m, 5H), 6.96 (d, ³J = 7.6 Hz, 4H), 6.51 (dd, ³J = 7.6 Hz, ⁴J = 5.2 Hz, 2H), 6.04 (s, 2H), 4.39 (s, 1H), 2.05 (sept, ³J = 6.8 Hz, 4H), 0.94 (d, ³J = 6.8 Hz, 12H), 0.97 (d, ³J = 6.8 Hz, 12H). ¹³C NMR (C₆D₆, 100 MHz, 25 °C): δ 145.1, 140.1, 134.2, 131.2, 128.8, 127.0, 124.3, 122.5, 121.9, 121.4, 28.7, 24.6, 23.7. Anal. Calcd for C₅₈H₅₃N₄CuPt·0.21(C₇H₈): C, 62.58; H, 5.58; N, 5.67. Found: C, 62.22; H, 5.59; N, 5.55.

2.5 Synthesis of RuCp*LPtPh₂ (6)

2.5.1 Method 1

To a solution of 2 (50 mg, 61.7 µmol) in 3 mL of THF was added a suspension of [RuCp*(μ₃-Cl)]₄ (16.8 mg, 15.4 µmol) in 8 mL of THF. The resulting brown suspension was left to sit overnight. A yellow/beige precipitate was removed by filtration and the solvent of the filtrate was removed under vacuum to yield the compound 6 (46.0 mg, 61.1 µmol, 99% yield). X-ray quality crystals of 6 were obtained by diffusing pentanes into a solution of toluene at -33 °C.
2.5.2 Method 2

To 1 unit equiv. of solid [PtPh$_2$(µ-SMe$_2$)$_n$]$_n$ (22.4 mg, 54 µmol) was added 5 (19.2 mg, 47.6 µmol) in 2 mL of THF. The resulting brown solution was left to sit overnight. The resulting solution contained orange and yellow precipitate. The suspension was filtered and the precipitate collected on the filter washed thoroughly with THF. The volatiles of the filtrate were removed under reduced pressure and the resulting orange/brown residue was washed with hexanes and dried under vacuum to yield 6 (21.4 mg, 28.4 µmol, 60% yield). $^1$H NMR (C$_6$D$_6$, 600 MHz, 25 °C): δ 8.22 (dd, $^3$J = 4.2 Hz, $^4$J = 1.2 Hz, 2H), 8.15-8.12 (m, $^3$J$_{Pt-H}$ = 77.4 Hz, 3H), 7.40-7.35 (m, 5H), 7.23-7.19 (m, 2H), 7.07 (dd, $^3$J = 8.4 Hz, $^4$J = 1.2 Hz, 2H), 5.99 (dd, $^3$J = 8.4 Hz, $^3$J = 4.2 Hz, 2H), 4.72 (s, 1H), 1.20 (s, 15H).

2.6 Synthesis of [RuCp*(L$_p$H)$_2$Cl$_2$ (7)]

[RuCp*(µ$_3$-Cl)$_4$]$_4$ (10 mg, 9.2 µmol) was dissolved in 12 mL of THF, and L$_p$H (14 mg, 36.8 µmol) was dissolved in 8 mL of THF. The L$_p$H solution was carefully layered on top of the [RuCp*(µ$_3$-Cl)$_4$]$_4$ solution, resulting in a purple solution. Slow evaporation of the THF solvent yielded orange crystals of 7 suitable for X-ray crystallographic analysis. After 8 days the supernatant was decanted; the crystals were washed with cold THF and dried under vacuum (10.8 mg, 8.3 µmol, 45% yield). $^1$H NMR (DMSO-$d_6$, 400 MHz, 25 °C): δ 8.75 (d, $^3$J = 5.47 Hz, 2H), 7.70-7.59 (m, 10H), 7.50 (dd, $^3$J = 7.55 Hz, $^3$J = 5.44 Hz, 2H), 7.40 (d, $^3$J = 7.59 Hz, 2H), 4.16 (t, $^3$J = 7.40 Hz, 1H), 1.86-1.80 (m, 2H), 1.11 (d, $^3$J$_{H-P}$ = 1.23 Hz, 15H), 0.18-0.14 (m, 2H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz, 25 °C): δ 160.7, 152.2, 138.4, 133.9, 133.5, 133.1 (d, $^3$J$_{C-P}$ = 11.8 Hz), 132.9, 130.8, 129.2 (d, $^3$J$_{C-P}$ = 9.6 Hz), 127.05, 84.4 (d, $^3$J$_{C-P}$ = 1.8 Hz), 67.4, 25.6, 9.0. $^{31}$P NMR (DMSO-$d_6$, 162 MHz, 25 °C): δ 37.7. Anal. Calcd for C$_{33}$H$_{32}$N$_2$PtRu·0.33(C$_7$H$_8$): C, 54.15; H, 4.46; N, 3.58. Found: C, 53.86; H, 4.64; N, 3.60.
2.7 Synthesis of [RuCp*L\text{p}]_2 (8)

2.7.1 Method 1

L\text{p}H (50 mg, 131.4 µmol) and KO\text{t}Bu (14.7 mg, 131.4 µmol) were dissolved in 2 mL of THF and stirred for 2 h, resulting in a purple solution of KL\text{p}. To the solution of KL\text{p} was added solid [RuCp*(µ_3-Cl)]_4 (35.7 mg, 32.9 µmol), and the mixture was stirred for 2 h. The solvent was removed under vacuum, leaving a brown residue, which was extracted into 10 mL of toluene and filtered. The brown toluene solution was heated at 100 °C overnight, resulting in a bright green solution. The green solution was filtered, and the solvent was removed under vacuum to give complex 8 (60 mg, 74% yield). X-ray diffraction quality crystals can be grown by either vapor diffusion of hexanes into a benzene solution of (8) or vapor diffusion of pentane into a DME solution (8∙(C_5H_{12})).

2.7.2 Method 2

To 7 (18.6 mg, 14.25 µmol) was added 1 mL of a 29.7 µmol/mL solution of KO\text{t}Bu, and the mixture was left to sit overnight at room temperature to yield a green solution. The solvent and volatiles were removed under vacuum, and the residue was extracted into toluene, filtered, and dried under vacuum to give complex 8 (16.2 mg, 13.2 µmol, 92% yield). ^1H NMR (C_6D_6, 300 MHz, 25 °C): δ 7.85 (d, J = 4.72 Hz, 2H), 7.71–7.65 (m, 4H), 7.35–7.26 (m, 6H), 7.23 (dd, J = 7.22 Hz, J = 1.39 Hz, 2H), 6.95 (dd, J = 7.76 Hz, J = 4.71 Hz, 2H), 2.54–2.44 (m, 2H), 1.37 (d, J = 1.37 Hz, 15H), −0.55 to −0.66 (m, 2H). ^13C NMR (C_6D_6, 100 MHz, 25 °C): δ 142.5, 135.2, 134.9, 134.6, 133.5 (d, J_C−P = 10.59 Hz), 129.1 (d, J_C−P = 1.74), 126.5, 124.3, 121.8, 116.8, 95.1 (d, J_C−P = 9.89 Hz), 82.4 (d, J_C−P = 2.18 Hz), 9.9. ^31P NMR (C_6D_6, 121.5 MHz, 25 °C): δ 38.0. Anal. Calcd for C_70H_70N_4P_2Ru_2∙(C_4H_{10}O_2): C, 67.25; H, 6.10; N, 4.24. Found: C, 66.79; H, 5.90; N, 4.31.

2.8 Synthesis of [Cu(IMes)L\text{p}]_2 (9b)

KO\text{t}Bu (22 mg, 197.2 µmol) and L\text{p}H (75 mg, 197.2 µmol) were dissolved in 8 mL of THF and the resulting purple solution was stirred for 3 hours. A solution of Cu(IMes)Cl (80 mg, 197.2 µmol) in 3 mL of THF was then added and a colour change to green was observed. The reaction mixture was stirred for an additional 12 hours. The solvent was then evaporated under vacuum
and a green powder was obtained. The green powder was then dissolved in toluene and filtered through Celite. The solvent was evaporated to reveal a green residue (64.2 mg, 85.9 µmol, 90% yield). X-ray diffraction quality crystals of 9b(Et₂O) were obtained by diffusing diethyl ether into a DME solution of the compound at -33 °C for two weeks. The poor solubility of compound 9b in common NMR solvents hindered the collection of ¹³C NMR data. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 7.49-7.30 (br, 3H), 7.10-6.83 (m, 5H), 6.74-6.48 (m, 5H), 6.05 (s, br, 2H), 2.78 (s, br, 1H), 2.10 (s, br, 6H), 1.88 (s, br, 12H). ³¹P NMR (C₆D₆, 161 MHz, 25 °C) δ -7.77, -10.73. Anal. Caled for C₄₆H₄₄N₄CuP·0.16Et₂O·0.05DME: C, 73.66; H, 6.08; N, 7.34. Found: C, 73.15; H, 6.42; N, 7.10.

2.9 Synthesis of PtPh₂LₚCu(IPr) (10a)

2.9.1 Method 1

To a solution of 1 unit equiv of 9a (18.2 mg, 21.9 µmol) was added 1 unit equiv. of [PtPh₂(µ-SMe₂)]ₙ (9 mg, 21.9 µmol) in 5 mL of benzene. The solution was stirred for 48 hours to yield an orange-green solution. The solution was filtered and the solvent was removed under reduced pressure to yield an orange-green solid (20.7 mg, 17.5 µmol, 80% yield). Diffusion of pentanes into a solution of benzene yielded orange crystals of 10a·(C₆H₆)₂ suitable for X-ray diffraction.

2.9.2 One-pot synthesis

LₚH (13.9 mg, 36.46 µmol) and KO'Bu (4.1 mg, 36.46 µmol) were dissolved in 3 mL of THF and stirred for 3 hours. The purple KLₚ solution was added to 1 equiv of Cu(IPr)Cl (17.8 mg, 36.46 µmol) and 1 unit equiv. of [PtPh₂(µ-SMe₂)]ₙ (15 mg, 36.46 µmol) to yield a blue-green solution. This was stirred for 2 days and a orange-green solution was observed. The solvent was evaporated and the light yellow-green residue obtained was dissolved in C₆H₆. This benzene solution was filtered and the solvent evaporated to yield an orange-green residue of complex 10a that upon recrystallization from benzene and pentanes appears orange (38.8 mg, 32.8 µmol, 90%). The poor solubility of compound 10a in common NMR solvents hindered the collection of ¹³C NMR data. ¹H NMR (C₆D₆, 300 MHz, 25 °C): δ 7.91-7.77 (m, 6H), 7.74-7.62 (br, 2H), 7.37-7.28 (m, 3H), 7.22-6.97 (m, 12 H), 6.89-6.74(m, 3H), 6.69 (d, J = 5.1 Hz, 2H), 6.40-6.19 (m, 6H), 2.86-2.71 (m, 2H), 2.61 (m, 4H), 2.33-2.14 (m, 2H), 1.19 (d, ³J = 6.9 Hz, 12H), 1.06 (d, ³J
2.1 Synthesis of PtPh$_2$L$_P$Cu(IMes) (10b)

2.1.1 Method 1

1 unit equiv. of 9b (18.2 mg, 24.3 µmol) and 1 unit equiv. of [PtPh$_2$(µ-SMe)$_2$)$_n$ (10 mg, 24.3 µmol) were dissolved in 5 mL of benzene. The green solution was stirred for 48 hours to yield a light green solution with precipitate. The solution was filtered and the solvent was removed under vacuum to obtain a light green residue (18.2 mg, 16.6 µmol, 68% yield). Dark green X-ray diffraction quality crystals of 10b·(C$_6$H$_6$) were obtained by vapour diffusion of hexanes into the benzene solution. The solvent was pipetted off and the crystals were washed with cold toluene. (10 mg, 9.12 µmol, 37% yield). When the crystals were broken under a microscope they were yellow under the green surface. When 10b was recrystallized by vapour diffusion of hexanes into the DME solution, the other polymorph with three-coordinate Cu centres was obtained.

2.1.2 One-pot synthesis

L$_P$H (20 mg, 52.6 µmol) and KO'Bu (5.9 mg, 52.6 µmol) were dissolved in 3 mL of THF and stirred for 3.5 hours. To the resulting purple solution of KL$_P$ was added to a mixture of Cu(IMes)Cl (21.2 mg, 52.6 µmol) and [PtPh$_2$(µ-SMe)$_2$]]$_n$ (21.6 mg, 52.6 µmol). A colour change to green was observed and the solution was stirred for 2 days to yield a yellow-green solution. The solvent was evaporated under vacuum and the green residue was dissolved in benzene and filtered through Celite. The solution was concentrated under vacuum and hexanes was diffused into the solution to yield green crystals of 10b (33 mg, 30.1 µmol, 57% yield). The poor solubility of compound 10b in common NMR solvents hindered the collection of $^{13}$C NMR data.

$^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 7.90-7.84 (m, 4H), 7.80 (dd, $^3$J = 8.0 Hz, $^4$J = 1.2 Hz, 2H), 7.72-7.64 (m, $^3$J$_{Pt-H}$ = 65.2 Hz, 2H), 7.21-7.11 (m, 6H), 7.10-7.04 (m, 2H), 7.0 (dd, $^3$J = 8.0 Hz, $^3$J = 4.8 Hz, 2H), 6.86-6.80 (m, 2H), 6.77 (d, $^4$J = 0.4 Hz, 4H), 6.73-6.66 (m, 1H), 6.29-6.16 (m, 5H), 6.08 (s, 2H), 2.92-2.87 (m, 2H), 2.33 (dt, $^2$J$_{Pt-H}$ = 26.0 Hz, $^3$J$_{H-H}$ = 7.2 Hz, 2H), 2.12 (s, 6H), 2.07 (s, 12H). $^{31}$P NMR (C$_6$D$_6$, 162 MHz, 25 °C): δ 37.96 ($^1$J$_{Pt-P}$ = 1977 Hz). Anal. Calcd for C$_{58}$H$_{54}$N$_4$CuPPt: C, 63.52; H, 4.96; N, 5.11. Found: C, 63.29; H, 5.14; N, 4.78.
2.11 Synthesis of PtPh$_2$(L$_{\text{Mes}}$H) (11)

In the glovebox L$_{\text{Mes}}$H (51 mg, 126.1 µmol) and 1 unit equiv. of [PtPh$_2$(µ-SMe$_2$)]$_n$ (51.9 mg, 126.1 µmol) were dissolved in 6 mL THF and left to sit for 2 hours. The resulting orange solution was concentrated to 5 mL under vacuum. Yellow block-shaped crystals of 11 were obtained by vapour diffusion of hexanes into the solution of THF overnight (72 mg, 95.5 µmol, 76% crystalline yield). $^1$H NMR (CDCl$_3$, 500 MHz, 25 °C): δ 8.03 (d, $^3J = 8.0$ Hz, 2H), 7.13 (d, $^3J = 8.0$ Hz, 2H), 6.83-6.75 (m, $^3J_{\text{Pt-H}} = 76.0$ Hz, 3H), 6.44 (s, 4H), 6.26-6.19 (m, 6H), 4.20 (s, 2H), 2.14 (s, 6H), 2.05 (s, 12H). $^{13}$C NMR (CDCl$_3$, 126 MHz, 25 °C): δ 162.9, 161.8, 138.0, 137.3, 135.8, 135.0, 134.5, 133.9, 133.9, 128.6, 128.5, 125.3, 119.7, 34.8, 21.1, 20.9. Anal. Calcd for C$_{41}$H$_{38}$N$_2$Pt∙1.5(C$_4$H$_8$O): C, 65.48; H, 5.85; N, 3.25. Found: C, 65.30; H, 5.70; N, 3.38.

2.12 Synthesis of [PtPh$_2$(L$_{\text{Mes}}$)][K(DME)$_2$] (12)

2.12.1 Method 1

Complex 11 (45.1 mg, 59.8 µmol) and KO'Bu (7.2 mg, 64.2 µmol) were suspended in 2 mL of THF. The resulting purple solution was left to sit for 3 hours after which the solvent was removed under vacuum. The pink residue was dissolved in a 2:1 solution of DME:THF. The solvent was removed under reduced pressure to yield purple crystals of 12 (49.1 mg, 50.5 µmol, 85% yield).

2.12.2 Method 2

L$_{\text{Mes}}$H (50 mg, 123.6 µmol) and KO'Bu (13.9 mg, 123.6 µmol) were dissolved in 3 mL of THF and stirred for 3 hours. The red solution of KL$_{\text{Mes}}$ was added to 1 unit equiv. of [PtPh$_2$(µ-SMe$_2$)]$_n$ (50.8 mg, 123.6 µmol). The mixture was stirred overnight to yield a purple solution. The solvent was removed under vacuum and the resulting purple residue was dissolved in a 5:1 DME:THF solution. The solution was filtered and hexanes was left to vapour diffuse into the filtrate. Needle-shaped purple crystals of 12 were obtained, washed with hexanes and dried under vacuum (84.6 mg, 87.0 µmol, 70% crystalline yield). $^1$H NMR (DMSO-$d_6$, 400 MHz, 25 °C): δ 7.91 (d, $^3J = 8.0$ Hz, 1H), 7.83 (d, $^3J = 8.0$ Hz, 1H), 7.01-6.93 (m, 3H), 6.91 (s, 1H), 6.84 (s, 1H), 6.68 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 2H), 6.58 (d, $^3J = 8.0$ Hz), 6.50 (s, 1H), 6.47-6.38 (m, 3H), 6.36-6.30 (m, 2H), 6.24 (t, $^3J = 7.6$ Hz, 2H), 6.12 (s, 1H), 6.28-6.20 (m, 1H), 2.33 (s, 3H), 2.29
(s, 3H), 2.23 (d, J = 3.2 Hz, 6H), 2.04 (s, 3H), 0.57 (s, 3H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz, 25 °C): δ 148.8, 147.2, 145.0, 142.70, 140.6, 140.5, 139.3, 138.0, 137.9, 136.3, 135.3, 135.1, 134.8, 134.7, 134.7, 129.4, 127.8, 127.7, 127.2, 127.0, 126.4, 125.0, 124.1, 124.0, 120.2, 119.8, 117.4, 117.2, 79.3, 21.67, 21.12, 21.0, 20.8, 20.5, 19.1. $^{195}$Pt NMR (DMSO-$d_6$, 600 MHz, 25 °C): δ -3722.9. Anal. Calcd for C$_{41}$H$_{47}$N$_2$PtK∙2.1(C$_4$H$_{10}$O$_2$): C, 60.47; H, 5.96; N, 2.86. Found: C, 59.97; H, 5.84; N, 2.86.

2.13 Synthesis of Cp(NMe$_2$)Zr(µ-NMe$_2$)$_2$PtPh$_2$ (13)

To 1 unit equiv. of solid [PtPh$_2$(µ-SMe$_2$)]$_n$ (40 mg, 97.2 µmol) a solution of ZrCp(NMe$_2$)$_3$ (29.6 mg, 102.6 µmol) in 1 mL of toluene was added. The reaction was heated at 45 °C for 5 hours at which point everything was dissolved. The solution was layered with 19 mL of hexanes and placed in the -33 °C freezer. After 5 days colourless crystals of 13 were obtained, washed with minimum hexanes, and dried under reduced pressure (35.5 mg, 55.6 µmol, 57% crystalline yield). $^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 7.67 (dd, $^3$J = 8.0 Hz, $^4$J = 1.6 Hz, J$_{Pt-H}$ = 70.6 Hz, 4H), 7.26-7.17 (m, 4H), 7.04-6.95 (m, 2H), 5.71 (s, 5H), 3.31 (s, 6H), 2.36 (s, J$_{Pt-H}$ = 24.0 Hz, 6H), 2.17 (s, J$_{Pt-H}$ = 28.8 Hz, 6H). $^{13}$C NMR (C$_6$D$_6$, 100 MHz, 25 °C): δ 148.9, 137.1, 127.4, 122.7, 112.3, 49.2, 47.8, 43.5. Anal. Calcd for C$_{23}$H$_{33}$N$_3$PtZr: C, 43.31; H, 5.21; N, 6.59. Found: C, 43.60; H, 5.95; N, 7.31.

2.14 $^1$H NMR data for Cp*Ru(L$_{Mes}$) (14)

$^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 7.35 (d, $^3$J = 8.8 Hz, 2H), 6.98 (s, 4H), 6.74 (d, $^3$J = 8.8 Hz, 2H), 4.82 (s, 1H), 2.39 (s, 12H), 2.24 (s, 6H), 1.50 (s, 15H).

2.15 Synthesis of Cp*Ru(L$_{Mes}$)PtPh$_2$ (15)

2.15.1 Method 1

Compound 14 (50 mg, 78.14 µmol) and 1 unit equiv. of [PtPh$_2$(µ-SMe$_2$)]$_n$ (32.1 mg, 78.14 µmol) were dissolved in 10 mL of THF. The resulting red solution was left overnight. The volatiles were removed under vacuum to obtain a red film. The red film was dissolve in 10 mL of toluene and pentanes was diffused into the solution. Red crystals of 15 were obtained, washed with hexanes and dried under vacuum (20.2 mg, 20.4 µmol, 26% crystalline yield).
2.15.2 Method 2

Compound 12 (35 mg, 36 µmol) and [RuCp*(µ$_3$-Cl)]$_4$ (9.8 mg, 9 µmol) were suspended in 5 mL of THF and left to sit overnight to yield a red solution. Volatiles were removed under vacuum and the compound was extracted into toluene and filtered to remove KCl. The solvent was removed under vacuum to yield 15 as a red residue (32.5 mg, 32.8 µmol, 91% yield). X-ray diffraction quality crystals of 15 were obtained by diffusing pentane into a solution of toluene.

$^1$H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 7.41 (dd, $^3$J = 8.0 Hz, $^4$J = 1.6 Hz, $^3$J$_{Pt-H}$ = 73.6 Hz, 3H), 7.17 (d, $^3$J = 8.8 Hz, 2H), 6.68 (s, 2H), 6.64 (t, $^3$J = 7.6 Hz, $^3$J = 6.8 Hz, 4H), 6.58-6.53 (m, 2H), 6.40 (s, 2H), 6.31 (d, $^3$J = 8.8 Hz, 2H), 4.75 (s, 1H), 2.40 (s, 6H), 2.14 (s, 6H), 2.10 (s, 6H), 1.72 (s, 15H).

$^{13}$C NMR (C$_6$D$_6$, 100 MHz, 25 °C): δ 162.7, 138.1, 138.0, 137.1, 136.2, 136.0, 135.7, 133.0, 129.3, 128.7, 125.6, 124.8, 120.3, 113.4, 85.4, 84.2, 57.7, 21.6, 21.2, 20.4, 11.3. Anal. Calcd for C$_{51}$H$_{52}$N$_2$PtRu: C, 61.93; H, 5.30; N, 2.83. Found: C, 62.41; H, 5.43; N, 2.89.

2.16 Synthesis of Cp*Ru(L$_{Mes}$)FeCl$_2$ (16)

Compound 14 (48 mg, 75.0 µmol) and FeCl$_2$∙(thf)$_{1.5}$ (17.6 mg, 74.9 µmol) were suspended in 3 mL of THF and left to sit overnight. Volatiles were removed under vacuum to yield a red residue. Crystals of 16(C$_7$H$_8$) were obtained by diffusing hexanes into a solution of toluene (22.6 mg, 29.5 µmol, 39% crystalline yield). $^1$H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 54.55 (s, 2H), 4.52 (s, 2H), 3.98 (s, 2H), 3.06 (s, 15H), 1.46 (br, 6H), 0.17 (s, 6H), -1.57 (br, 2H), -3.32 (br, 5H), -12.07 (br, 2H). Anal. Calcd for C$_{39}$H$_{42}$N$_2$Cl$_2$FeRu·1.4(C$_7$H$_8$): C, 65.44; H, 5.99; N, 3.13. Found: C, 65.33; H, 5.89; N, 3.39.

2.17 Synthesis of Cp*Ru(L$_{Mes}$)CoCl$_2$ (17)

Compound 14 (83.1 mg, 129.9 µmol) and CoCl$_2$∙(thf)$_{1.5}$ (31 mg, 130.2 µmol) were suspended in 3 mL of THF and left to sit overnight. The resulting dark brown solution was filtered to remove blue solids and the solvent was removed under vacuum to yield a dark brown residue. Dark brown crystals of 17 were obtained by diffusing pentanes into a solution of DME (56 mg, 72.8 µmol, 56% crystalline yield). $^1$H NMR (CDCl$_3$, 600 MHz, 25 °C): δ 50.30 (s, 2H), 22.87 (s, 1H), 6.12 (s, 15H), 3.43 (s, 4H), 1.48 (s, 2H), 1.21 (s, 1H), -0.71 (s, 2H), -0.99 (s, 1H), -2.05 (2, 6H), -2.91 (s, 2H), -(3.05-3.56) (m, 6H). Anal. Calcd for C$_{39}$H$_{42}$N$_2$Cl$_2$CoRu: C, 60.86; H, 5.50; N, 3.64. Found: C, 60.68; H, 5.63; N, 3.63.
2.18 Synthesis of Cp*Ru(L_{Mes})CuCl (18)

Compound 14 (76.2 mg, 119.1 µmol) and CuCl (13 mg, 131.3 µmol) were suspended in 5 mL of THF and left to sit overnight. The resulting red solution was filtered to remove excess CuCl. Solvent from the filtrate was removed under vacuum to yield a red residue. Crystals of 18·0.5(C_{4}H_{10}O_{2}) were obtained by vapour diffusing hexanes into a DME solution (55.0 mg, 74.4 µmol, 62% crystal yield). \(^1\)H NMR (C_{6}D_{6}, 400 MHz, 25 °C): δ 7.34 (d, \(^3\)J = 8.8 Hz, 2H), 6.92-6.78 (m, 4H), 6.60 (d, \(^3\)J = 8.8 Hz, 2H), 4.82 (s, 1H), 2.56 (br, 6H), 2.12 (s, 12H), 1.49 (s, 15H). \(^{13}\)C NMR (C_{6}D_{6}, 100 MHz, 25 °C): δ 161.3, 138.4, 136.7, 129.5, 122.0, 87.8, 83.7, 57.6, 21.2, 14.3, 11.1. Anal. Calcd for C_{39}H_{42}N_{2}ClCuRu: C, 63.40; H, 5.73; N, 3.79. Found: C, 63.19; H, 5.82; N, 3.88.

2.19 X-ray diffraction analysis

2.19.1 General Considerations

The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer, and processed with the Bruker Apex 2 software package.\(^{65}\) Data was collected with graphite monochromated Mo Kα radiation (\(\lambda = 0.71073 \) Å), at 150 K controlled by an Oxford Cryostream 700 series low temperature system. The structures were solved by the direct methods or Patterson and refined using SHELX-2013.\(^{66}\) Disordered portions of DME ligands of complex 2 were successfully modelled over two positions. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated using the riding model. The disordered Cu centre in 10b obtained from DME/hexanes was modelled successfully over two positions. The diffuse electron density in the crystal lattice of 8 obtained from DME/pentanes and of 10b obtained from DME/hexanes was removed with the SQUEEZE function of PLATON\(^{67}\) and its contribution was excluded from the formula.
### 2.19.2 Crystallography Data

<p>| Table 1: Crystallographic data for compounds 1 to 7. |
|---------------------------------|-------------|-----------|-----------|-----------|-----------|
| Formula | C$<em>{23}$H$</em>{18}$N$<em>2$Pt | C$</em>{33}$H$<em>{27}$N$<em>2$O$<em>2$PtNa | C$</em>{33}$H$</em>{46}$N$<em>4$PtRu | C$</em>{33}$H$</em>{46}$N$<em>2$PtCu | C$</em>{33}$H$_{46}$N$_2$PtCu |
| F.W. | 517.48 | 809.82 | 1060.72 | 752.76 | 1304.29 |
| T (K) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| Space group | P2$_1$/c | C2/c | P2$_1$2$_1$2$_1$ | Pt | P2$_1$/c |
| a (Å) | 6.7555(4) | 18.3296(11) | 12.1488(8) | 12.0472(7) | 17.5777(5) |
| b (Å) | 16.3786(9) | 17.6541(10) | 20.0623(14) | 14.7379(11) | 13.3783(4) |
| c (Å) | 16.1010(8) | 12.0217(8) | 20.5295(16) | 15.9362(11) | 17.4924(4) |
| α (°) | 90 | 90 | 90 | 97.095(3) | 90 |
| β (°) | 98.714(3) | 113.916(2) | 90 | 91.064(3) | 118.8860(10) |
| γ (°) | 90 | 90 | 90 | 101.555(3) | 90 |
| V (Å$^3$) | 1760.94(17) | 3556.1(4) | 5003.7(6) | 2748.2(3) | 3654.59(17) |
| Z | 4 | 4 | 4 | 4 | 2 |
| D$_c$ (g·cm$^{-3}$) | 1.952 | 1.513 | 1.408 | 1.819 | 1.185 |
| μ (mm$^{-1}$) | 7.976 | 4.002 | 3.258 | 5.659 | 0.568 |
| no. reflns collcd | 13480 | 13313 | 38782 | 48190 | 31449 |
| no. indept reflns | 3082 | 3138 | 8805 | 12579 | 8240 |
| GOF on F$^2$ | 1.022 | 1.038 | 1.028 | 1.011 | 1.023 |
| R [I &gt; 2σ(I)] | R$_1$ = 0.0200 | R$_1$ = 0.0227 | R$_1$ = 0.0613 | R$_1$ = 0.0364 | R$_1$ = 0.0418 |
| wR$_2$ = 0.0420 | wR$_2$ = 0.0491 | wR$_2$ = 0.1516 | wR$_2$ = 0.0640 | wR$_2$ = 0.1163 |
| R (all data) | R$_1$ = 0.0265 | R$_1$ = 0.0274 | R$_1$ = 0.0800 | R$_1$ = 0.0595 | R$_1$ = 0.0609 |
| wR$_2$ = 0.0441 | wR$_2$ = 0.0507 | wR$_2$ = 0.1629 | wR$_2$ = 0.0708 | wR$_2$ = 0.1238 |</p>
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<th>10a (benzene)₂</th>
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Table 3: Crystallographic data for compounds 10b to 15.

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Table 4: Crystallographic data for 16 to 18.

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3 4,5-Diazafluorenide Chemistry

3.1 Syntheses and Structures of Mononuclear Complexes

3.1.1 Syntheses and Structures of \( \text{PtPh}_2(\text{LH}) \) and \([\text{PtPh}_2\text{L}][\text{Na(DME)}_3]\)

When \( \text{LH} \) was reacted with one unit equiv. of \([\text{PtPh}_2(\mu-\text{SMe})]\)_n, an insoluble amorphous yellow precipitate formed instantly. In order to obtain X-ray diffraction quality crystals of the product, DCM solutions of \( \text{LH} \) and \([\text{PtPh}_2(\mu-\text{SMe})]\)_n were carefully layered on top of one another along with toluene (Scheme 14). After the layers slowly mixed yellow block-shaped crystals of \( \text{PtPh}_2(\text{LH}) \) (1) formed and were examined using X-ray crystallography (Figure 1). Compound 1 crystallized in the space group \( P2_1/c \). The Pt\(^{II} \) centre is coordinated to the N,N-chelate of the LH ligand. The Pt-N distances are 1.991(3) and 1.996(3) Å, and the N-Pt-N bite angle is 81.3(1)°. Complex 1 is soluble enough in CDCl\(_3\) to obtain an \(^1\)H NMR spectrum where the peaks are less intense than the carbon satellite peaks observed around the CDCl\(_3\) peak.
The reaction between \([\text{PtPh}_2(\mu-\text{SMe}_2)]_n\) and NaL in THF gives a precipitate, which can be treated with DME to give \([\text{PtPh}_2\text{L}][\text{Na(DME)}_3]\) (2). The solid-state structure of 2 has been confirmed by X-ray crystallography (Figure 2). The \([\text{PtLPh}_2]\) anion has a crystallographically imposed \(C_2\) symmetry. The Pt centre is coordinated to the N,N-chelate site of the L’ ligand. The N-Pt bond lengths are 2.169(2) Å, longer than in 1 (1.991(3) and 1.996(3) Å) and the N-Pt-N angle is 82.0(1)°. The \(\text{Na}^+\) cation is sequestered by three molecules of DME. In the \(^1\text{H NMR}\) spectrum of 2 in DMSO-\(d_6\), the proton at the 9-position of diazafluorenide displays a singlet at 6.15 ppm, suggesting the aromaticity of the C$_5$ ring. If 2 is placed under vacuum overnight, the \(^1\text{H NMR}\) showed that only 2 equiv. of DME remained. During the synthesis of 2, a small amount of yellow precipitate was removed by filtration, which was confirmed to be 1 by \(^1\text{H NMR}\) spectroscopy.

Figure 1. Crystal structure of 1. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [°]: Pt1-N1 2.159(3), Pt1-N2 2.166(3), Pt1-C18 1.991(3), Pt1-C12 1.996(3), N1-Pt1-N2 81.3(1), N1-Pt1-C12 92.9(1), C12-Pt1-C18 93.1(1), C18-Pt1-N2 92.8(1).
Figure 2. Crystal structure of 2. All hydrogen atoms are omitted for clarity. Only one orientation of the disordered DME is shown. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [°]: Pt1-C7 1.993(3), Pt1-N1 2.169(2), C7-Pt1-C7’ 89.6(2), C7-Pt1-N1 94.2(1), N1-Pt1-N1’ 82.0(1).

3.2 Syntheses and Structures Heterobimetallic Complexes

3.2.1 Synthesis and Structure of Cu(IPr)LPtPh₂

Scheme 15. Synthetic routes to 4.
The reaction of 2 with 1 equiv. of Cu(IPr)Cl in toluene yielded 4 (Scheme 15). The molecular structure of 4 was revealed by X-ray crystallography (Figure 3). Compound 4 is a Cu-Pt heterodinuclear complex of the L’ ligand with the Cu centre bound to the carbon donor of the Cp-moiety and the Pt centre bound to the N,N-chelate site. The two-coordinate Cu\(^1\) centre is bound to the L’ ligand in an \(\eta^1\) fashion via the carbon at the 9-position with a Cu1-C28 bond length of 1.979(7) Å, within the typical bonding distance. The Cu1-C29 and Cu1-C32 distances are 2.612(7) and 2.569(7) Å, respectively, beyond the typical bonding distance.\(^{68,69}\) The Cu1-C28-C32 and Cu1-C28-C29 bond angles are 95.8(5) and 97.3(5)°, respectively; the Cu1-C28-C\(_5\)\(^{\text{centroid}}\) angle is \(\sim99°\). These metric parameters suggest that the Cu centre is bound to the Cp-moiety in a \(\pi\)-type \(\eta^1\) fashion rather than \(\sigma\)-type \(\eta^1\) fashion.\(^{70,71}\) In contrast, the analogous Cu1-C28-C\(_5\)\(^{\text{centroid}}\) angle in [PdLCl(PPh\(_3\))]\(_2\), Pd-C5-C\(_5\)\(^{\text{centroid}}\) (where the \(\sigma\)-type \(\eta^1\) coordination mode was observed) is \(\sim115°\).\(^{29}\) The coordination geometry of the Cu centre is slightly off linear with the C1-Cu1-C28 angle of 176.0(5)°. The Pt centre has a typical square planar coordination geometry displaying typical bond lengths and angles. The Cu and the Pt were separated by 5.543(1) Å, significantly closer together than in complexes 10a and 10b.

![Crystal structure of 4](image)

**Figure 3. Crystal structure of 4. All hydrogen atoms except for that on the 9-position of L’ and the isopropyl groups are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [°]:**

- Pt1-C39 1.989(8), Pt1-C45 1.994(8), Pt1-N4 2.153(7), Pt1-N3 2.177(6), Cu1-C1 1.886(7), Cu1-C28 1.979(7), C39-Pt1-C45 93.9(3), C39-Pt1-N4 91.1(3), C45-Pt1-N4 174.4(3), C39-Pt1-N3 173.1(3), C45-Pt1-N3 92.8(3), N4-Pt1-N3 82.4(2), C1-Cu1-C28 175.5(3), C1-Cu1-Pt1 112.8(2), C28-Cu1-Pt1 63.2(2).
The $^1$H NMR spectrum of 4 in C$_6$D$_6$ showed broad peaks at room temperature in the aromatic region. The proton at 9-position of the L$^-$ ligand resonates at 4.39 ppm, indicating the decreased aromaticity. Below -5°C in toluene-$d_8$, only one set of sharp diazafluorene signals can be observed (Figure 4).

![NMR spectra at different temperatures](image)

**Figure 4. Variable temperature $^1$H NMR spectra of 4 in toluene-$d_8$ at 600 MHz.**

It is conceivable that the stepwise approach can be done in the other metallation sequence, i.e., metallate the L$^-$ ligand with Cu prior to Pt. Previously, we reported CuL(IPr) (3) $^{34}$ where Cu$^I$ is coordinated to the N,N-chelate site leaving the Cp$^-$ moiety vacant for the possible coordination of a second metal. If the metallation of the Cp-moiety with Pt occurs, an isomer of 4 could potentially be achieved. To our surprise, the reaction of [PtPh$_2$(µ-SMe)$_2$]$_n$ and 3 also gives complex 4 (Scheme 15). The Ph$_2$Pt$^{II}$ unit replaced the (IPr)Cu$^I$ unit from the N,N-chelate site of the L$^-$ ligand, and the (IPr)Cu$^I$ unit migrated to the Cp-moiety of the L$^-$ ligand. This encouraging result prompted us to examine the one-pot synthesis of 4, because even if the ligand mistakenly binds Cu on the N,N-chelate site initially, the mistake can be corrected automatically, leading to
the formation of 4. Indeed, the one-pot reaction of NaL, [Cu(IPr)Cl], and [PtPh₂(μ-SMe₂)]ₙ in THF produces 4 with decent yield. Compound 4 is thermally unstable in solution at room temperature, but is stable in the solid state and can be stored in solution at -33 °C.

3.2.2 Synthesis and Structure of RuCp*LPtPh₂

![Scheme 16. Synthetic routes to 6.](image)

The [PtPh₂] unit of complex 2 occupies the N,N-chelate site leaving the Cp moiety of the diazafluorene backbone vacant for the coordination of the second metal. The [RuCp*]⁺ fragment has demonstrated the affinity to bind to π systems, and its coordination to the vacant Cp moiety of complex 2 was explored. When 0.25 equiv. of [Cp*Ru(μ₁-Cl)]₄ was added to 2 in THF the expected heterobimetallic Cp*RuLₚₜ₃H₂ (6) formed selectively. Compound 6 can also be synthesized by adding 1 unit equiv. of [PtPh₂(μ-SMe₂)]ₙ to RuCp*L (5) (Scheme 16).

The ¹H NMR spectrum of 6 in C₆D₆ showed that the chemical shift of the proton in the 9-position moved upfield to 4.72 ppm from 6.87 ppm in complex 2. Similarly, the ¹³C NMR spectrum showed that the chemical shift of the carbon in the 9-position moved upfield to 57.7 ppm in CDCl₃ from 79.2 ppm in complex 2 in DMSO-d₆. These upfield shifts suggest a π interaction between the Ruᴵᴵ centre and the corresponding carbon. The chemical shift for the proton in the 9-position of 4 was at 4.39 ppm, and the analogous proton in 5 appears at 4.81 ppm in C₆D₆.

The crystal structure of 6 (Figure 5) confirms that the Ptᴵᴵ centre adopts a square-planar geometry to the N,N-chelate and the [RuCp*]⁺ fragment is coordinated in an η²-fashion to the Cp moiety of the diazafluorene backbone. The Pt-N bond lengths (2.155(4) and 2.172(5) Å) are comparable to the Pt-N bond lengths in complex 2 (2.169(2) Å) and in complex 4 (2.153(7) and
The metallocene moiety of 6 is slightly bent with a \((C_5 \text{ ring of Cp}^*)^{\text{centroid}}\)-Ru-(C_5 \text{ ring of diazafluorenyl})^{\text{centroid}} angle of \(\sim 178.49^\circ\), more linear than the analogous angle in 5 (176.41(3)^\circ), but very similar to the analogous angle in a Ru\(^{\text{II}}\)-Pd\(^{\text{II}}\) heterotrimetallic complex (\(\sim 178.79^\circ\)). The Pt\(^{\text{II}}\) and Ru\(^{\text{II}}\) are separated by 4.1347(6) Å, with a Ru-(C_5 \text{ ring of diazafluorenyl})^{\text{centroid}}-Pt angle of \(\sim 88.24^\circ\). A Cp*Co(4,5-diazafluorenone) metallocene-like compound have also been seen. To the best of our knowledge this is the first example of an \(\eta^5, \kappa^2\) heterobimetallic complex using a 4,5-diazafluorenide derivative.

Figure 5. Crystal structure of 6. All hydrogen atoms and the second molecule from the asymmetric unit have been omitted for clarity. Ellipsoids are drawn at 50\% probability level. Selected distances [Å] and angles [°]: Pt1-N1 2.155(4), Pt1-N2 2.172(5), Pt1-C22 1.989(5), Pt1-C28 1.995(5), Ru1-C6 2.156(7), Ru1-C7 2.151(6), Ru1-C8 2.154(6), Ru1-C9 2.154(6), Ru1-C10 2.164(5), Ru1-C14 2.244(7), Ru1-C15 2.195(6), Ru1-C16 2.226(6), Ru1-C20 2.215(5), Ru1-C21 2.235(5), Ru1-Pt1 4.1347(6), N1-Pt1-N2 83.5(2), N1-Pt1-C22 89.7(2), C22-Pt1-C28 95.7(2), N2-Pt1-C28 91.1(2).
4  9-(2-(Diphenylphosphino)Ethyl)-4,5-Diazafluorene Chemistry

4.1  Syntheses and Structures of Homonuclear Complexes

4.1.1  Syntheses and Structures of [Cp*Ru(L₆H)]₂Cl₂ and [Cp*RuL₆]₂

The coordination chemistry between the phosphine functionalized derivative of 4,5-diazafluorene and a [RuCp*]⁺ fragment was explored. The addition of two equivalents of L₆H and 0.5 equivalents of [RuCp*(μ₃-Cl)]₄ yields a purple solution containing an orange microcrystalline precipitate of [Cp*Ru(L₆H)]₂Cl₂ (7) (Scheme 17). Complex 7 is soluble in DMSO, sparingly soluble in THF and insoluble in toluene, benzene, hexanes, and pentanes. X-ray diffraction quality crystals of 7 are obtained from a THF solution with slow evaporation, the structure is shown in Figure 6.

The crystal structure of 7 revealed that the compound exists as a head-to-tail dimer. The dimer contains a crystallographically imposed inversion centre and the two diazafluorenyl moiety are antiparallel with an interplane separation distance of ~5.52 Å. C11 retained sp³ hybridization and a tetrahedral geometry. The Ru₁-P₁ bond length is 2.315(1) Å. Both Ru-N bond lengths are
similar (2.169(2) and 2.174(2) Å). The Ru\textsuperscript{II} centre adopted a pseudo octahedral geometry where the two N-donors of one diazafluorenyl, the phosphine of the second diazafluorenyl, and the Cp* occupy the coordination sites of the metal centre.

The \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectra suggest that 7 retains the head-to-tail structure in solution. The \(^{31}\text{P}\) NMR spectrum shows a singlet at 37.65 ppm, suggesting that the phosphine remains coordinated to the Ru\textsuperscript{II} centre in solution. A triplet can be observed in the \(^1\text{H}\) NMR spectrum at 4.16 ppm for the proton at the 9-position of the diazafluorenyl moiety and the ethyl protons of the pendent arm appear as multiplets at 1.84 and 0.16 ppm. Only one set of diazafluorenyl peaks are observed in the \(^1\text{H}\) NMR spectrum suggesting that in solution the Ru\textsuperscript{II} centre does not favor one nitrogen donor.

To explore the coordination chemistry of \(\text{L}_p^-\), two equivalents of \(\text{KL}_p\) was added to 0.5 equivalents of \([\text{RuCp}^*\text{(μ}_3\text{-Cl})_4\text{]}\) and allowed to react at room temperature overnight. The reaction progress of the resulting brown mixture was monitored by NMR spectroscopy in \(\text{C}_6\text{D}_6\). Multiple singlets were observed in the \(^{31}\text{P}\) NMR spectrum at ~82 ppm, 42.77 ppm, 39.95 ppm, and the
major peak appeared at 38.02 ppm. Refluxing the solution in THF for 9 hours did not fully convert the mixture to a single species by $^{31}$P NMR spectroscopy. Removal of the volatiles under reduced pressure, extracting into toluene and heating was required to convert the mixture to a single species by $^{31}$P NMR spectroscopy, with a single peak observed at 38.03 ppm belonging to $[\text{RuCp}*\text{L}_p]^2$ (8).

Once the mixture was completely converted to 8 the resulting solution was a vibrant green and the KCl precipitate was observed. A non-polar organic solvent such as toluene was probably needed to encourage the precipitation of KCl during the assembly of 8. The reaction could not solely take place in toluene due to the insolubility of KL_p and RuCp*(µ_3-Cl)]_4, making the solvent switch during the reaction necessary. Complex 8 could also be synthesized by deprotonating 7 with KOtBu in THF (Scheme 17). Full conversion of 7 to 8 was observed by NMR spectroscopy and a solvent switch was unnecessary, probably due to the molecule being already assembled. The minor peaks observed in the $^{31}$P NMR spectrum during the synthesis of 8 may correspond to intermediate species between L_p^- and the [RuCp*Cl] unit. Attempts to isolate these potential intermediate species were unsuccessful.

Compound 8 is soluble in benzene, toluene, THF, and DME and insoluble in hexanes, pentanes and DMSO. The $^{31}$P NMR spectrum of 8 suggests that the phosphine is coordinated to the Ru$^{II}$ centre in solution with a singlet observed at 38.03 ppm, similar to what was seen in the $^{31}$P NMR spectrum of 7 (37.65 ppm). The ethyl protons of the pendent arm appear as multiplets at 2.48 and -0.61 ppm in the $^1$H NMR spectrum, similar to what was seen in the $^1$H NMR spectrum of 7 (1.84 and 0.16 ppm). The $^1$H and $^{31}$P NMR spectra suggest that compound 8 has adopted a similar head-to-tail structure as 7.

Crystals of 8 can be obtained by diffusing hexanes into a C_6H_6 solution (Figure 7A) or pentanes into a DME solution (Figure 7B). The crystal structures of 8 revealed the structure to be a head-to-tail dimer. The carbons in the 9-position have adopted trigonal planar geometries due to the sp$^2$ hybridization. The crystal structure obtained from C_6H_6 does not possess a crystallographically imposed inversion centre, resulting in a dihedral angle of ~13° between the diazafluorenyl moieties. The intramolecular separation distance between the diazafluorenyl moieties is ~4.80 Å. The crystal structure obtained from DME crystallized with a
crystallographically imposed inversion centre in the middle of the molecule, therefore the diazafluorenyl moieties are antiparallel with an interplane distance of ~4.69 Å. Due to the planar geometry around the sp² hybridized carbon in the 9-position of the diazafluorenyl moieties of 8 the interplane distance between the ligand frameworks is a lot smaller than in 7 (~4.69 Å vs. ~5.52 Å).

![Figure 7](image_url)

**Figure 7.** Crystal structures of 8 from C₆H₆/Hex (A) and DME/Pent (B). All hydrogen atoms are omitted for clarity. For (B) the second molecule from the asymmetric unit was omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected distances [Å] and angles [°] for A): Ru1-N1 2.171(3), Ru1-N2 2.197(2), Ru1-P2 2.3301(9), Ru1-C26 2.193(3), Ru1-C27 2.176(4), Ru1-C28 2.196(3), Ru1-C29 2.171(3), Ru1-C30 2.189(3), Ru2-N3 2.178(3), Ru2-N4 2.180(2), Ru2-P1 2.3261(9), Ru2-C61 2.193(3), Ru2-C62 2.178(3), Ru2-C63 2.167(4), Ru2-C64 2.186(3), Ru2-C65 2.176(3), N1-Ru1-N2 80.2(1), N1-Ru1-P2 86.81(7), N2-Ru1-P2 88.85(7), N3-Ru2-N4 80.5(1), N3-Ru2-P1 90.44(7), N4-Ru2-P1 85.25(7); for B): Ru1-N1 2.182(3), Ru1-N2 2.174(3), Ru1-P1 2.3360(9), Ru1-C26 2.178(4), Ru1-C27 2.177(4), Ru1-C28 2.169(4), Ru1-C29 2.192(5), Ru1-C30 2.199(3), N1-Ru1-N2 80.2(1), N1-Ru1-P1 84.98(7), N2-Ru1-P1 88.62(7).

The Ru-N bond lengths are 2.171(3), 2.197(2), 2.178(3), and 2.180(2) Å for the crystal from C₆H₆. The Ru-N bond lengths are 2.182(3) and 2.174(3) Å for the crystal from DME. The Ru-N bond lengths of 8 are very similar to the Ru-N bond lengths seen in 7 (2.169(2) and 2.174(2) Å). The Ru-P bond lengths of 8 (2.3301(9) and 2.3261(9) Å for the C₆H₆ crystal and 2.3360(9) Å for the DME crystal) are longer than the Ru-P bond lengths of 7 (2.315(1) Å).

L⁻ₚ and HLₚ are binucleating ligands, both possessing a phosphine moiety and an N,N-chelate at opposite ends of the ligand framework. As what has been previously reported of coordination-
driven self-assembly with ditopic ambidentate ligands,\textsuperscript{42,73,74} head-to-tail dimers appear to form selectively instead of a mixture of oligomers.

### 4.1.2 Synthesis and Structure of [Cu(IMes)L\(_{\text{p}}\)]\(_2\)

![Diagram of synthesis and structure of [Cu(IMes)L\(_{\text{p}}\)]\(_2\)](image)

**Scheme 18. Synthesis and monomer-dimer equilibrium for 9a and 9b.**

Similar to the synthesis of 9a,\textsuperscript{36} the reaction of Cu(IMes)Cl (IMes = N,N’-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) with KL\(_{\text{p}}\) yielded a green solution of 9b (Scheme 18). Broad peaks were seen in the \(^1\)H NMR spectrum of 9b at room temperature, suggesting that the compound is dynamic. Variable temperature \(^{31}\)P NMR spectroscopy was used to examine the solution behaviour of 9b (Figure 8). Between 268 and 298 K two peaks can be seen at ~ -7.7 and -13.6 ppm, suggesting the co-existence of the monomer (9b\(^+\)) and dimer (9b). These peaks coalesce at 313 K into a broad peak around -8.7 ppm, which becomes a sharp peak at -9.7 ppm at 328 K, suggesting the complete conversion to the monomer. When the temperature is lower than 268 K, the limited solubility of 9b makes it difficult to record a meaningful NMR spectrum. We tentatively assign the peak at -13.6 ppm at 298 K to the monomer, because the \(^{31}\)P NMR signal observed for the monomeric 9a was at -14.2 ppm.\textsuperscript{36,75}
Figure 8. Variable temperature $^{31}$P NMR spectra of 9b in toluene-$d_8$ at 243 MHz.

Analogous to 9a, complex 9b is a head-to-tail dimer in the solid state as confirmed by X-ray crystallography (Figure 9). The copper centre adopts a highly distorted tetrahedral geometry with two N-donors from one L$_p$ ligand, the C-donor from IMes, and the P-donor of the phosphine from the other L$_p$ ligand occupying the four coordination sites. The Cu-P bond lengths in 9b are 2.252(2) and 2.253(2) Å, slightly shorter than that in 9a (2.285(1) Å). Similar to 9a, each Cu centre in 9b is unsymmetrically bound to the N,N-chelate sites of the L$_p$ ligands, with Cu-N bond lengths of 2.290(5) and 2.193(4) Å for Cu2 and 2.439(5) and 2.116(4) Å for Cu1, respectively. The diazafluorenyl moieties are separated by an interplane distance of ~5.05 Å, greater than that in 9a (~4.54 Å).
Figure 9. Crystal structure of 9b. All hydrogen atoms and the mesityl groups of the NHC ligands are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [°]: Cu1-C26 1.947(6), Cu1-P1 2.252(2), Cu1-N1 2.439(5), Cu1-N2 2.116(4), Cu2-C72 1.934(6), Cu2-P2 2.253(2), Cu2-N5 2.290(5), Cu2-N6 2.193(4), C26-Cu1-N2 116.3(2), C26-Cu1-P1 133.2(2), N2-Cu1-P1 102.5(1), C26-Cu1-N1 119.5(2), N2-Cu1-N1 81.6(2), P1-Cu1-N1 90.0(1), C72-Cu2-N6 116.4(2), C72-Cu2-P2 138.0(2), N6-Cu2-P2 96.0(1), C72-Cu2-N5 113.5(2), N6-Cu2-N5 83.3(2), P2-Cu2-N5 95.4(1).

4.2 Syntheses and Structures of Heterobimetallic Complexes

4.2.1 Syntheses and Structures of PtPh$_2$L$_p$Cu(NHC)

Due to the dynamic behaviour of 9a and 9b the phosphine-carbanion coordination site of the L$_p$-ligand is still available for metal binding in solution at room temperature. Indeed, when 9a and 9b were reacted with [PtPh$_2$(µ-SMe)$_2$]$_n$ in benzene, hetero-dinuclear complexes 10a and 10b (Scheme 19) were formed, respectively. Both 10a and 10b are air-stable in the solid state and in solution. The solid-state structures of 10a and 10b have been confirmed by X-ray crystallography (Figure 10 and Figure 11). Two types of crystals were obtained for 10b: Figure 11A shows the structure of the crystals obtained from C$_6$H$_6$/hexanes and Figure 11B shows the structure of the crystals obtained from DME/hexanes.
Scheme 19. Synthetic routes to 10a and 10b.

The Cu\(^1\) centre in 10a possesses a trigonal-planar geometry with two nitrogen donor atoms of the \(L_p^-\) ligand and a carbon donor from IPr ligand occupying the coordination sites. The sum of the bond angles around Cu1 is 359.3(3)°. The two Cu-N distances are 2.190(6) and 2.060(6) Å, shorter than those in 9a. Each Pt centre adopts a typical square-planar geometry with \(cis\)-(P,C) chelate and two \(cis\)-Ph ligands occupying the four coordination sites.

Figure 10. Crystal structure of 10a. All hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [°]: Pt1-C26 2.036(8), Pt1-C32 2.061(8), Pt1-C11 2.231(7), Pt1-P1 2.253(2), Cu1-C38 1.872(7), Cu1-N1 2.060(6), Cu1-N2 2.190(6), C26-Pt1-C32 88.7(3), C26-Pt1-C11 175.5(3), C32-Pt1-C11 93.0(3), C26-Pt1-P1 95.1(2), C32-Pt1-P1 174.3(2), C11-Pt1-P1 83.4(2), C38-Cu1-N1 140.7(3), C38-Cu1-N2 132.9(3), N1-Cu1-N2 85.7(2).
Similarly, the Pt centre in 10b is also bound to the P,C-chelate site of the L$_p^-$ ligand, while the Cu centre is coordinated at the nitrogen donor site. Interestingly, the two crystal structures of 10b show different coordination geometries for the Cu centres: two- and three-coordinate for crystals from C$_6$H$_6$/hexanes (Figure 11A) and DME/hexanes (Figure 11B), respectively. The coordination geometry of two-coordinate Cu centre of 10b is off linear with the N-Cu-C bond angle of 164.6(2)$^\circ$. The sum of the bond angles around the three-coordinate Cu centre of 10b is 350.3(4)$^\circ$, slightly off from planarity. The Cu-N distances of the three-coordinate Cu centre are 1.956(9) Å and 2.427(8) Å. The $^1$H NMR spectrum of 10b shows only one set of diazafluorenide peaks, suggesting that in solution the Cu does not favour one nitrogen. The unsymmetrical arrangements in both crystal structures are likely due to the crystal packing effects.

![Figure 11. Crystal structures of 10b from C$_6$H$_6$/hexanes (A) and from DME/hexanes (B). All hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected distances [Å] and angles [$^\circ$] for A: Pt1-C32 2.038(4), Pt1-C26 2.049(4), Pt1-C11 2.249(4), Pt1-P1 2.275(1), Cu1-C38 1.879(5), Cu1-N2 1.911(4), C32-Pt1-C26 87.7(2), C32-Pt1-C11 178.3(2), C26-Pt1-C11 91.7(2), C32-Pt1-P1 97.2(1), C26-Pt1-P1 174.8(1), C11-Pt1-P1 83.4(1), C38-Cu1-N2 164.6(2); for B: Pt1-C26 2.033(7), Pt1-C32 2.072(6), Pt1-C11 2.266(7), Pt1-P1 2.267(2), Cu1-C38 1.886(9), Cu1-N1 1.956(9), Cu1-N2 2.427(8), C26-Pt1-C32 84.7(3), C26-Pt1-C11 177.4(3), C32-Pt1-C11 94.2(3), C26-Pt1-P1 97.8(2), C32-Pt1-P1 175.4(2), C11-Pt1-P1 83.2(2), C38-Cu1-N1 148.0(4), C38-Cu1-N2 119.9(3), N1-Cu1-N2 82.4(3).

The orientations of the imidazolylidene rings relative to the diazafluorenide moieties are different in 10a and 10b, with the dihedral angles of ~14$^\circ$ for 10a and ~59$^\circ$ (from C$_6$H$_6$/hexanes)
and ~73° (from DME/hexanes) for 10\textit{b}. The Pt-Cu distances in both complexes are quite long: 6.224(1) Å for 10\textit{a}, 6.0540(7) Å (from C\textsubscript{6}H\textsubscript{6}/hexanes) and 5.709(7) Å (from DME/hexanes) for 10\textit{b}. In both 10\textit{a} and 10\textit{b}, one of the phenyl ligands on the Pt centre is oriented towards the Cu centre with the shortest Cu-C distance of ~4.5 Å in 10\textit{a} and ~3.4 Å (from C\textsubscript{6}H\textsubscript{6}/hexanes) and ~3.2 Å (from DME/hexanes) in 10\textit{b}.

Complexes 10\textit{a} and 10\textit{b} show similar \textsuperscript{31}P NMR signals: a singlet at 37.90 and 37.93 ppm, respectively, with platinum satellites. The \textsuperscript{1}J\textsubscript{Pt-P} coupling constants for 10\textit{a} and 10\textit{b} are 1965 and 1977 Hz, respectively. The Pt-P coupling constants observed for 10\textit{a} and 10\textit{b} are similar to other five membered chelate rings with two anionic phenyl ligands on the platinum. \textsuperscript{76} It is worth pointing out that although the larger \textsuperscript{1}J\textsubscript{Pt-P} for 10\textit{b} normally suggests a shorter Pt-P bond compared to 10\textit{a}, the crystallography data show the opposite, i.e., the Pt-P distances in 10\textit{b} are 2.275(1) and 2.267(2) Å for crystals obtained from C\textsubscript{6}H\textsubscript{6}/hexanes and DME/hexanes, respectively, longer than that in 10\textit{a} (2.253(2) Å). Such a discrepancy might be due to crystal packing effects.

Previously, we observed the transfer of L\textsubscript{p} ligand from the Cu\textsuperscript{1} centre in 9\textit{a} to the Rh\textsuperscript{1} and Au\textsuperscript{1} centres in [Rh\textsuperscript{1}]-Cl and [Au\textsuperscript{1}]-Cl starting materials resulting in macrocycle formation accompanied by the release of Cu(IPr)Cl. \textsuperscript{36} Herein, the presence of labile SME\textsubscript{2} ligands in [PtPh\textsubscript{2}(\mu-SME\textsubscript{2})\textsubscript{n}] and lack of halides prevent the L\textsubscript{p} ligand transfer and allow for the isolation of heterobimetallic complexes 10\textit{a} and 10\textit{b}.

Due to the distinct properties observed for both coordination sites within the L\textsubscript{p} ligand, a one-pot synthesis was carried out where KL\textsubscript{p} was added to a mixture of [PtPh\textsubscript{2}(\mu-SME\textsubscript{2})\textsubscript{n}] and Cu(NHC)Cl in THF (Scheme 19). Both the \textsuperscript{1}H and \textsuperscript{31}P NMR spectra showed the clean formation of the desired hetero-dinuclear complexes, 10\textit{a} and 10\textit{b}. When L\textsubscript{p} is used, the Ph\textsubscript{2}Pt\textsuperscript{II} unit is selectively bound to the P,C-chelate site and the (NHC)Cu\textsuperscript{1} unit is coordinated to the N,N-chelate site. In case of L\textsuperscript{-}, the regioselectivity of the metallation is reversed: the Ph\textsubscript{2}Pt\textsuperscript{II} unit is coordinated to the N,N-chelate, while the (NHC)Cu\textsuperscript{1} unit is bound to the carbanion site in an \textit{η}\textsuperscript{1} fashion. Presumably the \textit{d}\textsuperscript{10} metal, Cu\textsuperscript{1}, has no strong preference when coordinating to the ambidentate ligands, while the preference of the Pt\textsuperscript{II} centre determines the overall regioselectivity. In the L\textsubscript{p} case (complexes 10\textit{a} and 10\textit{b}), the P,C-site wins with both its softness
and the chelate effect. In L^- case however (complex 4), the chelate effect of the N,N-site outcompetes the soft but monodentate carbanion site for Pt^{II}. The regioselectivity in the metallation of these ligands enabled the one-pot syntheses of Pt^{II}-Cu^1 hetero-dinuclear complexes.
5 3,6-Dimesityl-4,5-Diazafluorenide Chemistry

5.1 Syntheses and Structures of Homonuclear Complexes

5.1.1 Syntheses and Structures of PtPh₂(LMesH) and [PtPh₂L₄ Mes][K(DME)₂]

Scheme 20. Synthetic routes to 11 and 12.

We set out to construct mononuclear PtⅡ complexes of LMesH and LMes in order to compare the coordination chemistry with LH and L⁻. LMesH was mixed with 1 unit equiv. of [PtPh₂(m-SMe₂)]ₙ in THF to form PtPh₂(LMesH) (11) (Scheme 20). Compound 11 is air stable and can be synthesized in air. Compound 11 is poorly soluble in toluene and hexanes but soluble in THF, DCM, and in CHCl₃. Bright yellow block-shaped crystals of 11 can be obtained by diffusing hexanes into a THF solution (Figure 12A).

The Pt-N bonds in 11 (2.191(2) and 2.189(2) Å) are longer than the Pt-N bonds in 1 (1.991(3) and 1.996(3) Å). The entire molecule is quite contorted, the angles between the plane of the C₅ ring of the diazfluorenyl moiety and the planes of the pyridyl moieties are ~6.73° and ~7.03°. The angle between the plane of the C₅ ring of the diazfluorenyl moiety and the mean plane defined by N1, N2, Pt1, C30, and C36 is ~19.18°. The [PtPh₂] unit and the mesityl rings are flexed in opposite directions (Figure 12B). The dihedral angles between the planes of the pyridyl rings and the plane of their corresponding mesityl groups are ~68.64° and ~66.61°.
Figure 12. A) Crystal structure of 11. B) The side view of 11 with one of the mesityl groups omitted for clarity. For A) and B) the non-hydrogen atoms are shown as 50% probability ellipsoids, and H atoms are shown as spheres of arbitrary radius. Selected distances [Å] and angles [°]: Pt1-N1 2.191(2), Pt1-N2 2.189(2), Pt1-C30 1.997(3), Pt1-C36 1.992(3), N1-Pt1-N2 80.64(8), N1-Pt1-C36 96.0(1), C36-Pt1-C30 86.3(1), N2-Pt1-C30 96.3(1).

Compound 11 can be deprotonated with KOtBu to form [PtPh₂L₉Mes][K(DME)]₂ (12). Compound 12 can also be synthesized by reversing the order of addition of the base and the metal starting material (Scheme 20). The ¹H and ¹³C NMR spectra in DMSO-d₆ of compound 12 revealed that the compound is completely unsymmetrical in solution. Initially it was hypothesized that there were multiple species present, however only one peak at 6.12 ppm in the ¹H NMR spectrum, and one peak at 79.3 ppm in the ¹³C NMR spectrum correlate to the C-H group at the 9-position of the coordinated L₉Mes⁻ ligand. Compound 12 was also examined using ¹⁹⁵Pt NMR spectroscopy and only one peak was observed at -3722.9 ppm suggesting that there was only one species present. The DMSO-d₆ displaces the DME ligands bound to the K⁺ ion in solution.

Compound 12 was also studied using X-ray crystallography (Figure 13). The crystal structure reveals that the [PtPh₂] unit is coordinated with a square planar geometry to the N,N-chelate. The Pt-N bond lengths of 12 (2.19(1) and 2.21(2) Å) are comparable to 2 (2.169(2) Å). The diazafluorenide backbone is slightly flexed with an angle of ~5.83° and ~5.52° between the plane of the Cp moiety and both planes of the pyridyl moieties. Similar to 11, the Pt²⁺ centre does not lie in the plane of the C₅ ring of diazafluorenyl. The angle between the mean plane define by N1, N2, Pt1, C30, and C36 and the plane of the C₅ ring of diazafluorenyl is ~8.01°. Unlike complex 2 where the Na⁺ cation is sequestered from the [PtPh₂L]⁺ anion by three DME molecules, the crystal structure of 12 shows that the K⁺ cation is sandwiched between both phenyl ligands of Pt²⁺.
and two DME molecules. It is possible that the $K^+$ cation coordinated to DMSO in solution creates the asymmetry observed by NMR spectroscopy as it is unknown if the $K^+$ cation is sequestered from the $[\text{PtPh}_2\text{L}_{\text{Mes}}]^-$ anion of 12 in the same manner that the $Na^+$ cation was sequestered from the $[\text{PtPh}_2\text{L}]^-$ anion of 2.

![Crystal structure of 12](image)

Figure 13. Crystal structure of 12. All hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected distances [Å] and angles [°]: Pt1-N1 2.19(1), Pt1-N2 2.21(2), Pt1-C30 2.00(2), Pt1-C36 2.05(2), N1-Pt1-N2 83.2(5), N1-Pt1-C30 95.9(7), C30-Pt1-C36 83.8(8), C36-Pt1-N2 97.0(6).

5.2 Syntheses and Structures of Heterobimetallic Compounds

5.2.1 Synthesis and Structure of $\text{Cp(NMe}_2\text{)Zr(µ-NMe}_2\text{)}_2\text{PtPh}_2$

![Scheme 21](image)

Scheme 21. Synthetic attempt to construct a Zr-Pt heterobimetallic complex.
Complex 11 was added to ZrCp(NMe$_2$)$_3$ in THF in an attempt to synthesize a Zr-Pt heterobimetallic complex containing L$_{Mes}$$. Instead the formation of complex 13 and free L$_{Mes}$H were observed (Scheme 21). Therefore complex 13 was independently synthesized in pure form by reacting 1 unit equiv. of [PtPh$_2$(µ-SMe)$_2$]$_n$ with ZrCp(NMe$_2$)$_3$ in toluene (Scheme 22). Compound 13 can be crystallized by layering the toluene solution with hexanes and chilling at -35 °C. The crystal structure of 13 can be seen in Figure 14.

The crystal structure of 13 revealed that the amide ligands were bridging both metal centers, with a Zr-Pt distance of 2.8117(5) Å. The Zr-N bond lengths are slightly shorter than the Pt-N bond lengths with the N atoms from the bridging amides, 2.148(3)/2.148 Å and. 2.214(3)/2.198(3) Å respectively. The Pt$^{II}$ centre has adopted the expected square planar geometry and the Zr$^{IV}$ centre has adopted a pseudo octahedral geometry with two bridging amide ligands, a terminal amide ligand, and the Cp ligand occupying the coordination sites. The $^1$H NMR spectrum shows three different singlets, each integrating to 6, for the methyl amide protons (3.31, 2.36, and 2.17 ppm). The two upfield peaks have platinum satellite peaks with $^3$$J_{Pt-H}$ coupling constants measuring 24.0 and 28.8 Hz. This suggests that the solid-state structure is retained in solution with two bridging amide ligands and one terminal amide ligand on the Zr$^{IV}$ centre. Platinum satellite peaks for the ortho-phenyl protons are observed with a $^3$$J_{Pt-H}$ coupling constant of 70.6 Hz. The $^3$$J_{Pt-H}$ coupling constant for the ortho-phenyl protons for 13 is very similar to the same protons in 11 ($^3$$J_{Pt-H}$ = 76.0 Hz). To the best of our knowledge this is the first example of amide ligands bridging group 4 and group 10 metals.
5.2.2 Synthesis and Structure of RuCp*L$_{\text{Mes}}$PtPh$_2$

Similar to complex 2, the diazafluorenyl Cp moiety of 12 is also vacant. When 12 is added to 0.25 equivalents of [Cp*Ru(μ$_3$-Cl)]$_4$ in THF the heterobimetallic compound Cp*Ru(L$_{\text{Mes}}$)PtPh$_2$ (15) was isolated. Compound 15 can also be synthesized by adding 1 unit equiv. of [PtPh$_2$(μ-$\text{SMe}_2$)]$_n$ to 14 (Scheme 23). Compound 15 is stable in air and is soluble in toluene, $C_6H_6$, THF, and DCM, and is insoluble in hexanes.

Figure 14. Crystal structure of 13. All hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected distances [Å] and angles [°]: Zr1-Pt1 2.8117(5), Zr-C1 2.508(5), Zr1-C2 2.516(5), Zr1-C3 2.533(5), Zr1-C4 2.524(5), Zr1-C5 2.509(5), Zr1-N1 2.148(3), Zr1-N2 2.148(3), Zr1-N3 2.032(4), Pt1-N1 2.214(3), Pt1-N2 2.198(3), Pt1-C6 2.012(3), Pt1-C12 2.012(5), N1-Zr1-N2 96.7(1), N1-Zr1-N3 110.0(1), N2-Zr1-N3 111.5(1), N1-Zr1-centroid(C1-C5) 115.38, N2-Zr1-centroid(C1-C5) 113.52, N3-Zr1-centroid(C1-C5) 109.32, N1-Pt1-N2 93.3(1), N1-Pt1-C6 90.1(1), C6-Pt1-C12 88.3(2), N2-Pt1-C12 88.3(2).
Figure 15. Crystal structure of 15. All hydrogen atoms are omitted for clarity. Only one orientation of the disordered Cp* is shown. Ellipsoids are drawn at 50% probability level. Selected distances [Å] and angles [°]: Pt1-N1 2.193(5), Pt1-N2 2.247(6), Pt1-C30 2.002(8), Pt1-C36 1.995(8), Ru2-C4 2.248(6), Ru2-C5 2.235(6), Ru2-C6 2.233(6), Ru2-C7 2.252(7), Ru2-C11 2.193(7), Ru2-C42 2.14(2), Ru2-C43 2.13(2), Ru2-C44 2.13(1), Ru2-C45 2.14(1), Ru2-C46 2.15(1), Ru2-Pt1 4.2571(7), N1-Pt1-N2 81.2(2), N1-Pt1-C30 96.0(2), C30-Pt1-C36 85.2(3), N2-Pt1-C36 97.4(3).

The crystal structure of 15, shown in Figure 15, reveals that the [PtPh₂] unit is coordinated to the N,N-chelate and the [Cp*Ru]+ fragment is coordinated to the C₅ ring of the diazafluorenone backbone in an η⁵-fashion. The Pt-N bond lengths of 15 (2.193(5) Å and 2.247(6) Å) are slightly longer than the Pt-N bond lengths of structurally related complex 6 (2.155(4) Å and 2.172(5) Å). The metallocene moiety of 15 is slightly bent with a (C₅ ring of Cp*)centroid-Ru-(C₅ ring of diazafluorenyl)centroid angle of ~178°, similar to the analogous angle of 14 (~177°). The Ru-Pt distance in complex 15 is 4.2571(7) Å, slightly longer than the Ru-Pt distance in complex 6 (4.1347(6) Å). The Ru- (C₅ ring of diazafluorenyl)centroid-Pt angle is ~90.98°, slightly larger than for 6 (~88.24°). The steric strain imposed by the mesityl groups have pushed the planes of the pyridyl moieties out of the plane defined by the C₅ ring of diazafluorenyl by ~10.73° and ~8.97°.
pulling the [PtPh₂] unit farther away from the RuІІ centre. The dihedral angles between the planes of the pyridyl rings and the planes of their corresponding mesityl groups are ~69.77° and ~75.23°.

The proton in the 9-position of the coordinated LMes⁻ ligand of complex 15 resonates at 4.75 ppm in the ¹H NMR spectrum in C₆D₆, slightly upfield from the analogous proton in 14 (4.82 ppm) and almost the same as 6 (4.72 ppm). In complex 15 the mesityl groups are unable to freely rotate. Since the [RuCp*]⁺ fragment is coordinated to one face of the diazafluorenide backbone the mesityl methyl protons at the 2- and 6- positions, and the mesityl protons at the 3- and 5- positions are no longer equal and separate peaks can be seen in the ¹H NMR spectrum.

5.2.3 Syntheses and Structures of RuCp*LMesMCl₂ (M = Fe, Co)

![Scheme 24. Synthetic route to 16 and 17.](image)

The metalloligand complex 14 can also be reacted with 1 equiv. of either FeCl₂·(thf)₁.₅ or CoCl₂·(thf)₁.₅ to yield Cp*RuLMesFeCl₂ (16) or Cp*RuLMesCoCl₂ (17) respectively (Scheme 24). Compounds 16 and 17 are both paramagnetic, and gave paramagnetically shifted and broadened peaks in the ¹H NMR spectra. Both complexes 16 and 17 have similar solubilities. They are soluble in THF, DME, CDCl₃, slightly soluble in toluene, and poorly soluble in benzene.

Crystals of 16 can be obtained by diffusing hexanes into a solution of toluene, and crystals of 17 are obtained by diffusing pentanes into a solution of DME. The crystal structures of 16 and 17 are shown in Figure 16 and Figure 17, respectively.
The selected bond lengths and angles of 16 and 17 are shown in Table 5. The crystal structures of 16 and 17 reveal that the [RuCp*]⁺ fragment remained coordinated in an η⁵-fashion to the C₅ ring of diazafluorenyl. Both the Feᴵᴵ and Coᴵᴵ centres at the N,N-chelate adopt a distorted tetrahedral geometry. Both N-donors and both chloride ligands occupy the four coordination sites around each metal centre. The N1-M1-N2 angles for complexes 16 and 17 are 84.3(1)° and 86.3(2)° respectively. The Cl1-M1-Cl2 angles for complexes 16 and 17 are 129.33(7)° and 123.9(1)° respectively. The angles between the mean planes defined by N1-M1-N2 and by Cl1-M1-Cl2 are ~89.84° and ~86.69° for complexes 16 and 17 respectively. The dihedral angles between the pyridyl planes and the planes of their corresponding mesityl rings are ~80.78° and ~84.06° for 16 and ~84.93° and ~85.35° for 17. The mesityl rings are more perpendicular to the diazafluorenyl backbone than in 14 (~66.39° and ~55.03°). The diazafluorenide backbones are slightly flexed with angles between the planes of the pyridyl moieties and the planes defined by the C₅ rings of the diazafluorenyl of ~5.93° and ~5.71° for 16 and ~4.91° and ~5.14° for 17. The ruthenocene portions are slightly bent with (C₅ ring of Cp*)centroid-Ru1-(C₅ ring of diazafluorenyl)centroid angles of ~175.56° and ~176.51° in complexes 16 and 17 respectively. The Ru1-(C₅ ring of diazafluorenyl)centroid-Fe1 angle in complex 16 is ~98.63°. The analogous Ru1-(C₅ ring of diazafluorenyl)centroid-Co1 angle in complex 17 is ~99.11°. This bent nature of the
ruthenocene could be due to the steric clash between the Cp* ring and the Cl ligands. The Ru1-Fe1 distance is 4.4269(7) Å and the Ru1-Co1 distance is 4.359(1) Å.

**Figure 17.** Crystal structure of 17. All hydrogen atoms and the second molecule from the asymmetric unit have been omitted for clarity. Ellipsoids are drawn at 50% probability level.

### 5.2.4 Synthesis and Structure of RuCp*L\textsubscript{Mes}CuCl

![Scheme 25. Synthetic route to 18.](image)

The addition of CuCl to 14 in THF yields Cp*Ru(L\textsubscript{Mes})CuCl, 18 (Scheme 25). Compound 18 is very soluble in THF, DME, toluene, and benzene. The crystal structure of 18, Figure 18, reveals that the [RuCp*]\textsuperscript{+} fragment remained coordinated in an η⁵-fashion and the CuCl coordinated in
an off linear geometry to one N-donor. Two enantiomers were seen in the asymmetric unit of the crystal structure (18A and 18B). The selected bond lengths and angles are seen in Table 5. The Cu\(^1\) centers were slightly bent with N-Cu-Cl angles of 171.0(1)° (18A) and 169.7(1)° (18B). The (C\(_5\) ring of Cp*)\(^{\text{centroid}}\)-Ru-(C\(_5\) ring of diazafluorenyl)\(^{\text{centroid}}\) angles are slightly bent at ~177.68° for (18A) and ~177.66° for (18B), similar to the analogous angle of complex 14 (~177°).\(^{35}\) The diazafluorenide backbone is slightly off planarity with angles of ~3.58° and 3.24° (18A) and ~2.72° and ~3.69° (18B) between the planes defined by the C\(_5\) ring of diazafluorenyl and the planes of the pyridyl moieties. The dihedral angles between the planes of the pyridyl moieties and the planes of their corresponding mesityl rings are ~67.34° and ~84.36° for (18A) and ~83.83° and ~60.95° for (18B).

![A) and B) are enantiomers in the asymmetric unit. Ellipsoids are drawn at 50% probability level.](image)

**Figure 18.** Crystal structures of 18A and 18B. All hydrogen atoms have been omitted for clarity. A) and B) are enantiomers in the asymmetric unit. Ellipsoids are drawn at 50% probability level.

The \(^1\)H NMR spectrum in C\(_6\)D\(_6\) shows that the proton in the 9-position appears at 4.82 ppm, unchanged from complex 14. Only one set of diazafluorenyl peaks are observed suggesting that the [CuCl] unit does not favour one N-donor in solution. The peaks at 6.92-6.78 ppm and 2.56 ppm correspond to the mesityl protons at the 3- and 5- positions and the mesityl methyl protons at the 4-position respectively. These peaks are broad suggesting the mesityl rings are not locked in position.
Table 5. Selected distances [Å] and angles [°] for 16, 17, 18A, and 18B.

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6 Conclusion and Future Outlook

6.1 Conclusion

We have explored the use of three different 4,5-diazafluorenyl derivatives as binucleating ligands for the syntheses heterobimetallic complexes. Nine heterobimetallic complexes were synthesized, eight used 4,5-diazafluorenyl derivatives. The following section will provide a brief summary of each chapter with the exceptions of chapters 1 and 2.

6.1.1 Chapter 3

$L^-$ was used to construct monometallic Pt$^{II}$ species (1 and 2) as well as Pt$^{II}$-Cu$^1$ (4) and Ru$^{II}$-Pt$^{II}$ (6) heterobimetallic complexes. The [PtPh$_2$] unit coordinated to the N,N-chelate in both complexes 4 and 6. The [Cu(IPr)]$^+$ fragment coordinated to the carbanion in the 9-position of the diazafluorenyl backbone in an $\eta^1(\pi)$-fashion in complex 4, and the [RuCp*]$^+$ fragment coordinated to the Cp moiety of diazafluorenyl in an $\eta^5$-fashion in complex 6. Complex 4 could be synthesized using a stepwise or a one-pot approach.

6.1.2 Chapter 4

$L_p$H and $L_p^-$ were used to synthesize Ru$^{II}$ homobimetallic macrocycles (7 and 8). $L_p^-$ was used to synthesize a dynamic Cu$^1$ complex (9b) and two Pt$^{II}$-Cu$^1$ heterobimetallic complexes (10a and 10b). The [PtPh$_2$] unit coordinated to the softer P,C-chelate and the [Cu(NHC)]$^+$ fragment coordinated to the N,N-chelate. Complexes 10a and 10b could be synthesized using a stepwise or a one-pot approach.

6.1.3 Chapter 5

The bulky $L_{Mes}^-$ diazafluorenyl derivative was used to synthesize four heterobimetallic Ru$^{II}$-M (M = Pt (15), Fe (16), Co (17), Cu (18)) complexes. The [RuCp*]$^+$ coordinated to the Cp moiety of diazafluorenyl in an $\eta^5$-fashion and the second metal coordinated to the N-donors. In an attempt to synthesize a Pt$^{II}$-Zr$^{IV}$ heterobimetallic species containing a binucleating $L_{Mes}^-$ unit a serendipitous Pt$^{II}$-Zr$^{IV}$ heterobimetallic complex (13) was synthesized where two amide ligands were bridging both metal centres.
6.2 Future Outlook

This thesis has explored the use of 4,5-diazafluorenyl derivatives as binucleating ligands for the syntheses of heterobimetallic complexes. However, an in depth study of the reactivity and catalytic applications has not been performed and this project still exhibits a lot of potential. This final section will outline some possible directions for this project and will include preliminary findings.

6.2.1 CO₂ Reactivity

Scheme 26. Size selective encapsulation through reversible small molecule activation.

The cavities between the diazafluorenyl moieties of complexes 7 and 8 changed size depending on whether the carbon in the 9-position was sp² or sp³ hybridized. It would be interesting if the size of the cavity can be changed through reversible small molecule activation. If the carbanion at the 9-position of complex 8 could reversibly bind to CO₂ then the size of the cavity would enlarge. This strategy of reversibly altering the size of a macrocycle cavity could be applied to host-guest chemistry, or the synthesis of other supramolecular architectures such as rotaxanes or catenanes. Ideally the guest would be able to fit and interact with the macrocycle cavity when CO₂ was bound to L⁻. π-π stacking interactions between L⁻ and the guest could be one possible strategy for the host and guest to interact. Removing CO₂ could trap the guest inside the macrocyclic host leading to size selective encapsulation of guest through reversible small
molecule activation (Scheme 26). Modifications can be made to 8 to change the size of the cavity such as adding carbons to the pendent arm.

### 6.2.2 Acetonitrile Activation

![Scheme 27. Proposed reaction scheme for isolated heterotrimetallic complex.](image)

In an attempt to synthesize an Fe$^{II}$-Pt$^{II}$ heterobimetallic analogue of 6 (Scheme 27), a suspension containing dark crystals and a yellow precipitate was observed. The dark crystal, analyzed by X-ray crystallography, revealed a heterotrinuclear species (Figure 19). The complex unexpectedly contained a bridging CO ligand as the CO ligands were thought to have all been removed from the Fe$^{II}$ starting material by photolysis. The starting material therefore contained an unknown number of CO ligands. It can be seen that the sp hybridized carbon of the acetonitrile ligand underwent a nucleophilic attack by the [PtPh$_2$L]$^-$ anion of complex 2 to activate the C≡N triple bond, which resulted in the N atom coordinating to two Fe$^{II}$ centres. The crystal structure obtained suggested that yellow precipitate observed during the synthesis of the trinuclear species is probably 1.

![Figure 19. The preliminary crystal structure of (μ-CO)(FeCp$^*$)$_2$(NC(CH$_3$))L PtPh$_2$.](image)
Our group has extensively explored the reactivity between diazafluorenyl derivatives and CO$_2$\textsuperscript{33, 34}. In some cases the reversible formal insertion of CO$_2$ into the remote C-H bond at the 9-position of the ligand framework has been observed.\textsuperscript{33, 34} Reversible CO$_2$ activation has also been explored using dearomatized PNN and PNP pincer ligands.\textsuperscript{77, 78} More recently the reversible activation of C≡N triple bonds using a Rhenium PNP pincer complex has been reported by Milstein and coworkers.\textsuperscript{79} Our group has yet to explore the reactivity of diazafluorenyl derivatives with nitriles and it possible that heteromultimetallic systems are one viable strategy to activate the C≡N triple bond of nitriles.

6.2.3 Five coordinate Pt$^{IV}$ Chemistry

![Scheme 28. Proposed route to five coordinate Pt$^{IV}$ complex from 6 and 15.](image)

Five coordinate Pt$^{IV}$ complexes have been long proposed intermediates in reductive elimination and oxidative addition reactions, however stable complexes have only been isolated in the past decade.\textsuperscript{80} A variety of nacnac ligands,\textsuperscript{81, 82, 83, 84} anilido-imine ligands,\textsuperscript{85} and pyridylpyrrole ligands\textsuperscript{86} have been used to synthesize five coordinate Pt$^{IV}$ species. A five coordinate Pt$^{IV}$ species has also been synthesized where the five coordination sites were occupied by two hydrides, a trialkyl silane, and two N-donors a trispyrazolylborate ligand.\textsuperscript{87} These unsaturated Pt$^{IV}$ species have led to some very interesting reactivity.\textsuperscript{82, 83, 84, 85, 86} It is possible that the addition of a methylating agent (e.g. MeOTf or MeI) could oxidize the Pt$^{II}$ centre in complexes 6 and 15 to form a five coordinate Pt$^{IV}$ centre (Scheme 28). If this novel heterobimetallic species is isolable it could lead to some very interesting reactivity.
6.3 Final Remark

This thesis explored the use of three different 4,5-diazafluorenyl derivatives as binucleating ligands for the syntheses of heterobimetallic complexes. Although a variety of heterobimetallic complexes have been synthesized this work only covers the exploratory phase of the project. The next stage is indulging in the reactivity and catalytic applications of these diazafluorenyl heteromultimetallic species.
7 Bibliography


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