2014

Novel Coordination Cages from T-shaped Ligands

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Recommended Citation
Elguraish, Ismail Khalafalla, "Novel Coordination Cages from T-shaped Ligands" (2014). *Electronic Theses and Dissertations*. 5126.
https://scholar.uwindsor.ca/etd/5126

Novel Coordination Cages from T-shaped Ligands

By

Ismail Elguraish

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of **Chemistry & Biochemistry**
in Partial Fulfillment of the Requirements for
the Degree of **Master of Science**
at the University of Windsor

Windsor, Ontario, Canada

2014

Novel Coordination Cages from T-shaped Ligands

by

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May 26, 2014

DECLARATION OF CO-AUTHORSHIP

The primary contributions, synthesis, data collection, processing and interpretation were performed by the author.

In Chapter two, the initial design of the project was conceived by Dr. Kelong Zhu and Dr. Stephen J. Loeb. DFT studies for ligands were performed by Dr. Hazem Amarne.

All single crystal X-ray data was collected by Dr. Stephen J. Loeb, Dr. Kelong Zhu or Nicholas Vukotic. Crystal structure solutions and refinements were carried out by Dr. Stephen J. Loeb.

All the experimental work presented in this thesis was carried out in collaboration with Dr. Kelong Zhu.

I certify that I have properly acknowledged the contribution of other researchers to my thesis, and have obtained written permission from each to include the above material in my thesis.

I certify that, with the exceptions mentioned above, this thesis and the research presented therein is the product of my own work.

ABSTRACT

The coordination bond is very useful for supramolecular chemists because of its directionality and reversibility which lead to stable compounds.

This thesis describes the synthesis and characterization of new right-angled benzimidazole-based pyridyl ligands and the resulting assemblies that are formed when these ligands were combined with a *cis*-protected platinum(II) complex.

Chapter one gives a brief introduction about how coordination chemistry interfaces with supramolecular chemistry by utilizing coordination bonding in self-assemblies.

Chapter two describes the preparation and characterization of new T-shaped bipyridine ligands with a benzimidazole core and the surprising folded tetramers resulted from the combination of these ligands with a well-known platinum(II) metal corner.

Synthesis and characterization of another T-shaped tridentate pyridyl ligand built on the same benzimidazole framework is summarized in Chapter three. Reaction of this ligand with platinum(II) *cis*-protected complex resulted in a novel octahedral $\mathbf{M_6L_4}$ cage.

Chapter four provides conclusions and suggestions for future work.

DEDICATION

To my extended family

ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor Dr. Stephen Loeb for his guidance, advice, support and patience over the last couple of years. Thanks Steve for always being transparent, kind and generous.

I am beholden to Dr. Kelong Zhu for his continuous advice, support and help. Thank you Kelong; you are really unforgettable.

I am grateful to Dr. Jeremy Rawson who has helped me in many ways the least of which is being on my committee. Thanks Jeremy for your unlimited help, support and kindness.

I would also like to thank Dr. Barbara Zielinski for being on my committee and for reading my thesis.

I am also thankful to Dr. Holger Eichhorn and Dr. Charles Macdonald for their open doors, hearts and minds.

I would like to thank Dr. Hazem Amarne for performing DFT studies for ligands, Dr. Muhammad Usman Anwar for helping with IR and melting point measurements, Dr. Matthew Revington for advice and assistance with NMR, Dr. Janeen Auld for running MS and CHN, Nicholas Vukotic for collecting most of the X-ray crystal data, Rawson group members for offering a free access to their labs and equipment and Leslie Hernandez for re-running some reactions to confirm and complete NMR data.

Indeed thanks are due to Marlene Bezaire, Elizabeth Kickham, Catherine Wilson, Una Lee, Nedhal Al-Nidawy and Tina Lepine for their tremendous support to graduate students.

I would like to thank my sister Ammona, my family friends Roger and Sandra Chappus, my friend Elfadil Rahama for their help and encouragement from behind the scenes.

I would also like to thank present and past Loeb group members for being friendly and positive. Special thanks go to Ginny Loeb for administrative support.

Finally, I would like to express my love and gratitude to my wife RASHOYA and my four kids. Your love and smiles always empower me to face challenges and succeed.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF APPENDICES

LIST OF ABBREVIATIONS/SYMBOLS

^{o}	degree(s)
^{o}C	degree(s) Celsius
1D	one-dimensional
^{1}H	proton
2D	two-dimensional
3D	three-dimensional
a, b, c	cell dimensions (crystallography)
acac	acetylacetonato
ATR	attenuated total reflection
Br_2	bromine
CD_2Cl_2	deuterated dichloromethane/methylene chloride
$CDCl_3$	deuterated chloroform
$CHCl_3$	chloroform
cm	centimeter
Cs_2CO_3	cesium carbonate
d	doublet (NMR)
DCM	dichloromethane
dd	doublet of doublets (NMR)
ddd	doublet of doublet of doublets (NMR)

DFT	density functional theory
DMF	dimethylformamide
DMSO	dimetylsulfoxide
DNA	deoxyribonucleic acid
DOSY	diffusion ordered spectroscopy
dppp	1,3-bis(diphenylphosphino)propane
en	ethylenediamine
Et_2O	diethyl ether
EtOAc	ethyl acetate
EtOH	ethanol
g	gram(s)
g/mol	gram(s) per mole
h	hour(s)
Hz	Hertz
IR	infrared
J	dipole-dipole coupling constant/ scalar (NMR)
K_2CO_3	potassium carbonate
L	ligand
L1	7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole
L2	7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1Hbenzimidazole

L3	2,4,7-*tri*(pyridin-4-yl)-1H-benzimidazole
M	metal
m	multiplet (NMR)
MeCN	acetonitrile
$MeNO_2$	nitromethane
MeOH	methanol
mg	milligram(s)
$MgSO_4$	magnesium sulfate (anhydrous)
min	minute(s)
mL	milliliter(s)
mL/min	milliliter(s) per minute
mmol	millimole(s)
MP	melting point
M_r	molecular formula weight (crystallography)
MW	molecular weight
N_2	nitrogen
$NaBH_4$	sodium borohydride
nm	nanometer
NMR	nuclear magnetic resonance
OTf	trifluoromethanesulfonate

Ph	phenyl
ppm	part(s) per million
q	quartet (NMR)
RNA	ribonucleic acid
RT	room temperature
s	singlet (NMR)
THF	tetrahydrofuran
TLC	thin layer chromatography
V	cell volume (crystallography)
Z	formula units per unit cell (crystallography)
δ	chemical shift (NMR)
ν	wave number (IR)
α, β, γ	cell angles (crystallography)
μ	absorption coefficient (crystallography)
ρ	density

GENERAL COMMENTS

2,1,3-Benzothiadiazole was purchased from Aldrich and was used as received to synthesize 4,7-dibromo2,1,3-benzothiadiazole according to the literature method. 4-Fluorophenylboronicboronic acid, 4-*tert*-butylphenylboronic acid, 4-pyridylboronic acid, potassium carbonate, cesium carbonate and propionitrile were commercially obtained from Aldrich and used as received. Potassium tetrachloroplatinate(II) was purchased from STREM Chemicals. (1,3-Bis(diphenylphosphino)propane (**dppp**) was synthesized by an undergraduate student who used to work in Loeb's laboratory and was used to prepare the *cis*-protected metal corner **[Pt(dppp)][OTf]$_2$** using literature method. All deuterated solvents were obtained from Aldrich and used without further purification. Deionized water was purchased from Fischer Scientific. THF, DMSO, and MeOH were purchased from ACP Chemicals Inc. and were used as received. All other solvent were obtained from Aldrich and used as received. Thin layer chromatography was performed using Silicycle Ultrapure Silica Gel plates with 250 µm thickness and F-254 indicator and viewed under UV light. Silicycle Ultrapure Silica Gel (230 – 400 mesh) was used to perform column chromatography. NMR experiments were performed on a Brüker Avance (III) instrument (Broad Band Fluorine Optimized Probe) with a 500 MHz frequency, a Brüker Ultrashield Avance (US) instrument (Broad Band Probe) using a 300 MHz frequency, or a Brüker Avance (DPX) instrument with a 300 MHz frequency. ^{1}H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane Me_4Si ($\delta = 0.00$ ppm) and referenced to the residual solvent peak as an internal reference point. ^{31}P chemical shifts were referenced to 85% phosphoric acid H_3PO_4 (in water) ($\delta = 0.00$ ppm). ^{19}F chemical shifts were referenced to freon CCl_3F 80% (in deuterated chloroform $CDCl_3$) ($\delta = 0.00$ ppm). NMR spectra were initially processed using Topspin software. Final NMR spectra processing was performed using MestReNova 6 software. IR spectra were obtained using a Brüker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. Melting point measurements were performed using OptiMelt automated melting point system. All air-sensitive reactions were carried out under nitrogen using standard Schlenk line techniques. Single crystal data were collected using a Brüker D8 Venture diffractometer. Solutions and refinements of crystal structures were performed using SHELXTL library programs. Molecular graphics were prepared for publication using ORTEP-3, DIAMOND 3.0 or Mercury 3.3.

Chapter 1: INTRODUCTION

1.1 CHEMISTRY

Chemistry is the branch of natural sciences that studies the properties of substances, and most especially, the reactions responsible for the transformation of one substance to another.[1] Chemistry provides routes for exploring the properties and characteristics of existing materials to meet specific needs or applications as well as creating entirely new substances designed to have particular properties. Energy changes associated with chemical reactions are also of great importance to chemists. Chemistry is not only useful by itself but also fundamental to other scientific disciplines.[2] Biologists have used chemistry to understand many biological phenomena. Psychologists on the other hand have been influenced by chemistry as it unraveled the functioning of the nervous system. Engineers study chemistry to help them find materials with desired properties for desired applications. Chemistry is a central science that has contributed to the welfare of humanity, from food, clothing and health to smart phones and liquid crystals displays (LCDs). As years pass, more chemical compounds are synthesized or isolated. New materials are reported all over the world every day.

1.2 COORDINATION CHEMISTRY

Traditionally, chemistry branches have been organic, inorganic, physical and analytical chemistry. Over years, science has tremendously widened and expanded resulting in many new chemistry branches. The first explanation of the bonding in coordination complexes was given by Werner in 1893.[3] Werner's coordination theory was put forward before the electronic theory of valency and for this work he won the 1913 Nobel Prize in chemistry. Werner concluded that there are two different sorts of valency; primary or ionizable valency and secondary or non-ionizable valency. Alfred Werner (1866-1919) is undisputedly considered the founder of coordination chemistry.[4] In a coordination complex, a central atom or ion (usually of a transition metal) is coordinated by one or more molecules or ions (ligands) which act as Lewis bases, forming coordination bonds with the central atom or ion which acts as a Lewis acid.[5] The coordination bond arises from the donation of a lone pair of electrons from an orbital of one atom in the ligand (Lewis base) to occupy an empty orbital of another atom or ion (Lewis acid).[6] Ligand atoms that are directly bonded to the central atom or ion are known as "*donor atoms*". The number of donor atoms in a ligand used to coordinate to the central atom or ion is defined as the "*denticity*" of the ligand.[6] *Monodentate* ligands have one donor atom (e.g. NH_3 and PR_3), *bidentate* ligands have two (*e.g.* $[acac]^-$) and so on. Ligands may also be classified as neutral (*e.g.* NH_3 and PR_3) or anionic (e.g. $[acac]^-$ and Cl^-).

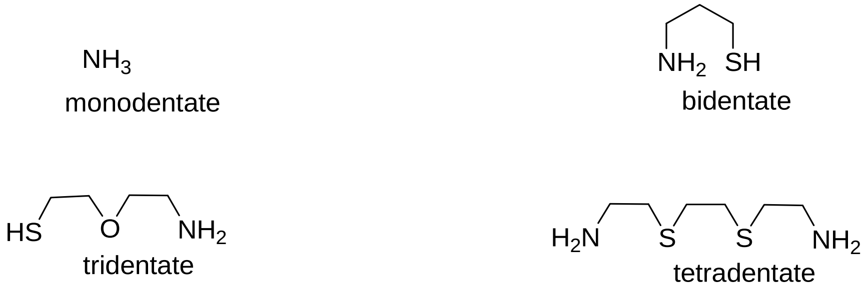


Figure 1. 1 – Ligand denticity

Ligand nature has a profound effect on the stability of coordination complexes.[6] When coordinated to a central atom or ion, polydentate ligands form a "*chelate ring*" leading to stable complexes due to what's known as the "*chelate effect*".[7]

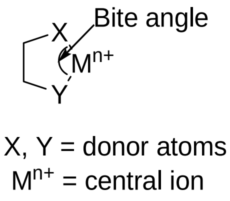


Figure 1. 2 – The chelate ring

Macrocyclic ligands form much stabilized complexes due to the "*macrocyclic effect*". A macrocyclic ligand (*e.g.* porphyrin and dibenzo-18-crown-6) contains three or more potential donor atoms in a ring of at least nine atoms.[8]

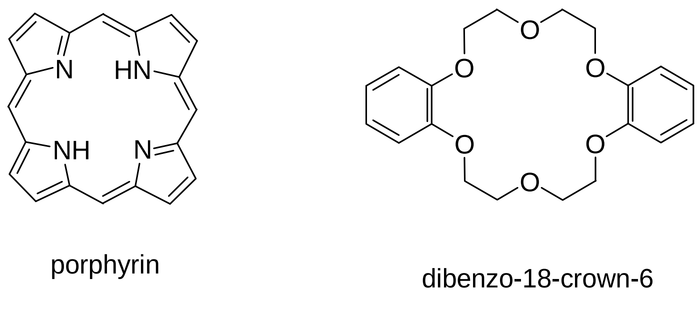


Figure 1. 3 – Examples of macrocyclic ligands

In *d*-block element complexes, *d* orbitals split (known as crystal field splitting) into two groups of different energy e_g and t_{2g}.[3] In addition to metal nature and oxidation state, the energy gap between these groups, Δ, depends on the nature of the ligand. Strong field ligands have large values for Δ while weak field ligands have small Δ values. Ligands arrangement in order of strength is called the "*spectrochemical series*".

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN <$ py (pyridine) $<$

$NH_3 <$en (ethylenediamine) $<$ bipy (2,2'-bipyridine) $<$ phen (1,10-phenanthroline) $< NO_2^- < PPh_3 <$

$CN^- \approx CO$

Figure 1. 4 – Spectrochemical series of common ligands

A reaction in which a ligand in a complex is replaced by another is called ligand substitution/exchange reaction.[6] Ligand substitution is usually reversible and leads to a stable complex. In addition to solvent, ligand substitution reactions (rates) are highly influenced by the ligand nature; *i.e.* strength, steric demand, chelate effect *etc.* for both leaving and entering groups.

1.3 SUPRAMOLECULAR CHEMISTRY

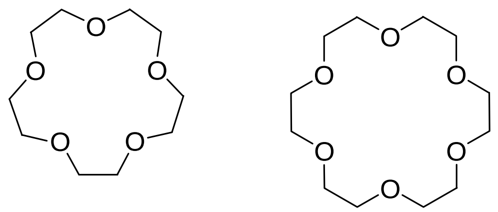
Founded in the 1980s, supramolecular chemistry is a new emerging domain lying amidst chemistry, biochemistry, physics and material technology.[9] Its founders Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen were awarded the Nobel Prize for chemistry in 1987 for their works on molecular recognition. Lehn defined supramolecular chemistry as "*the chemistry beyond the molecule*".[10] Another more specific definition – also given by Lehn – stresses the role of non-covalent interactions in supramolecular chemistry which are different from classical organic chemistry covalent interactions. Non-covalent interactions forcing the association of smaller molecules to form larger entities (self-assemblies) are characterized by much smaller energies than those of 200-400 kJ/mol typical for covalent chemical bonds.[9] Non-covalent bonding interactions are ion-ion interactions (100-350 kJ/mol), ion-dipole interactions (50-200 kJ/mol), dipole-dipole interactions (5-50 kJ/mol), hydrogen bonding (4-120 kJ/mol), cation-π (5-80 kJ/mol), π-stacking (0-50 kJ/mol), van der Waals forces (< 5 kJ/mol), close packing in solid state and hydrophobic effect.[11] Most of these interactions are directional and control the geometry of the assembly. Directional interactions govern orientations and relative distances in the assembly.[12] Whitesides defined molecular self-assembly as "*the spontaneous assembly of molecules into structured, stable, non-covalently joined aggregates*".[13] Whitesides considered understanding and controlling of the non-covalent connections between molecules as well as understanding and overcoming the intrinsically unfavourable entropy involved in bringing molecules together, the key to the synthesis of molecular self-assemblies.[13]

1.4 CAGES, SPHERES AND THE COORDINATION BOND

As mentioned above, the formation of self-assemblies is caused by weak non-covalent interactions. If these interactions are too weak, the spontaneous self-assembly does not take place and a mixture of kinetic oligomers results instead. To overcome such problems, Nature combines many weak interactions to form self-assemblies in biological systems. Emulating Nature, chemists have designed and prepared a vast array of self-assemblies using coordination and hydrogen bonds as the major driving force. Being strong enough, reversible and directional, coordination bonds are very useful in supramolecular chemistry as they lead to thermodynamically stable products. Coordination bonds have widely been used to achieve coordination cages and spheres with desired and predesigned architectures. Self-assembled coordination cages or spheres are three dimensional hollow compounds in which organic ligands serve as edges or faces and metal ions act as vertices to connect theses edges in a polyhedral structural fashion.[14]

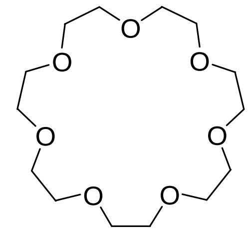
1.5 METALLOMACROCYCLES

The story of coordination self-assemblies traces back to 1967 when Pedersen accidently synthesized dibenzo[18]crown-6 which was the first crown ether. For this discovery, Pedersen gained the share of the 1987 Nobel Prize.[11] Pedersen observed the ability of the crown ether to dissolve alkali metals and their salts (*e.g.* $KMnO_4$) giving coloured solutions in organic solvents. He eventually concluded that "*the potassium ion had fallen into the hole at the center of the molecule*".[11]This proved to be absolutely correct, although his statement was bold and highly imaginative at that time.



[15]crown-5
complementary to Na^+

[18]crown-6
complementary to K^+



[21]crown-7
complementary to Cs^+

Figure 1. 5 – Examples of crown ethers

In 1984, Maverick *et al.* reported the preparation, structural characterization and adduct formation reactions of the first co-facial binuclear complex using a bis(β-ketone) ligand.[15] In Maverick's **M_2L_2** self-assembly, two **Cu(II)** ion centers connect two bis(β-ketone) ligands to form a 2D metallomacrocycle.

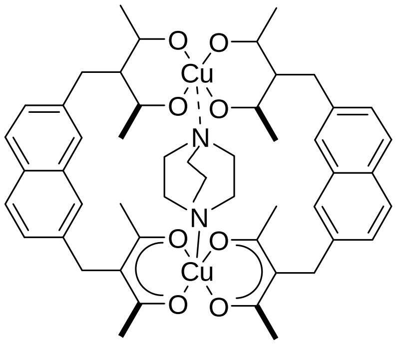


Figure 1. 6 – Maverick's M_2L_2 metallomacrocycle

Six years later in 1990, Fujita *et al.* reported the preparation of an **M_4L_4** self-assembled square macrocyclic complex using **$[Pd(en)]^{2+}$** as a *cis*-protected metal corner and a linear bidentate dipyridyl ligand.[16] The palladium block provides a 90° angle at each corner of the square. Using ^{1}H NMR experiments, Fujita proved that the complex is formed under thermodynamic control, which was very interesting. An important feature of Fujita's square is its molecular recognition ability for neutral organic molecules in aqueous media.

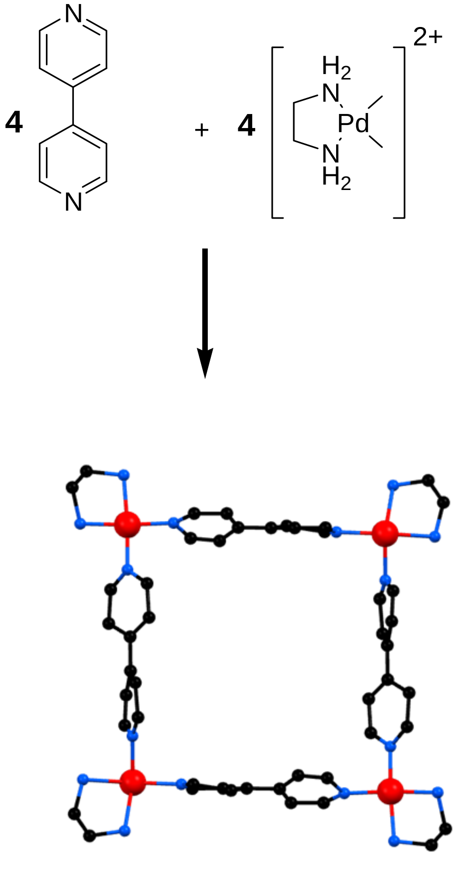
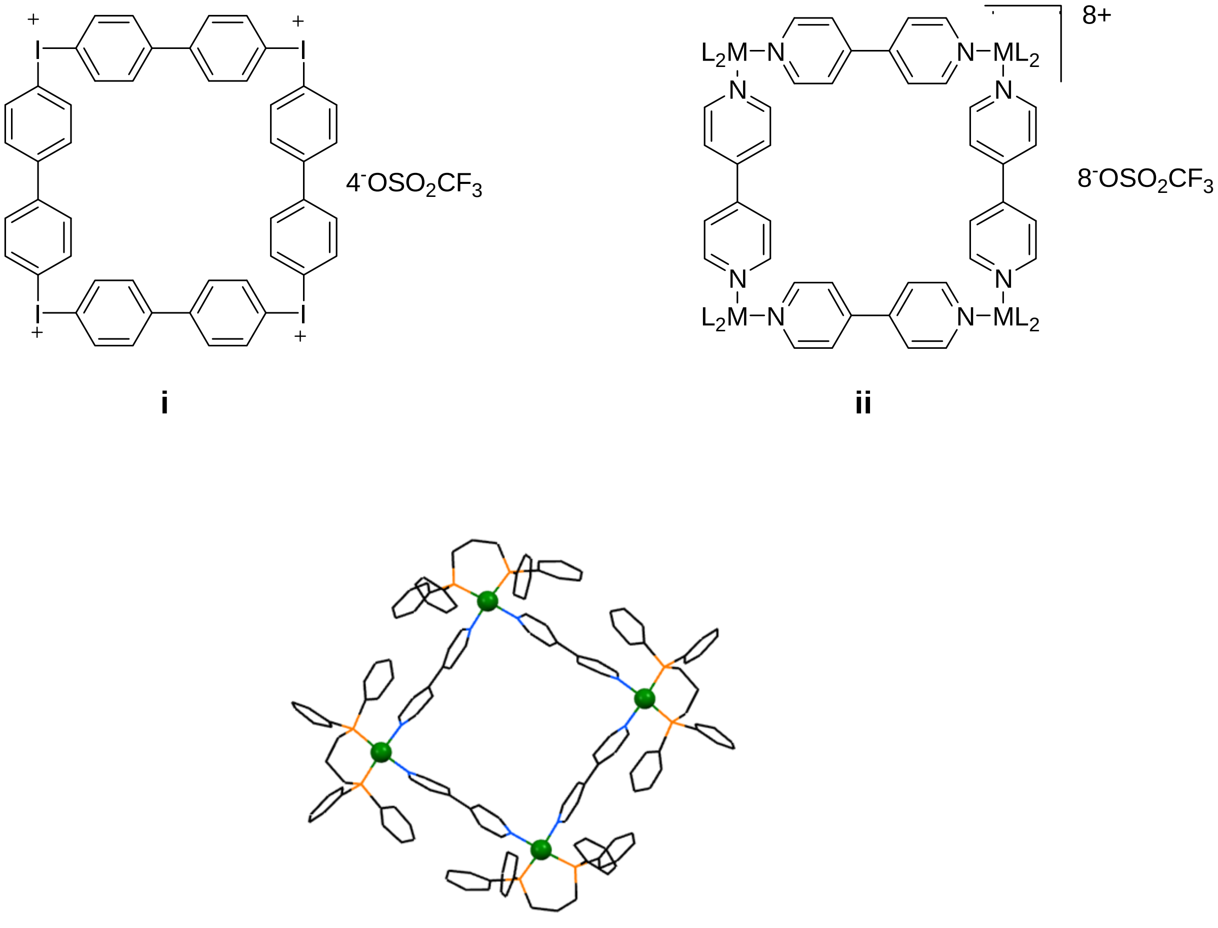


Figure 1. 7 – Fujita's M_4L_4 square

Following Fujita, Stang *et al*. were very active in the 1990s and were able to report many self-assembled metallacyclic complexes. In 1994, Stang and his group reported the preparation and characterization of **Pt(II)** and **Pd(II)** based tetranuclear macrocyclic complexes via self-assembly.[17] These were inspired by the preparation of the tetraaryl tetraiodonium macrocycle they reported in the previous year,[18] Stang's group used the same linear bidentate dipyridyl ligand (4,4'-bipyridine) previously used by Fujita, but different *cis*-protected metal corners with a chelating phosphine donor.



i

ii

iii

Figure 1. 8 – Stang's squares: (i) iodine-based, (ii) transitional metal-based (M = Pt or Pd), (iii) crystal structure of [Pt (dppp)(4,4'-dipyridine)]$_4^{2+}$

In 1996 Fujita *et al.* observed the formation of another component besides the square when 4,4'-bipyridine was replaced by a longer bridging ligand.[19] Two components, an $\mathbf{M_4L_4}$ square and an $\mathbf{M_3L_3}$ triangle, were assembled from $\mathbf{[Pd(en)(NO_3)_2]}$ and bis(4-pyridyl)acetylene (and similar ligands). The triangle is favoured by entropy effects while the square is stabilized by enthalpy effects. The square component is more dominant at higher concentrations while the triangle species dominates at lower concentrations. Needless to say, the equilibrium is also dependent on other factors such as temperature, steric effects and solvent nature.

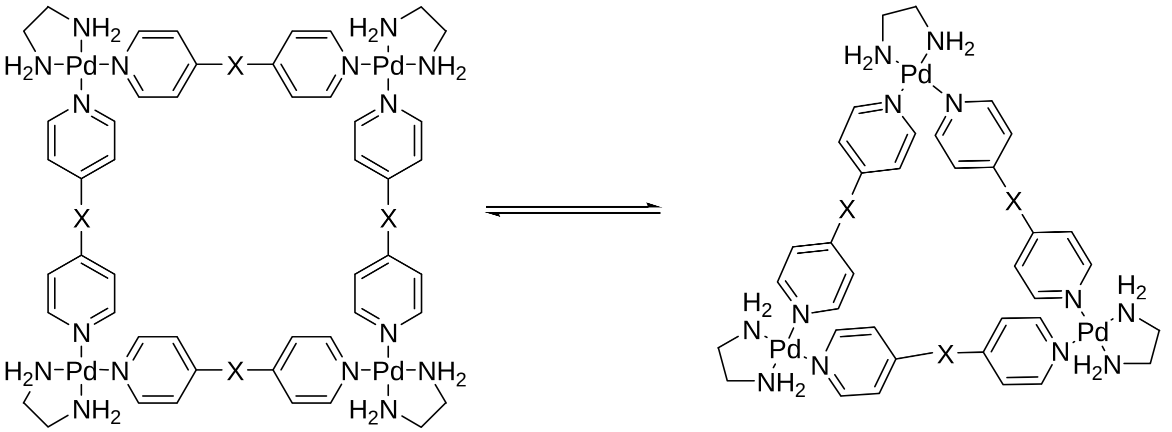


Figure 1. 9 – Fujita's square-triangle equilibrium

The first $\mathbf{M_2L_2}$ metallacycle assembled from a dipyridine ligand and a *cis*-protected metal corner was reported by Fujita *et al.* in 1993.[20] The treatment of flexible bis(4-pyridyl)-substituted ligands with a ***cis*****-**$\mathbf{[Pd(en)]^{2+}}$ complex resulted in high yields of macrocyclic dinuclear complexes. According to Fujita, "*the striking aspect of the macrocycle is its high ability for molecular recognition of electron-rich aromatic compounds with high shape specificity*".[20]

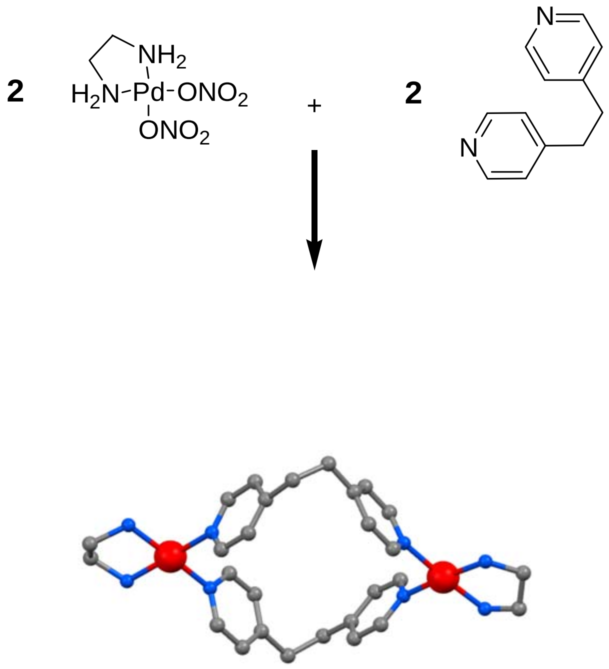


Figure 1. 10 – Fujita's M_2L_2 metallacycle

In 2002, Fujita designed a pentakis(*m*-phenylene) ligand with pyridine units at the two ends. The ligand is highly flexible and long enough to give an $\mathbf{M_1L_1}$ metallocyclic complex with *cis*-protected palladium corner. Non-functionalized *oligo*(*m*-phenylene)s do not favour double helical stacking due to the high entropic cost of the process. Formation of the mononuclear $\mathbf{M_1L_1}$ coordination ring reduces the entropy cost of the double helical stacking of the ligand leading to a reversible metal-linked catenation through aromatic stacking.

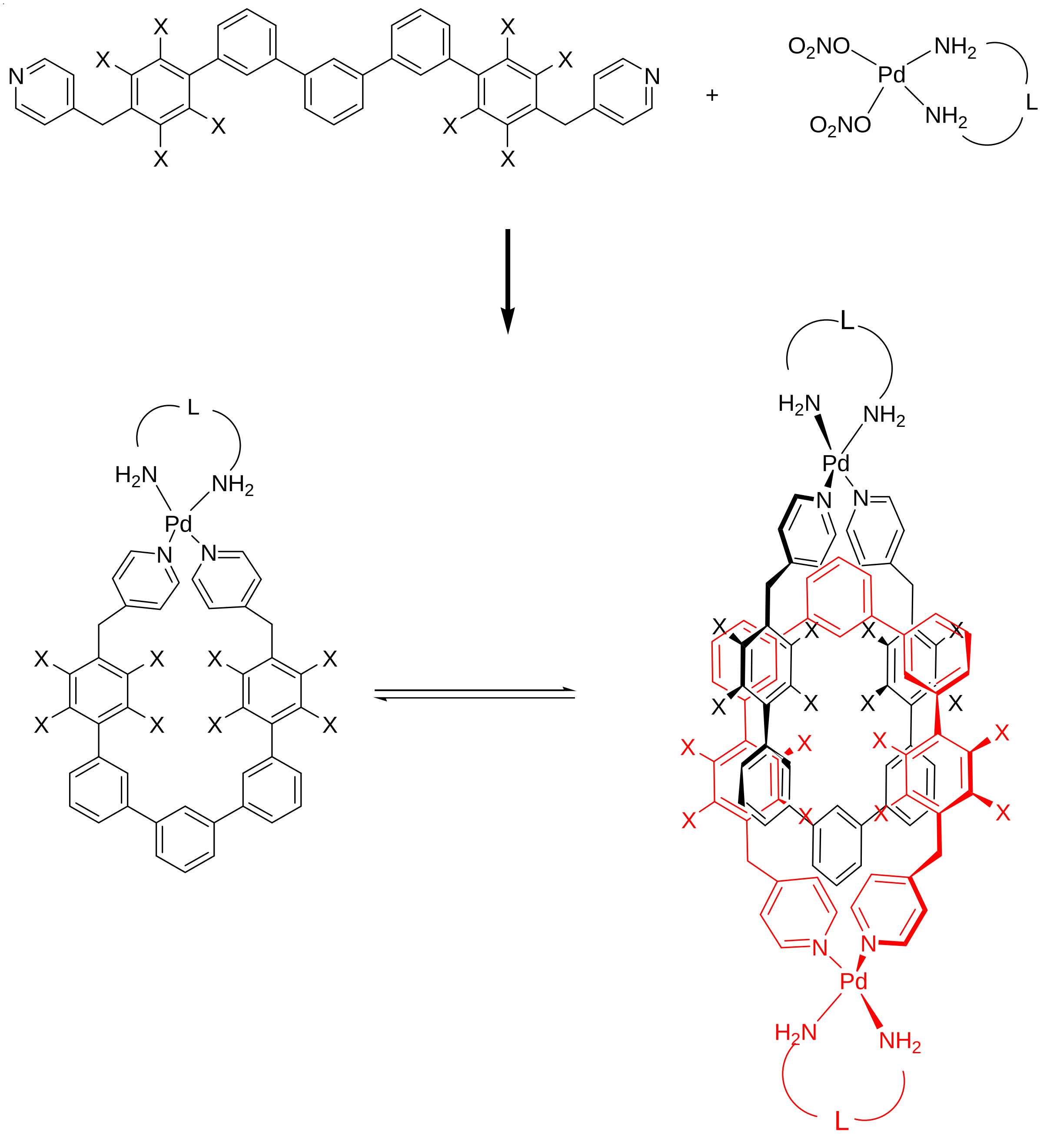


Figure 1. 11 – M_1L_1 metallacycle in equilibrium with a metal-linked catenane

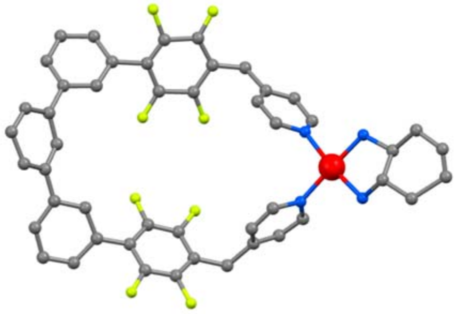


Figure 1. 12 – Crystal structure of Fujita's M_1L_1 metallacycle

1.6 TETRAHEDRONS

In 1988, Saalfrank *et al.* reported the first *T*-symmetric cluster of type $\mathbf{M_4L_6}$. Saalfrank's tetrahedral coordination complex was fortuitously assembled from six units of a *di-α-keto* acid ligand and four **Mg(II)** ions.[21] Later, a rational symmetrical-based synthetic approach was developed and a variety of divalent metals were embedded in the tetrahedral framework.[22] Metal ions occupy the four corners of the tetrahedron and are bridged by six bis-chelating ligands which form the tetrahedron edges. This distinct cage framework was also expanded by inserting a variety of spacers into the ligand.[22]

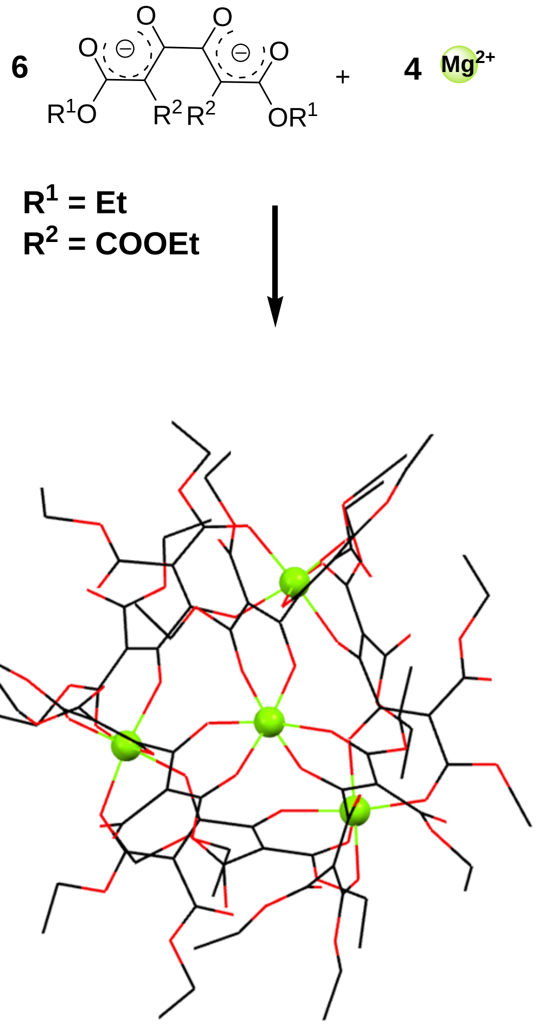


Figure 1. 13 – Saalfrank's M_4L_6 cluster

Raymond and coworkers made pronounced advancement on the chemistry of tetrahedral coordination cages. They demonstrated the possibility of employing strict geometric analysis in the design and synthesis of homochiral tetrahedral cages of the type $\mathbf{M_4L_6}$.[23] To avoid the formation of the $\mathbf{M_2L_3}$, which is entropically favoured, the designed ligand must be rigid enough to favour the formation of $\mathbf{M_4L_6}$. Raymond *et al.* used naphthalene-based catechol ligands ($\mathbf{H_4L}$) which, upon deprotonation, showed high affinity towards hard metals such as **Ga(III)** and **Fe(III)**. The naphthalene spacers' role is to keep the catechol binding sites apart to prohibit **M_2L_3** helix formation. They were also the first to show that assemblies of such nature can selectively encapsulate guests with remarkable discrimination.

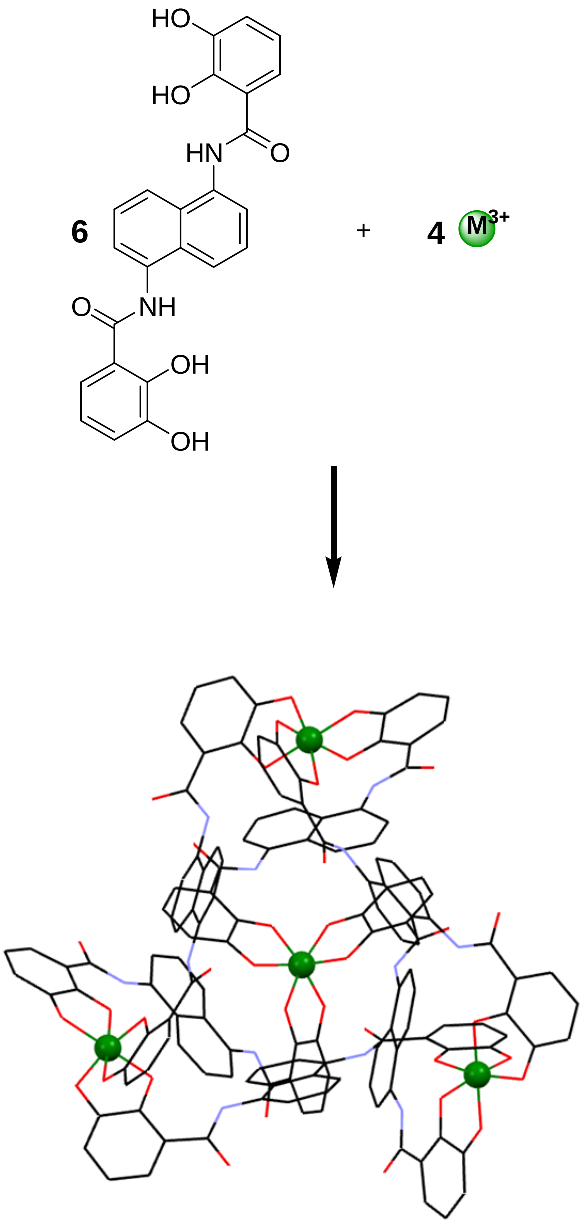


Figure 1. 14 – Raymond's M_4L_6 tetrahedral cage

1.7 MOLECULAR PANELLING, CAPSULES AND CAGES

The replacement of 1D linear and rod-type ligands with 2D panel-type ligands results in assemblies having more distinct capsule-like structures.[24] Metal ions serve as apices of a polyhedron while ligands represent faces rather than edges. This *"molecular paneling"* approach has been extensively utilized by Fujita and coworkers.[25] They showed that the simple combination of pyridine-bridged ligands and palladium (square planar geometry and 90 ° coordination angle) results not only in macrocycles and linked-ring molecules but also nanosized discrete organic cages and capsules.[25] They used triangular ligands as well as some square and rectangular ones.

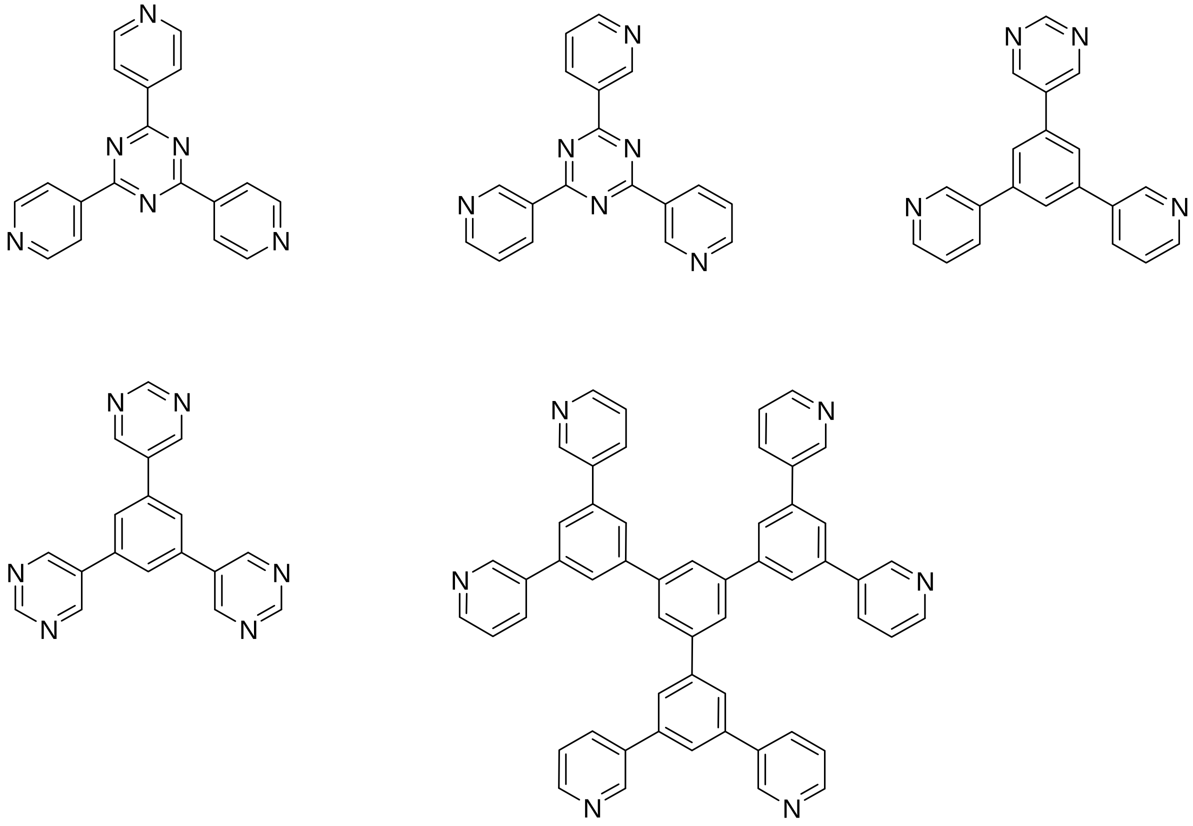


Figure 1. 15 – Fujita's triangular pyridyl ligands

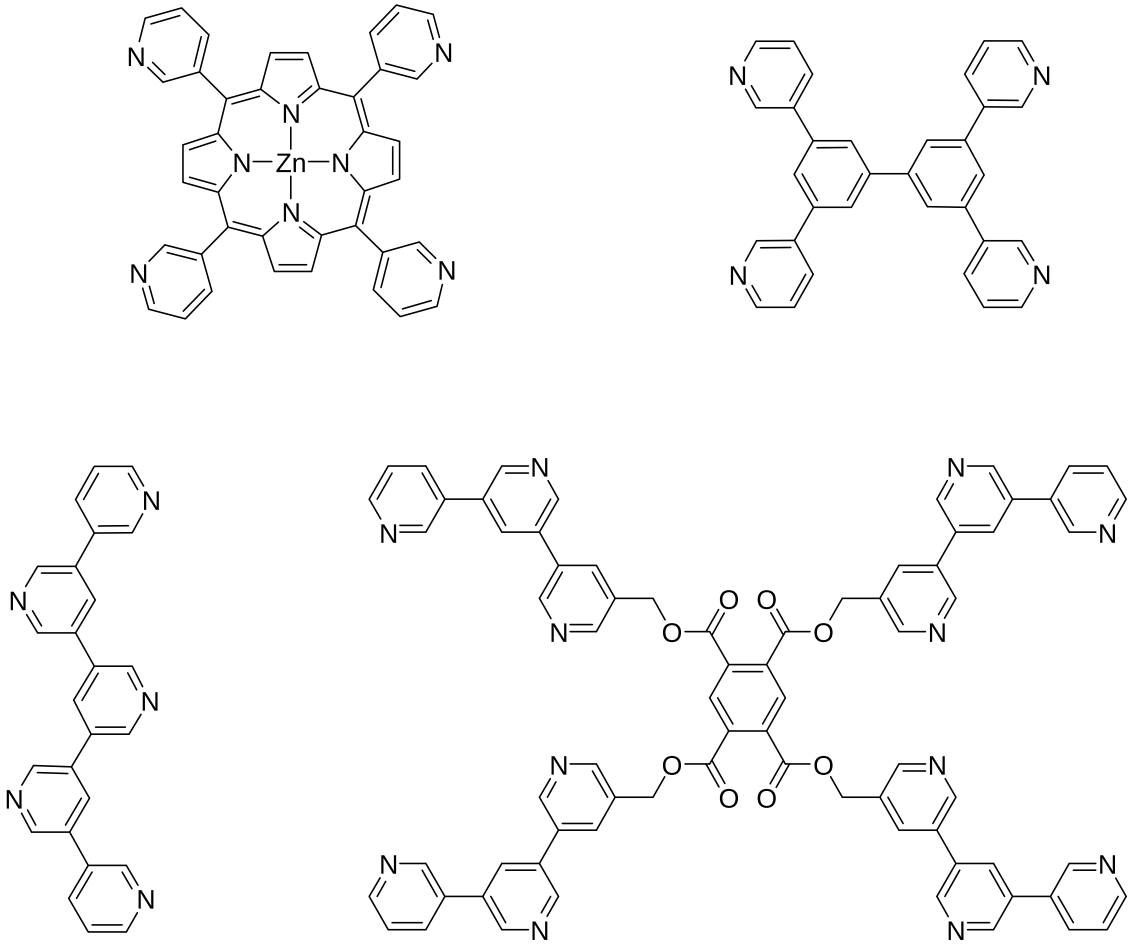


Figure 1. 16 – Fujita's square and rectangular pyridyl ligands

Fujita's cages and capsules have very large hydrophobic cavities and showed strong molecular recognition for neutral organic molecules in water. One of Fujita's cages (**M_4L_6, Pd-Pd** distance = 22 Å) is able to accommodate as many as four guests. Interestingly, these guests could be of same or different molecules. More interestingly, the shape and size of the guest molecule sometimes dictates the symmetry of the assembly. The **M_8L_4** example given below has a closed tetrahedral shape when a small guest **(CBr_4)** is encapsulated but it forms an open square-pyramidal cage with large guests (dibenzoyl). However, one disadvantage of guest molecules is that they add difficulties to the characterization and quantitative synthesis of some assemblies.[25]

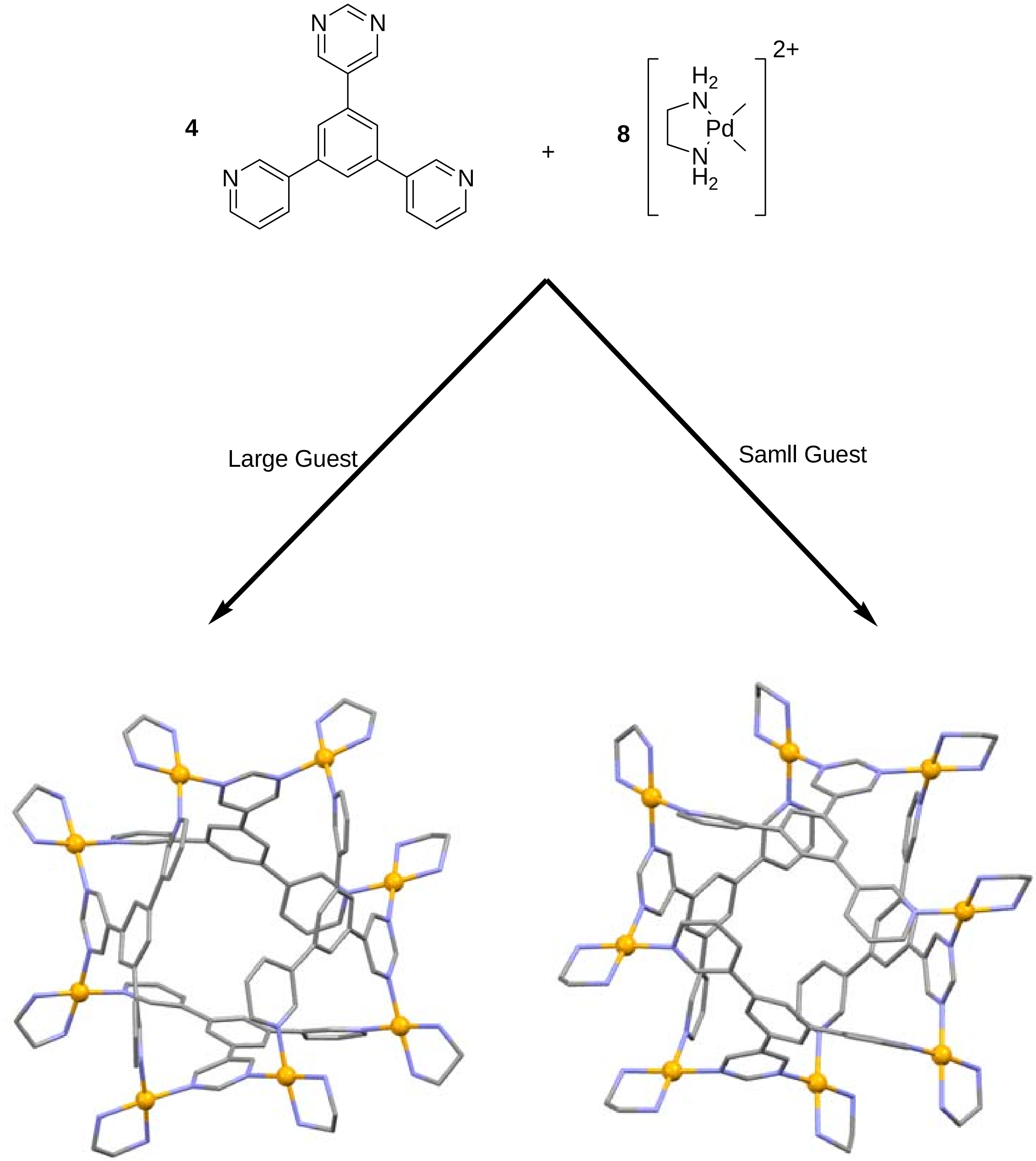


Figure 1. 17 – Effect of guest on assembly symmetry

1.8 COORDINATION SPHERES

In 1999, Robson and coworkers reported the synthesis of a coordination sphere using a trianionic ligand derived from 2,4,6-triazophenyl-1,3,5-trihydroxybenzene (H_3tapp) and **Cu(II)** ions.[26] Robson's sphere is built up of twenty building blocks and has an $\mathbf{M_{12}L_8}$ enclosure with cube-like topology in which the eight 3-connecting nodes are provided by the ligands rather than the **Cu(II)** ions. Crystal analysis revealed the diameter of the framework to be 1.3 nm and the void space inside the inner van der Waal's surface of the capsule (ca. **816 $\mathbf{Å^3}$**) is sufficient to accommodate six DMF molecules. The void space outside the outer van der Waal's surface of the capsule (**3190 $\mathbf{Å^3}$**) was found to be capable of accommodating twenty five DMF molecules. X-ray diffraction data indicated the presence of twenty four DMF molecules (both inside and outside the capsule), which agrees with crystal analysis.

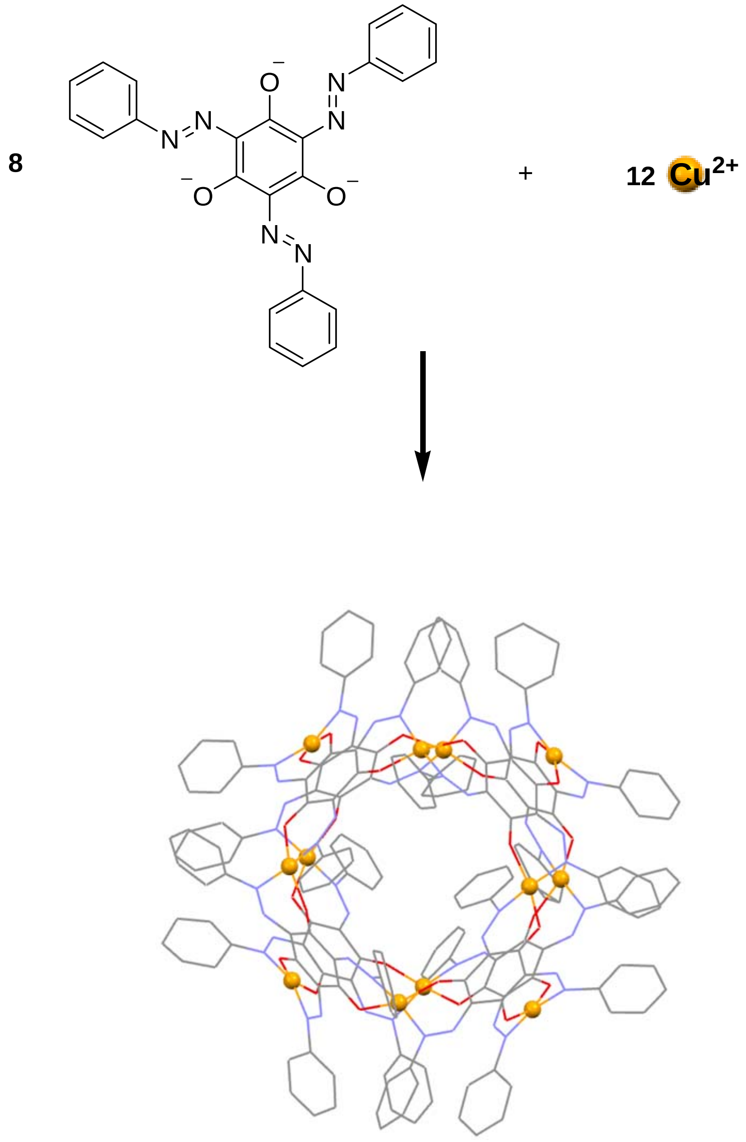


Figure 1. 18 – Robson's $M_{12}L_8$ sphere

In 2001, the groups of Yaghi and Zaworotko independently reported the synthesis of an **$M_{24}L_{24}$** cuboctahedral sphere from 1,3-benzenedicarboxylate (*m*-BDC) ligands which have a 120° angle between the functional groups, and **Cu(II)** ions.[27, 28] The internal cavity has a diameter of approximately **1.5 nm** and the volume is large enough to accommodate C_{60}.

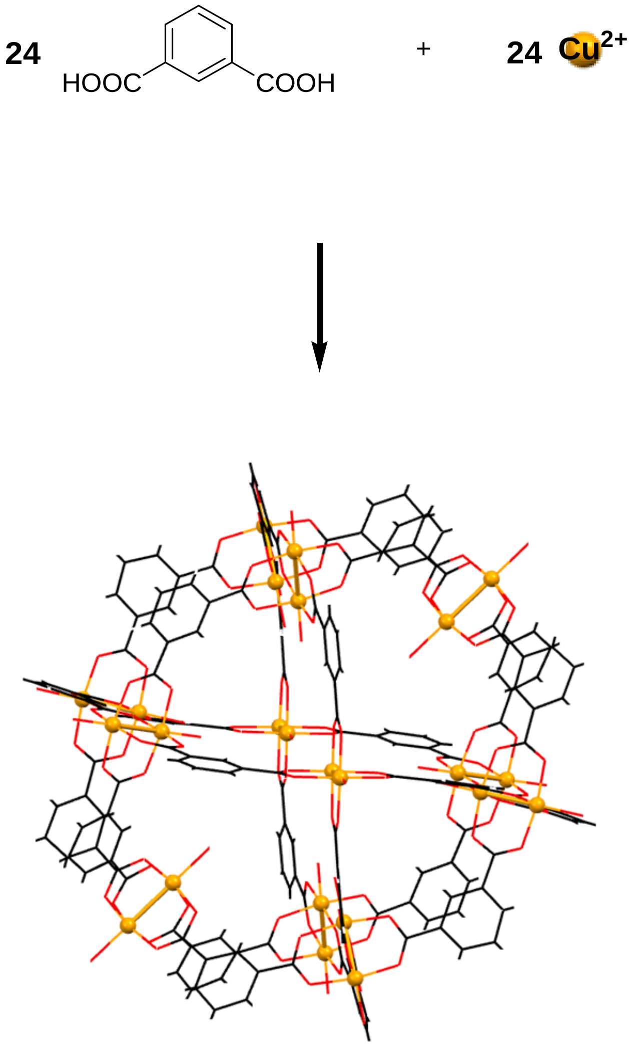


Figure 1. 19 – $M_{24}L_{24}$ coordination sphere

In 1999, Shinkai *et al.* showed that coordination spheres can be synthesized via the dimerization of calix[n]arenes.[29] Dimerization of two homo-oxacalix[3]arenes in the presence of three equivalents of **$[Pd(dppp)]^{2+}$** resulted in a very large coordination sphere. Shinkai and his group demonstrated the ability of their spheres to encapsulate C_{60} fullerene which was the first example of binding C_{60} in a capsule-like cage molecule.

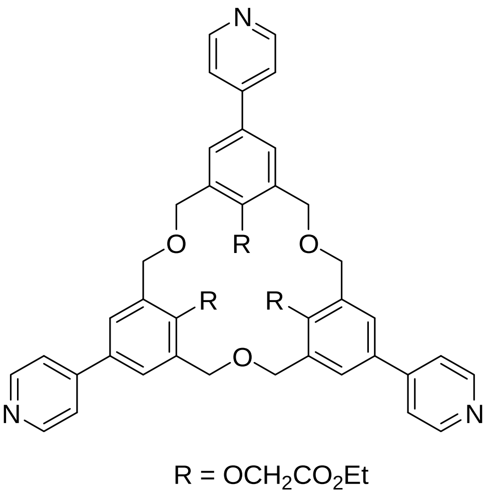


Figure 1. 20 – Shinkai's ligand

The same dimerization approach was used previously by Dalcanale *et al.* in 1997.[30] Dalcanale used a tetradentate ligand - bonding via cyano groups rather than pyridyl groups - and four equivalents of a *cis*-protected metal (**Pd** or **Pt**) complex. Both Dalcanale's and Shinkai's ligands are curved enough to facilitate the dimerization process.

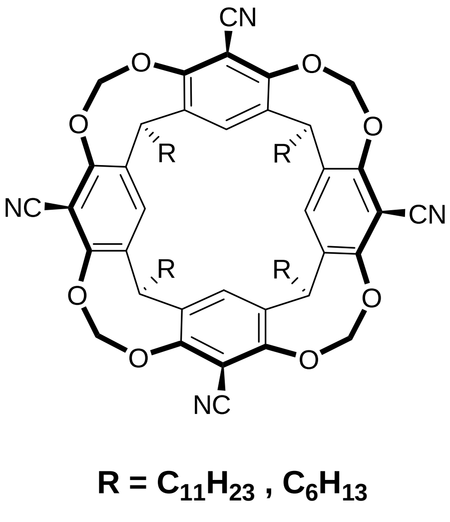


Figure 1. 21 – Dalcanale's ligand

Using the same ligand (pyrogallol[4]arene) and **Cu(II)** ions, Atwood and coworkers reported a large neutral pseudo-spherical **$M_{24}L_6$** coordination sphere in 2004.[31] Atwood's capsule has a diameter of **4 nm**. Atwood's group also constructed a hexameric (**L_6**) capsule from six calix[4]arene units connected by hydrogen bonds and showed for the first time that guest molecules in adjacent capsules adjust their spatial orientation in response to interactions between host capsules.[32]

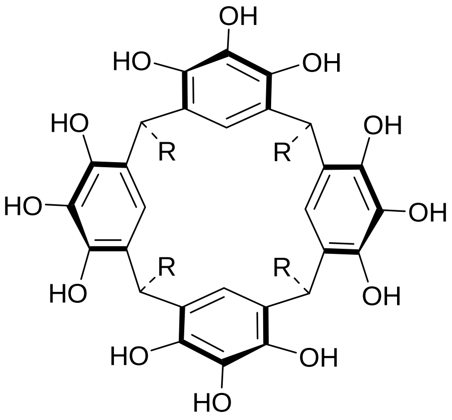


Figure 1. 22 – Atwood's ligand

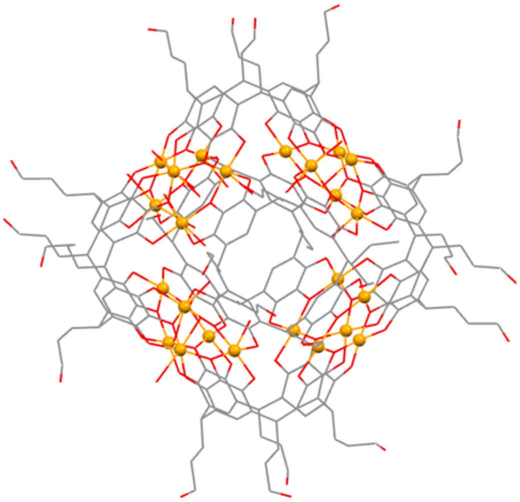


Figure 1. 23 – $M_{24}L_6$ sphere (M = Cu)

Inspired by the hollow spherical virus capsids and protein cages self-assembled by Nature, Fujita and coworkers performed a systematic study that lead to the preparation of a series of polyhedral spheres with the general formula $\mathbf{M_nL_{2n}}$.[33] Using simple bent bis(pyridine) bidentate ligands and **Pd(II)** ions, Fujita and his group succeeded in synthesizing several hollow complexes with **n = 6, 12, 24, 30 and 60**. The coordination angle was found to be the major factor in determining the value of n and hence the self-assembly size. Ligands with a larger bend angle formed larger $\mathbf{M_nL_{2n}}$ **capsules** with larger values of **n**. Table (1.1) below summarizes the correlation between **n** and coordination angle.

Table 1. 1 – Correlation between (n) and coordination angle

Coordination angle (^{0})	***Complex formula (M_nL_{2n})***
90	$\mathbf{M_6L_{12}}$
120 - 130	$\mathbf{M_{12}L_{24}}$
135 - 149	$\mathbf{M_{24}L_{48}}$

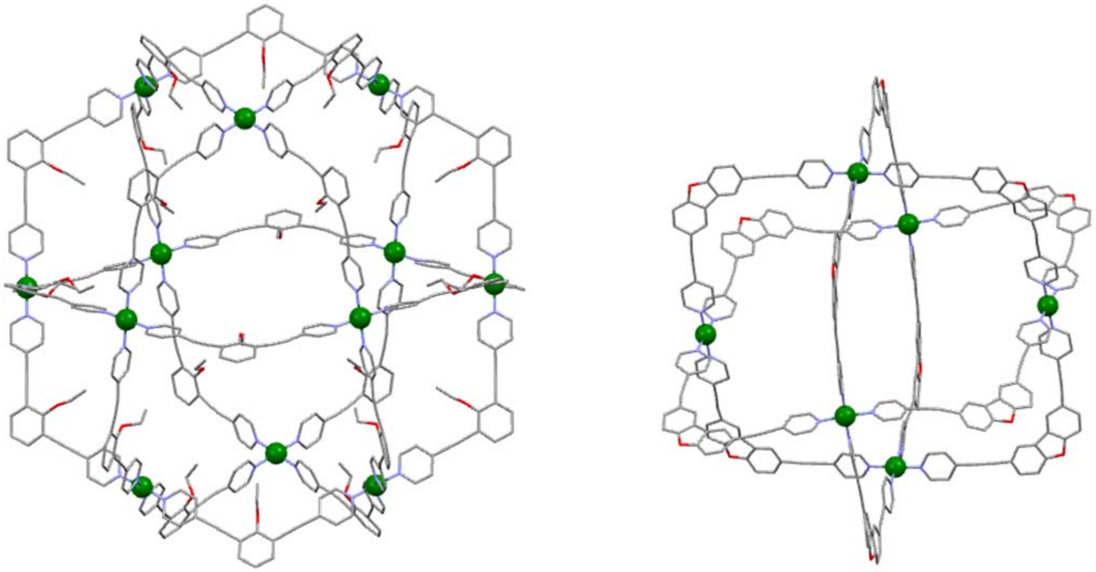


Figure 1. 24 – Examples of M_nL_{2n} cages
(M = Pd): M_6L_{12} (Right) [35] and $M_{12}L_{24}$ (left) [34]

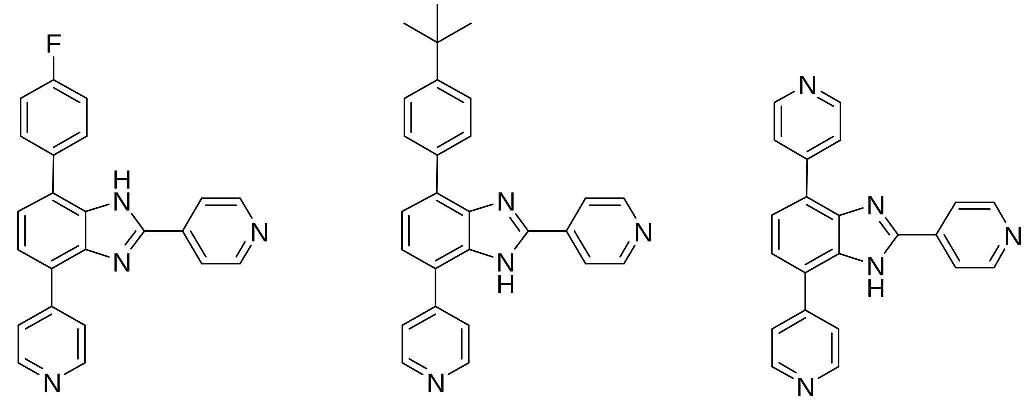
1.9 SCOPE OF THIS THESIS

In this thesis, a new set of pyridyl ligands based on a benzimidazole core were prepared and their coordination chemistry with **$[Pt(dppp)]^{2+}$** was explored. The unique feature that these ligands have in common is a 90° (right angle) defined by the substitution pattern of the benzimidazole unit.

In Chapter two, bidentate ligands **L1** and **L2** were prepared and characterized. Each of the two ligands was combined with **$[Pt(dppp)]^{2+}$** resulting in novel **M_4L_4-type** tetrahedral cages. The striking feature of the resulting cages is the formation of the tetrahedron from a single cyclic structure. Via coordination bonds, four ligand units are connected by four **Pt(II)** ions forming a macrocycle that is neatly folded to afford the tetrahedral shape.

In Chapter three, tridentate ligand **L3** was synthesized, characterized and combined with **[Pt(dppp)]$^{2+}$** resulting in an **M$_6$L$_4$-type** octahedral coordination cage. The longer dipyridyl portion forms the square base of an octahedron, while the shorter pyridyl "arms" coordinate to form the apices of the octahedron.

Both these simple ligand designs afford large and complex polyhedral architectures by utilizing divergent metal corners and the right angle of the ligand provided by the substitution pattern at the benzimidazole core. Thus, demonstrating the utility of this novel ligand design.



L1 **L2** **L3**

Figure 1. 25 – Ligands

Chapter 2: ASSEMBLY OF M4L4 CLUSTERS

2.1 INTRODUCTION

The ability of chemists to assemble large and complex structures from simple ligand and metal components has yielded a fascinating array of shapes and sizes from simple 2-dimensional (2D) triangles to giant 3-dimensional (3D) spheres. Supramolecular chemists have succeeded in preparing different molecular architectures such as squares, racks, ladders, helices, cages, capsules, bowels, tubes, polygons and polyhedra.[10] Functions and architectures of such complexes are dependent on the ligand design and the right choice of the metal ion.[36] In contrast, Nature often prefers to create larger structures by folding strands and simple oligomers. Deoxyribonucleic acid (DNA) - which is responsible for the encoding of the genetic instructions used in the development and functioning of all living organisms - and ribonucleic acid (RNA) are polymers of nucleotides.[37] The DNA double-helix is due to hydrogen bonding between two strands.[38] Proteins - the functions of which are very well-known - are another example of giant folded biochemical structures.

This chapter describes the preparation and characterization of new bis(pyridine) ligands built on a 2,4,7-triphenyl-(benzimidazole) scaffold that contains a rigid 90-degree angle, which is quite rare in the literature for an organic molecule. One of the ligands **(L1)** (Figure 2.1) was decorated with fluorine atoms which allowed the utilization of ^{19}F NMR spectroscopy for characterization and reaction monitoring. The other ligand **(L2)** (Figure 2.1) was decorated with *t*-butyl groups which provided an intense and sharp peak in ^{1}H

NMR spectra. Different NMR spectroscopic techniques as well as single crystal X-ray studies were performed to characterize these new ligands.

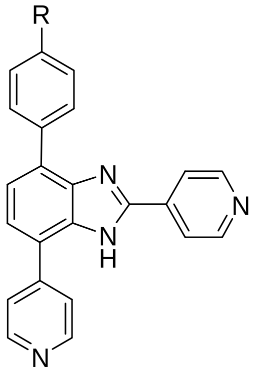
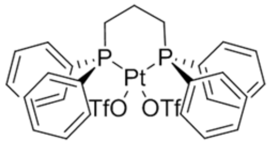


Figure 2. 1 - Ligand structure: L1: R = F; L2: R = *t*Bu

This chapter shows the surprising folded structure (Figure 2.28) that resulted when each of these ligands was combined with a standard **[Pt(dppp)]$^{2+}$** corner (Figure 2.2). Rather than yielding the simple square complex usually found from four right-angled components, the system folds into a large tetranuclear cluster.



Pt(dppp)(OTf)$_2$

Figure 2. 2 - Platinum corner

A single crystal X-ray study was performed to identify the tetrameric assembly in the solid state and 1D and 2D NMR experiments to verify retention of the cluster in solution.

2.2 EXPERIMENTAL: LIGANDS SYNTHESIS

2.2.1 Synthesis of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1)

2.2.1.1. Synthesis of 4,7-dibromobenzo[C][1,2,5]thiadiazole: [39]

2,1,3-Benzothiadiazole (10 g, 73.44 mmol, MW = 136.17 g/mol) was dissolved in HBr (48%, 150 mL). A solution of Br_2 in HBr (100 mL), containing (32.2 g, 201.50 mmol, 11.3 mL) of Br_2, was added very slowly; approximately (0.5 mL/min), (3.5 h). The resulting mixture was refluxed (90 ^oC) overnight. The mixture was then cooled to RT and an excess of sodium bisulphite ($NaHSO_3$) was added to remove any unreacted bromine. The mixture was filtered under vacuum, washed repeatedly with water and once with Et_2O. The pale yellow precipitate (4,7-dibromobenzo[C][1,2,5]thiadiazole) (Figure 2.3) was dried under vacuum for 24 h. **Yield:** 17.95 g, 83%, **MW** = 293.97 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.79 (s, 2H). **EA (CHN) (%):** calculated: C = 24.51; H = 0.69; N = 9.53; found: C = 24.97; H = 0.79; N = 9.54.

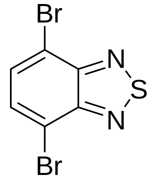


Figure 2. 3 - 4,7-Dibromobenzo[C][1,2,5]thiadiazole

2.2.1.2 Synthesis of 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (1)

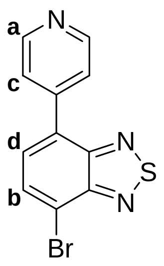
2.2.1.2.1 – Catalyzed by $Pd(PPh_3)_4$

4-Pyridylboronic acid (0.420 g, 3.42 mmol, MW = 122.92 g/mol), 4,7-dibromobenzo[C][1,2,5]thiadiazole (1.000 g, 3.40 mmol, MW = 293.97 g/mol), $Pd(PPh_3)_4$

(0.020 g, 0.02 mmol, MW = 1155.57 g/mol) and Cs_2CO_3 (0.400 g, 1.23 mmol MW = 325.82 g/mol) were added to a clean dry Schlenk flask. The flask was degassed and backfilled with N_2. A (1:1) mixture of dry toluene and DMF (40 mL) was added and the resulting mixture was refluxed (110 ^{o}C) under nitrogen for 1 day. The flask contents were cooled to RT, filtered and washed with DCM (60 mL) until a pale precipitate was formed. The solvent was removed using a rotary evaporator. Column chromatography was performed using DCM/EtOAc (1:2). A yellow product **(1)** resulted upon solvent removal. **Yield:** 0.050 g, 13%, **MW** = 292.15 g/mol.

2.2.1.2.2 Catalyzed by PEPPSI^{TM}-IPr

4-Pyridylboronic acid (0.420 g, 3.42 mmol, MW = 122.92 g/mol), 4,7-dibromobenzo[C][1,2,5]thiadiazole (1.000 g, 3.40 mmol, MW = 293.97 g/mol), PEPPSI^{TM}-IPr catalyst ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride) (0.046 g, 0.07 mmol, MW = 679.46 g/mol), and potassium carbonate (K_2CO_3) (2.35 g, 17.03 mmol, MW = 138 g/mol) were added to a clean dry 100-mL Schlenk flask. The flask was evacuated and backfilled with N_2 three times. A (1:1) 1,4-dioxane/water mixture (60 mL) was added to the reaction mixture. The flask contents were refluxed (90 ^{o}C) under nitrogen for 24h. The flask was cooled to RT. Extraction with DCM and drying over anhydrous $MgSO_4$ gave a greenish yellow solution. Solvent was removed using a rotary evaporator and the product was collected. Column chromatography was performed using DCM/EtOAc (2:1) and solvents removed. Product **(1)** is greenish yellow. **Yield:** 0.350 g, 35%, **MW** = 292.15 g/mol. **MP:** 178 ^{o}C. **IR** (ATR) (ν/cm^{-1}) = 3032, 1596, 1584, 1545, 1528, 1474, 1408, 1328, 1301, 1264, 1213, 1154, 1089, 1068, 992, 933, 880, 845, 814, 785, 748, 669, 626, 614, 560, 545, 517, 503, 463. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.03 (s, 1C), 152.56 (s, 1C), 150.41 (s, 2C), 143.91 (s, 1C), 132.21 (s, 1C), 130.99 (s, 1C), 128.99 (s, 1C), 123.54 (s, 2C), 115.44 (s, 1C). **EA (CHN) (%):** calculated: C = 45.22; H = 2.07; N = 14.38; found: C = 45.44; H = 2.35; N = 14.12.

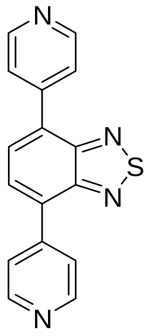


1

Table 2. 1 - ^{1}H NMR (300 MHz, $CDCl_3$) data of 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (1)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*d*	*8.77*	*2*	$^3J_{ac} = 5.3$
b	*d*	*7.96*	*1*	$^3J_{bd} = 7.6$
c	*m*	*7.88 – 7.80*	*2*	*-*
d	*d*	*7.67*	*1*	$^3J_{db} = 7.6$

In both cases above, another brown compound/by-product **(2),** characterization of which is given in section (3.2.1.1), was obtained by flushing the column with MeOH, drying over anhydrous $MgSO_4$ and recrystallization from MeCN.

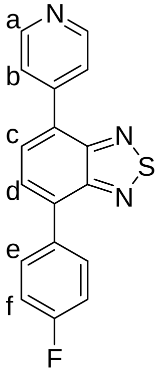


2

2.2.1.3 Synthesis of 4-(4-fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (3)

4-Fluorophenylboronic acid (0.166 g, 1.19 mmol, MW = 139.92 g/mol), PEPPSI^{TM}-IPr catalyst ([1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II)dichloride) (0.016 g, 0.02 mmol, MW = 679.46 g/mol), and potassium carbonate (K_2CO_3) (0.827 g, 5.99 mmol, MW = 138 g/mol) were added to a Schlenk flask. The flask was evacuated and kept under nitrogen for 5 min. 4-Bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(1)** (0.350 g, 1.20 mmol, MW = 292.15 g/mol) was dissolved in 1, 4-dioxane (20 mL) and added to the solids. Then water (20 mL) was added. The mixture was then refluxed under N_2 at 90 ^{o}C for 1 day. The product was extracted with $CHCl_3$. The solution was dried with anhydrous $MgSO_4$, filtered and then the solvent evaporated. Product **(3)** was recrystallized from MeOH. **Yield:** 0.368 g, 95%, **MW** = 307.06 g/mol. **MP:** 227 ^{o}C. **IR** (ATR) (v/cm^{-1}) = 3067, 3020, 2962, 1600, 1556, 1544, 1514, 1497, 1480, 1417, 1350, 1316, 1302, 1261, 1216, 1157, 1095, 1070, 1020, 1000, 957, 938, 889, 853, 811, 753, 719, 692, 670, 650, 632, 586, 550, 535, 516, 498, 481, 423. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.29 (s, 1C), 162.31 (s, 1C), 154.20 (s, 1C), 153.64 (s, 1C), 150.40 (s, 2C), 144.67 (s, 1C), 134.22 (s, 1C), 133.17 (s, 1C), 131.23 (d, *J* =

8.2 Hz, 1C), 130.42 (s, 1C), 128.90 (s, 1C), 127.82 (s, 1C), 123.68 (s, 2C), 115.99 (s, 1C), 115.82 (s, 1C). **EA (CHN) (%):** calculated: C = 66.44; H = 3.28; N = 13.67; found: C = 62.75; H = 3.81; N = 12.50.



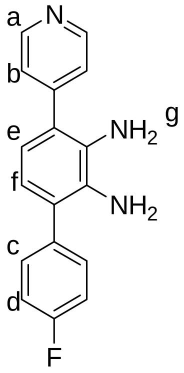
3

Table 2. 2 - ^{1}H NMR (300 MHz, $CDCl_3$) data of 4-(4-fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (3)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*dd*	*8.79*	2	$^3J_{ab} = 4.5$, $^5J_{ab} = 1.6$
b, c, d, e	*m*	*8.03 – 7.84*	6	-
f	*d*	*7.80*	2	$^3J_{fe} = 7.4$

2.2.1.4. Synthesis of 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (4)

4-(4-Fluorophenyl-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(3)** (0.348 g, 1.13 mmol, MW = 307.06 g/mol) was dissolved in EtOH (45 mL) and THF (15 mL) and transferred to a Schlenk flask. Cobalt(II) chloride hexahydrate (0.006 g, 0.02 mmol, MW = 236.9 g/mol) and sodium borohydride ($NaBH_4$) (0.065 g, 1.70 mmol, MW = 38 g/mol). The resulting mixture was refluxed (70 ^{0}C), monitored by running a TLC using DCM/EtOAc (2:1), and more sodium borohydride ($NaBH_4$) (0.065 g, 1.70 mmol, MW = 38 g/mol) added every 1 h until the reaction was complete (4 h); then cooled to RT. The product was extracted with DCM and filtered under N_2. The solvent was removed using a rotary evaporator. The white solid **(4)** was kept under N_2 to be used in the next step. **Yield:** 0.300 g, 95%, **MW** = 279.31. **MP:** 238 ^{o}C. **IR** (ATR) (v/cm^{-1}) = 3311, 2960, 2923, 2863, 2296, 2225, 1617, 1593, 1474, 1437, 1409, 1378, 1345, 1320, 1260, 1207, 1112, 991, 879, 864, 824, 808, 793, 748, 692, 648, 581, 520. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.35 (s, 1C), 161.39 (s, 1C),150.57 (s, 2C), 147.81 (s, 1C), 135.33 (s, 1C), 132.58 (s, 1C), 132.35 (s, 1C), 130.91 (d, *J* = 8.0 Hz, 1C), 128.67 (s, 1C), 125.53 (s, 1C), 124.11 (s, 2C), 121.38 (s, 1C), 120.58 (s, 1C), 116.12 (s, 1C), 115.95 (s, 1C).



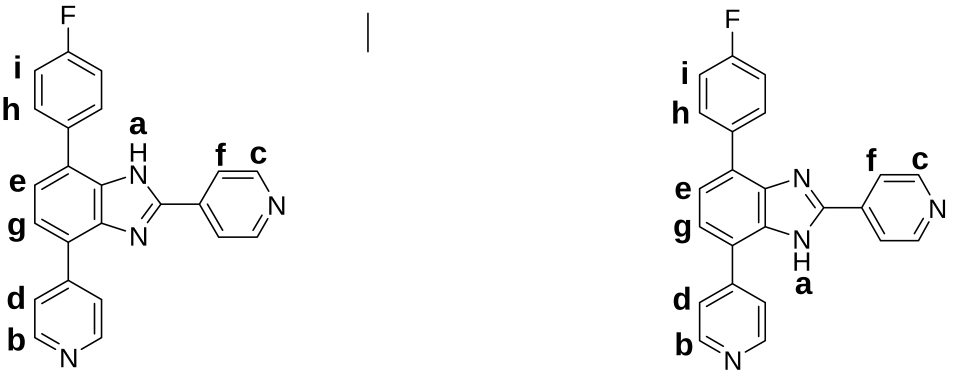
4

Table 2. 3 - ^{1}H NMR (300 MHz, $CDCl_3$) data of 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (4)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*d*	*8.79*	*2*	*$^3J_{ab}$ = 4.6*
b, c	*m*	*7.52*	*4*	-
d	*s*	*7.34*	*2*	-
e, f	*s*	*6.85*	*2*	-
g	*s (broad)*	*3.71*	*4*	-

2.2.1.5. Synthesis of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1)

4-Pyridinecarboxaldehyde (0.115 g, 1.07 mmol, MW = 107.11 g/mol) was weighed in a small vial, diluted with chloroform (10 mL) and added to the 3-(4-fluorophenyl-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** (0.300 g, 1.07 mmol, MW = 279.31 g/mol) in a round bottom flask. Zirconium tetrachloride ($ZrCl_4$) (0.0025 g, 0.01 mmol, MW = 233.6 g/mol) was added and the mixture was stirred overnight at RT. Solvent was removed using a rotary evaporator. The resulting solid was dissolved in THF and filtered and then the THF was evaporated from the filtrate. The resulting pale yellow product **(L1)** was recrystallized twice using MeCN. **Yield:** 0.195 g, 48%, **MW** = 366.39 g/mol. **MP:** 292 ^{o}C. **IR** (ATR) (v/cm^{-1}) = 3060, 3043, 2961, 1933, 1852, 1594, 1559, 1539, 1522, 1506, 1491, 1477, 1437, 1420, 1405, 1378, 1364, 1327, 1302, 1256, 1226, 1220, 1215, 1157, 1092, 1068, 1011, 999, 991, 861, 930, 870, 845, 831, 811, 801, 740, 731, 703, 695, 668, 651, 642, 614, 603, 583, 553, 528, 504, 447, 429. **EA (CHN) (%)**: calculated: C = 75.40; H = 4.13; N = 15.29; found: C = 71.43; H = 4.55; N = 13.82.



L1a **L1b**

L1

Table 2. 4 - ^{1}H NMR (500 MHz, CD_2Cl_2) data of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1b)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*s*	*10.78*	*1*	-
b	*m*	*8.80-8.75*	*2*	-
c	*d*	*8.73*	*2*	$^3J_{cf} = 4.5$
d, e	*m*	*8.22-8.14*	*3*	-
f	*dd*	*8.06*	*2*	$^3J_{fc} = 4.5$, $^5J_{ff} = 1.6$
g	*m*	*7.72-7.68*	*1*	-
h	*t*	*7.46*	*2*	$^3J_{hi} = 7.6$
i	*m*	*7.39 – 7.15*	*2*	-

Table 2. 5 ^{1}H NMR (500 MHz, CD_2Cl_2) data of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1a)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*S*	*9.81*	*1*	-
b	*m*	*8.80-8.75*	*2*	-
c	*d*	*8.68*	*2*	$^3J_{cf} = 4.5$
d, e	*m*	*8.22-8.14*	*3*	-
f	*dd*	*7.96*	*2*	$^3J_{fc} = 4.5$, $^5J_{ff} = 1.6$
g	*m*	*7.62-7.56*	*1*	-
h	*m*	*7.35-7.23*	*2*	-
i	*m*	*7.39 – 7.15*	*2*	-

2.2.2. Synthesis of 7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

2.2.2.1. Synthesis of 4-(4-tert-butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (5)

4-*tert*-Butylphenylboronic acid (0.182 g, 1.02 mmol, MW = 178.04 g/ mol), PEPPSI^{TM}-IPr catalyst ([1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride) (0.015 g, 0.02 mmol. MW = 679.46 g/mol), and potassium carbonate (K_2CO_3) (0.709 g, 5.14 mmol, MW = 138 g/mol) were added to a Schlenk flask. 4-Bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(1)** (0.300 g, 1.01 mmol, MW = 292.15 g/mol) was dissolved in 1, 4-dioxane (20 mL) and added to the solids followed by water (25 mL).

Then mixture refluxed under N_2 at 90 °C for 1 day. Extraction with hexane gave a greenish yellow product. A DCM/EtOAc (1:1) mixture was used for column chromatography to separate the yellow product **(5)**. **Yield:** 0.336 g, 95%, **MW** = 345.46 g/mol. **MP:** 150 °C. **IR** (ATR) (ν/cm^{-1}) = 3029, 2960, 2868, 1726, 1592, 1544, 1511, 1473, 1413, 1361, 1260, 1217, 1090, 1068, 1017, 991, 935, 893, 855, 833, 814, 794, 759, 728, 665, 636, 621, 591, 578, 546, 516, 483. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.32 (s, 1C), 153.65 (s, 1C), 152.09 (s, 2C), 150.34 (s, 1C), 144.81 (s, 1C), 135.27 (s, 1C), 134.23 (s, 1C), 129.92 (s, 1C), 129.06 (s, 1C), 129.00 (s, 1C), 127.65 (s, 2C), 125.88 (s, 2C), 123.65 (s, 2C), 34.91 (s, 1C), 31.45 (s, 3C).

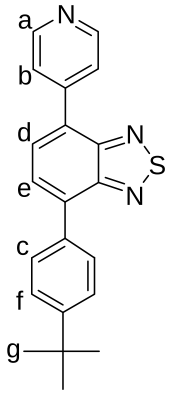


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Table 2. 6 - ^{1}H NMR (300 MHz, $CDCl_3$) data of 4-(4-*tert*-butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (5)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*s*	*8.78*	*2*	-
b, c, d	*m*	*8,01 - 7.86*	*5*	-
e	*d*	*7.82*	*1*	$^3J_{ed}$ = 7.4
f	*m*	*7.65 – 7.53*	*2*	-
g	*s*	*1.41*	*9*	-

2.2.2.2. Synthesis of 3-(4-tert-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (6)

4-(4-*tert*-Butylphenyl-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(5)** (0.350 g, 1.01 mmol, MW = 345.46 g/mol) was transferred to a round-bottom flask using EtOH (45 mL) and THF (15 mL). Cobalt(II) chloride hexahydrate (0.006 g, 0.02 mmol, MW = 236.9 g/mol) and sodium borohydride ($NaBH_4$) (0.058 g, 1.53 mmol, MW = 38 g/mol). The resulting mixture was refluxed (70 ^{o}C) and the progress of the reaction monitored by running a TLC using DCM/EtOAc (2:1).More sodium borohydride ($NaBH_4$) (0.058 g, 1.53 mmol, MW = 38 g/mol) was added every 1 h until the reaction was complete (6 h) and then cooled to RT. The product was extracted with Et_2O, filtered under N_2. Solvent was removed using a rotary evaporator. The off-white solid **(6)** was kept under N_2 to be taken to the next step. **Yield:** 0.250 g, 77%, **MW** = 317.19 g/mol. **MP:** 146 ^{o}C. **IR** (ATR) (ν/cm^{-1}) = 3417, 3362, 3287, 3213, 3069, 3027, 2960, 2860, 1627, 1592, 1550, 1517, 1497, 1478, 1439, 1401, 1362, 1314, 1259, 1217, 1089, 1066, 1014, 794, 763, 733, 691, 632, 620, 600, 591, 555, 525, 497, 437. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.56 (s, 1C), 150.39 (s, 1C), 150.26 (s, 1C), 148.15 (s, 1C), 136.39 (s, 1C), 132.62 (s, 1C), 132.36 (s, 1C), 129.79 (s, 1C), 129.15 (s, 1C), 128.87 (s, 1C), 127.68 (s, 1C), 126.01 (s, 1C), 125.12 (s, 1C), 124.20 (s, 1C), 123.72 (s, 1C), 121.46 (s, 1C), 120.52 (s, 1C), 34.79 (s, 1C), 31.48 (s, 3C).

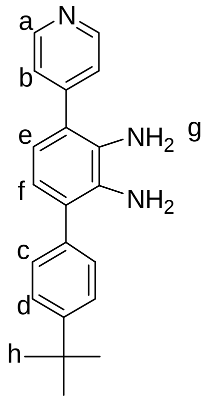

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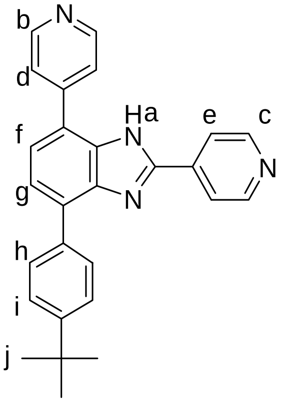
Table 2. 7 - ^{1}H NMR (300 MHz, CDCl$_3$) data of 3-(4-*tert*-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (6)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*dd*	*8.70*	*2*	$^3J_{ab} = 4.4$, $^5J_{ab} = 1.6$
b, c, d	*m*	*7.56 – 7.35*	*6*	-
e, f	*q*	*6.79*	*2*	$^3J_{ef} = {}^3J_{fe} = 7.9$
g	*s*	*3.65*	*4*	-
h	*s*	*1.38*	*9*	-

2.2.2.3. Synthesis of 7-(4-tert-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

4-Pyridinealdehyde (0.085 g, 0.79 mmol, MW = 107.11 g/mol) was weighed in a small vial, diluted with chloroform (10 mL) and added to the 3-(4-*tert*-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(6)** (0.250 g, 0.79 mmol MW = 317.19 g/mol) into a round bottom flask. Zirconium tetrachloride ($ZrCl_4$) (0.002 g, 0.008 mmol, MW = 233.6 g/mol) was added and the mixture was stirred overnight at RT. The solvent was removed using a rotary evaporator. The resultant solid was dissolved in THF and filtered. THF was evaporated from the filtrate. The resulting orange product **(L2)** was recrystallized twice using MeCN. **Yield:** 0.131 g, 41%, **MW** = 404.51 g/mol. **MP:** 236 ^oC. **IR** (ATR) (v/cm^{-1}) = 3030, 2960, 2918, 2850, 1599, 1534, 1525, 1476, 1437, 1364, 1327, 1289, 1259, 1091, 1066, 1017, 1001, 811, 741, 729, 706, 686, 666, 652, 627, 608, 584, 550, 526, 509, 458.

EA (CHN) (%): calculated: C = 80.17; H = 5.98; N = 13.85; found: C = 75.85; H = 6.05; N = 12.99.



L2

Table 2. 8 - ^{1}H NMR (300 MHz, $CDCl_3$) data of 7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*s*	*9.77*	*1*	-
b, c	*dd*	*8.78*	*4*	$^3J_{bd} = 6.3$, $^3J_{ca} = 6.1$
d	*d*	*8.15*	*2*	$^3J_{db} = 6.3$
e	*d*	*7.96*	*2*	$^3J_{ec} = 6.1$
f, g, h	*m*	*7.67 – 7.61*	*4*	-
i	*d*	*7.47*	*2*	$^3J_{ih} = 7.7$
j	*s*	*1.49*	*9*	-

2.3. Synthesis of [Pt(dppp)][OTf]$_2$

Potassium tetrachloroplatinate(II) (**$K_2[PtCl_4]$**) (0.300 g, 0.723 mmol, MW = 415.09 g/mol) was dissolved in water (2.5 ml) in a small vial. Propionitrile (C_2H_5CN) (0.3 ml, 0.040 g, 0.726 mmol, ρ = 0.772 g/ml, MW = 55.08 g/mol) was added to the solution. The mixture was left to stand for 3 days at RT. The resulting lemon-yellow rod-like crystals were filtered off, washed with water and dried at 70 ^{0}C (**MW** = 376.15 g/mol, **yield:** 234 mg, 86%).

The product **[PtCl$_2$(C$_2$H$_5$CN)$_2$]** (234g, 0.622 mmol, MW = 376.15 g/mol) was placed into a Schlenk flask, evacuated and backfilled with N$_2$ three times. DCM (5 mL) was added. In another Schlenk flask, 1,3bis(diphenylphosphino)propane (dppp) was weighed (256.5 mg, 0.642 mmol, MW = 412.44 g/mol) and dissolved by adding (5 mL) of DCM. **[PtCl$_2$(C$_2$H$_5$CN)$_2$]** solution was transferred to the flask with dppp solution by syringe. The mixture was stirred overnight (RT) under N$_2$. The reaction mixture was filtered and washed with Et$_2$O to produce the clean product **([PtCl$_2$(dppp)]**) (**MW** = 678.43 g/mol, **yield:** 363 mg, 88%)

[PtCl$_2$(dppp)] (0.363 g, 0.535 mmol, MW = 678.43) was weighed into a Schlenk flask and then evacuated and backfilled with N$_2$ three times. DCM (50mL) was added followed by Ag**OTf** (1.123 g, 4.37 mmol, MW = 256.94 g/mol). The mixture was stirred in the dark overnight (24 h). The volume of the solution was reduced to 5 mL and filtered quickly under N$_2$ to isolate the desired precipitate **[Pt(dppp)][OTf]$_2$** (**MW** = 905.66 g/mol, **yield:** 230 mg, 47%).

2.4. EXPERIMENTAL: COORDINATION

2.4.1. Synthesis of [Pt(dppp)(L1)]$_4$[OTf]$_8$

7-(4-Fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole **(L1)** (0.050 g, 0.136 mmol, MW = 366.39 g/mol) and **[Pt(dppp)][OTf]$_2$** (0.147 g, 0.162 mmol, MW = 905.66 g/mol) were dissolved in MeOH/MeNO$_2$ mixture (1:1, 30 mL). The mixture was stirred overnight at 70 ^{0}C, cooled to RT and filtered. The volume was then reduced to about 10 ml and diisopropyl ether added until a yellow precipitate formed. The resulting solid was collected using vacuum filtration and dissolved in diisopropyl/DCM mixture (1:1). Slow evaporation of the solution resulted in colorless crystals. The whole experiment was repeated scaling down the ligand **(L1)** mass to 0.010 g and reducing the stirring time to 2 h and the same result was attained. **MW** = 5088.25 g/mol. **MP:** 247 ^{0}C. **IR** (ATR) (ν/cm^{-1}) = 3479, 3056, 2969, 2926, 1615, 1486, 1436, 1379, 1244, 1222, 1155, 1101, 1065, 1027, 998, 975, 841, 813, 796, 744, 707, 692, 635, 572, 556, 514, 473, 436, 427. **^{31}P NMR** (202 MHz, CD$_2$Cl$_2$) δ -13.24 (d, *J* = 30.8 Hz), -15.70 (d, *J* = 30.8 Hz). **EA (CHN) (%)**: calculated: C = 49.10; H = 3.25; N = 4.40; found: C = 47.42; H = 3.89; N = 3.90.

2.4.2. Synthesis of [Pt(dppp)(L2)]$_4$[OTf]$_8$

7-(4-*tert*-Butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole **(L2)** (0.020 g, 0.049 mmol, MW = 404.51 g/mol) and **[Pt(dppp)][OTf]$_2$** (0.045 g, 0.049 mmol, MW = 905.66 g/mol) were dissolved in MeOH/MeNO2 mixture (1:1, 15 mL). The mixture was stirred for 2 h at 70 ^{0}C, cooled to RT and filtered. The solvent was evaporated slowly at RT. The resulting yellow solid was dissolved in DCM. Slow evaporation of DCM resulted in colorless crystals. **MW** = 5240.25 g/mol. **MP:** 217 ^{0}C.

2.5. RESULTS AND DISCUSSION

2.5.1. Synthesis of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1)

2.5.1.1. Synthesis of 4,7-dibromobenzo[C][1,2,5]thiadiazole:

2,1,3-Benzothiadiazole (Figure 2.4) has attracted considerable attention in materials chemistry because its π-extended derivatives have shown potential as constituents for organic light-emitting diodes (OLEDs), liquid crystals, solar cells, photovoltaic cells and dyes.[39] Therefore, this functional group compound was chosen based on its interesting properties in the design and synthesis of our right-angled targeted ligands.

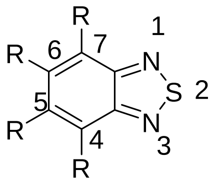
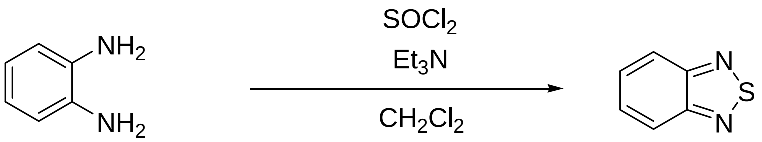


Figure 2. 4 - Unit of 2,1,3-benzothiadiazole

2,1,3-Benzothiadiazole can easily be synthesized by treating the commercially available *ortho*-phenylenediamine with thionyl chloride in a presence of a base (Scheme 2.1).[40, 41, 39]. However, it is also commercially available and the chemistry described in this thesis employed 2,1,3-benzothiadiazole (Aldrich) whose purity was checked by ^{1}H NMR prior to use.



Scheme 2. 1 - Synthesis of 2,1,3-benzothiadiazole

The dibromo derivative 4,7-dibromo-2,1,3-benzothiadiazole was synthesized according to the literature method (Scheme 2.2).[42] The reaction afforded high yields and was performed on a multi-gram scale. The yield was sensitive to the rate of bromine addition; when the bromine solution was added very slowly then the target dibromo derivative was generated in good yield. However, fast addition yielded the tetrabrominated derivative 4,5,6,7-tetrabromo-2,1,3-benzothiadiazole (Figure 2.5).[39]

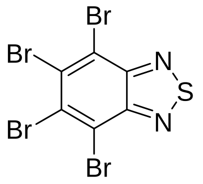


Figure 2. 5 - Tertabrominated 2,1,3-benzothiadiazole

Unreacted bromine was treated with sodium bisulphite and the product was washed with water and diethyl ether. The ^{1}H NMR spectrum (Figure 2.6) revealed the compound to be pure and the recovered yield (83%) was comparable with the literature value (88%).**[39]**

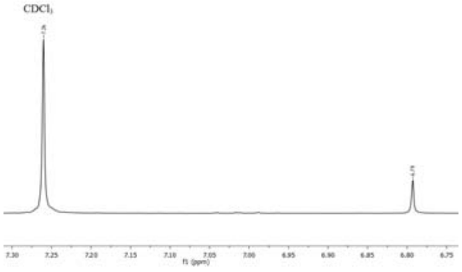
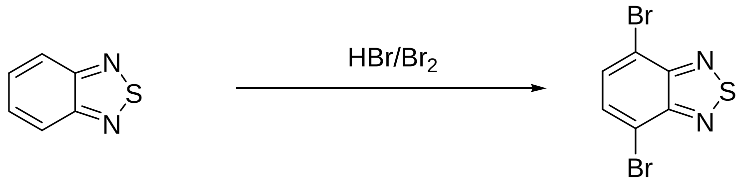
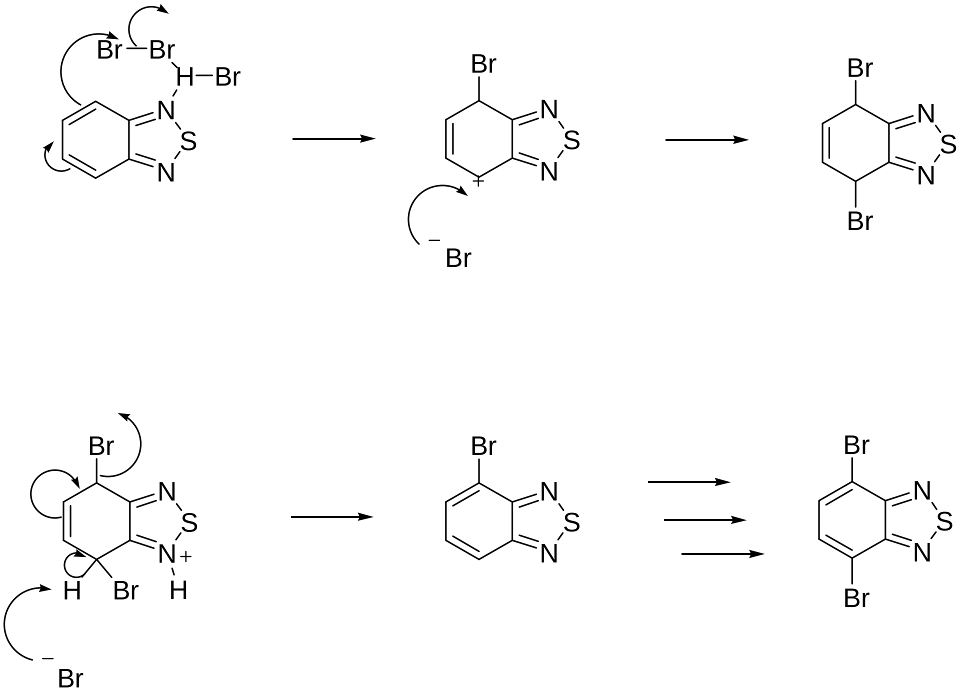


Figure 2. 6 - ^{1}H NMR spectrum of 4,7-dibromo-2,1,3-benzothiadiazole in CDCl$_3$



Scheme 2. 2 - Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole



Scheme 2. 3 - Plausible mechanism of the regioselective formation of 4,7-dibromo-2,1,3-benzothiadiazole[39]

2.5.1.2. Synthesis of 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (1)

Pyridyl derivatives of 2,1,3-benzothiadiazole can be readily prepared from dibromo-2,1,3-benzothiadiazole using a palladium-catalyzed cross-coupling reaction.[43] Bromide was preferred over other halides as a common and moderate leaving group.[44]

Synthesis of 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (1) was first attempted using tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ as a catalyst (Scheme 2.4 - top). The yield was very low (13%) probably because of coordination of the pyridyl fragments to palladium. When tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ was replaced by PEPPSI™-IPr catalyst (Scheme 2.4 - bottom), a better yield (35%) was attained.

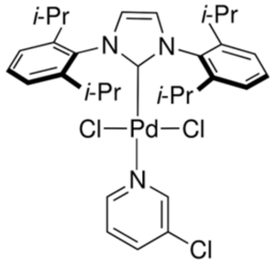
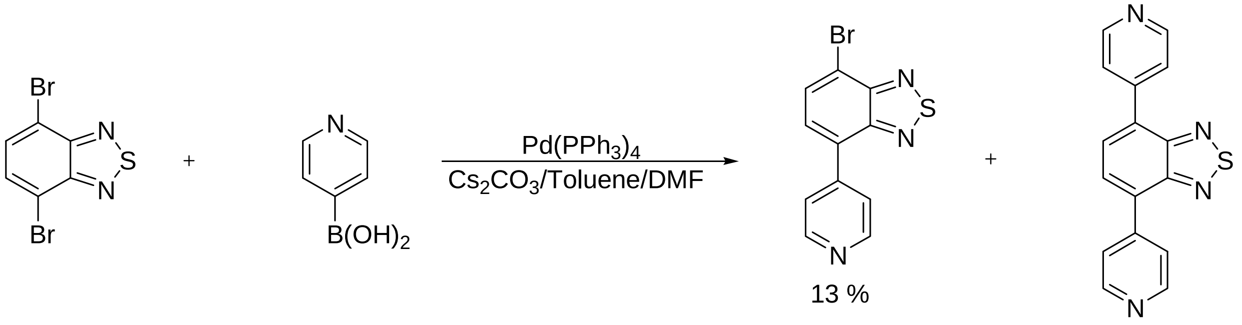
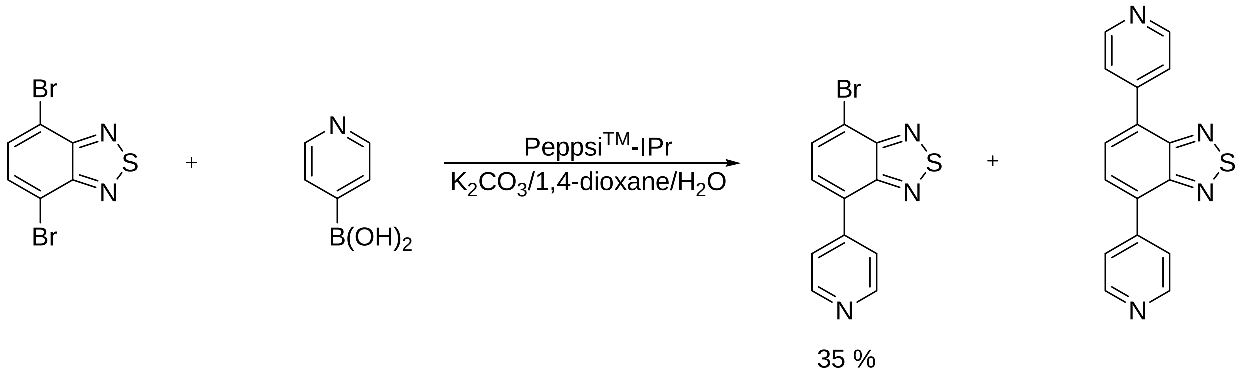


Figure 2. 7 - PEPPSI™-IPr catalyst

The new yield was also considered relatively low and was probably due to cross-coupling taking place at both the 4- and 7- positions of 4,7-dibromo-2,1,3-benzothiadiazole leading to considerable amounts of the di-substituted product 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(2)** which was characterized by ^{1}H NMR spectroscopy. The desired product **(1)** was obtained by column chromatography using DCM/EtOAc (2:1). Table (2.1) shows the major peaks of the ^{1}H NMR spectrum of the compound in $CDCl_3$. ^{13}C NMR chemical shifts of the product are summarized in section (2.2.1.2.2).



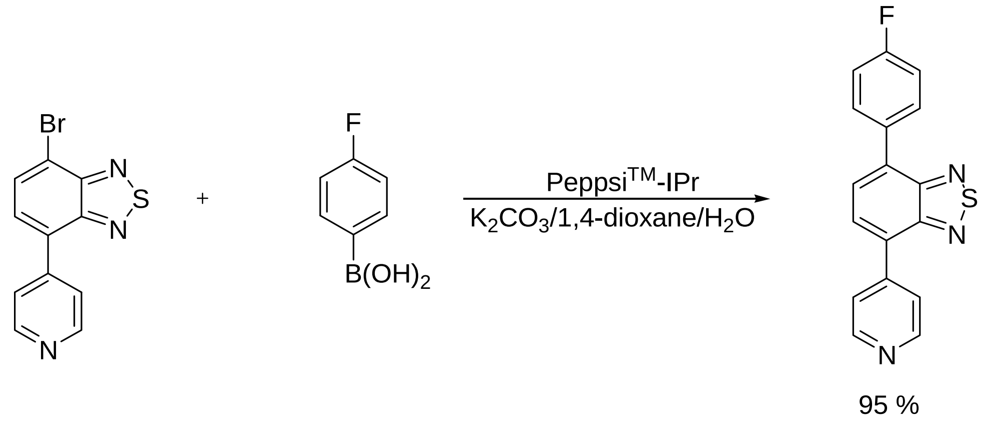
1 **2**



Scheme 2. 4 - Synthesis of 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (1)

2.5.1.3. Synthesis of 4-(4-fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (3)

4-(4-Fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(3)** was synthesized using a palladium-catalyzed cross-coupling (Scheme 2.5) from 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(1)** and 4-fluorophenylboronic acid. The product was purified by recrystallization from MeOH. The yield (95%) was much better; this time cross-coupling occurred at the 4-position- of the benzothiadiazole - only; since the 7-position is already occupied by the pyridyl group. Table (2.2) shows the major peaks of the ^{1}H NMR spectrum of the compound in $CDCl_3$. ^{13}C NMR data of the product are summarized in section (2.2.1.3). A comparison of ^{19}F NMR spectra of some fluorinated compounds including the ligand is given in (Figure 2.22).



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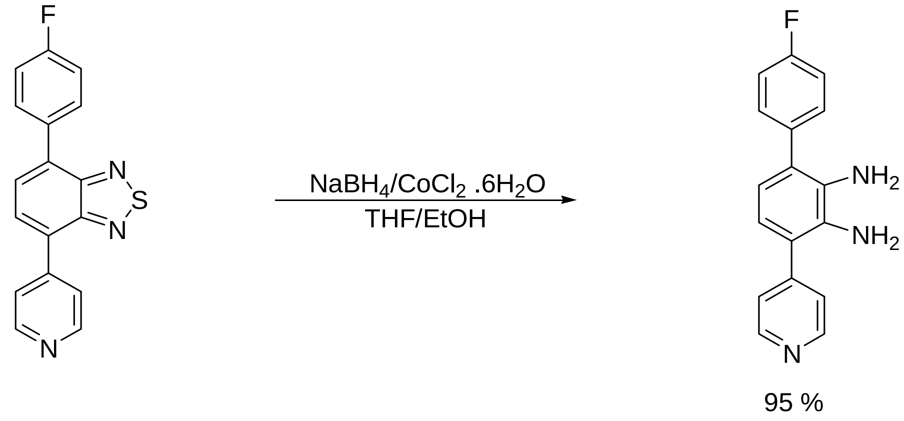
Scheme 2. 5 - Synthesis of 4-(4-fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (3)

2.5.1.4. Synthesis of 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (4)

An interesting property of benzothiadiazoles and their derivatives is the reductive sulfur extrusion reaction they undergo to yield the corresponding diamine. 3-(4-Fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** was synthesized by the reduction of 4-(4-fluorophenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(3)** using a slightly modified literature method (Scheme 2.6).[45] Cobalt(II) chloride hexahydrate $CoCl_2.6H_2O$ was used as a catalyst, sodium borohydride $NaBH_4$ as a reducing agent and a THF/EtOH (1:3) mixture as the solvent. The yield (95%) was high compared with the literature values (71 – 97%; depending on the nature of the R-groups at the 4- and 7-positions of the benzothiadiazole).[45] 3-(4-Fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic methods. The characteristic diamine peak (3350 – 3310 cm^{-1}) was clearly observed at 3311 cm^{-1} in the IR spectrum.

Some of the characterization data for the compound is given in section (2.2.1.4). Table (2.3) lists the major peaks of the ^{1}H NMR spectrum of the compound in $CDCl_3$.



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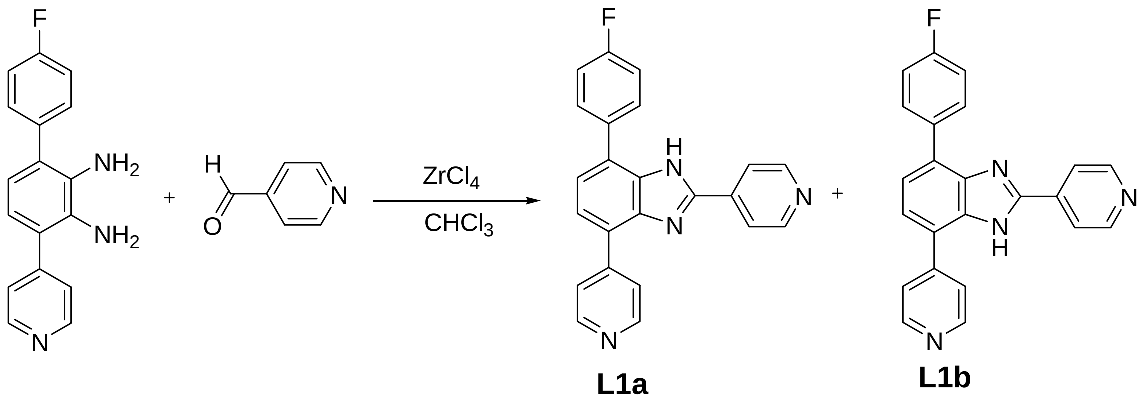
Scheme 2. 6 - Synthesis of 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (4)

2.5.1.5. Synthesis of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1)

Benzimidazoles can easily be synthesized via the cyclization condensation reaction of *o*-phenylenediamines with aldehydes which is catalyzed by Lewis acids.[46, 47] 7-(4-Fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole **(L1)** was synthesized using the condensation reaction of 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** and 4-pyridinecarboxaldehyde (Scheme 2.7). The reaction was catalyzed by zirconium tetrachloride.[47] The pure targeted ligand **(L1)** was obtained after a multiple recrystallizations from MeOH. The yield (48%) was likely only moderate because the reaction took place at ambient temperature and the relative instability of the diamine. The product was characterized using ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectroscopic methods. ^{1}H NMR (Figure 2.8) and ^{19}F NMR (Figure 2.9) spectra revealed the presence of two isomers **(L1a)** and **(L1b)** of the ligand. Tables (2.4) and (2.5) list the major peaks of the ^{1}H NMR spectra of the isomers in CD_2Cl_2.



Scheme 2. 7 - Synthesis of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1)

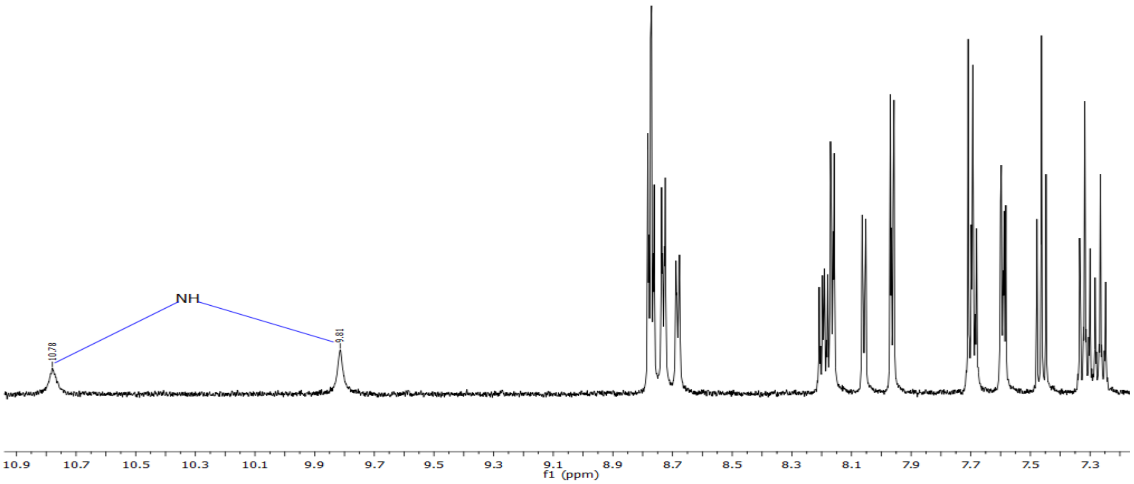


Figure 2. 8 - ^{1}H NMR spectrum of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1) in CD_2Cl_2 showing two isomers

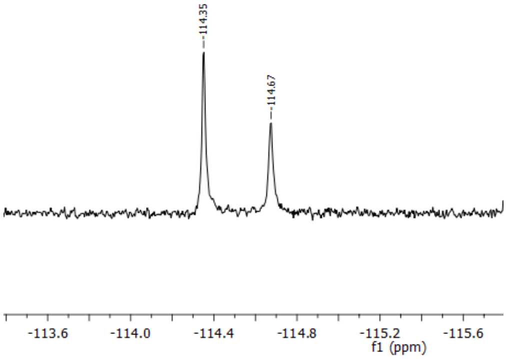


Figure 2. 9 - ^{19}F NMR spectrum of 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L1) showing two isomers

Slow evaporation of a solution of the isomers in $CDCl_3$ resulted in the formation of light brown crystals. A single crystal XRD study was performed and the structure obtained was found to be the **(L1a)** isomer. Some pictures of the crystal structure obtained are given in Figures (2.10) and (2.11) below. Table (2.9) contains the experimental crystal data. Geometric parameters are given in Appendix F.

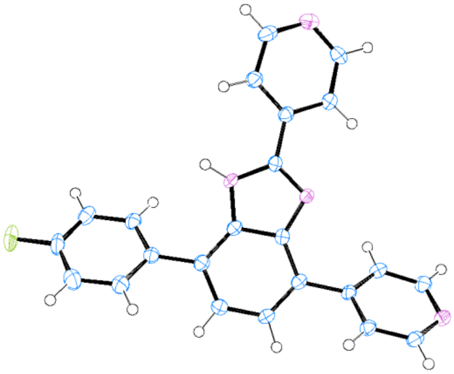


Figure 2. 10 - Crystal structure of (L1a) with 50% ellipsoid probability (one $CHCl_3$ molecule has been omitted for clarity)

Table 2. 9 - Single crystal data of (L1a)

CRYSTAL DATA	
Chemical formula	$C_{24}H_{17}Cl_3FN_4$
M_r	486.76
Crystal system, space group	Triclinic, P-1
Temperature (K)	173(2)
a, b, c (Å)	9.0898 (3), 10.2902 (3), 13.0414 (4)
α, β, γ (°)	80.2999 (11), 89.0859 (11), 64.1607 (10)
V (Å^3)	1079.91 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	4.09
Crystal size (mm)	0.28 x 0.30 x 0.34
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	empirical (SADABS)
Min. and max. transmission	0.5627, 0.6803
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12418, 3139, 2919
R_{int}	0.043
θ_{max} (°)	60.0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.562
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.148, 0.70
No. of reflections	3139
No. of parameters	289
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.66, -0.56

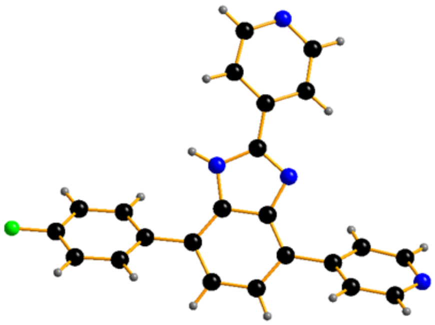


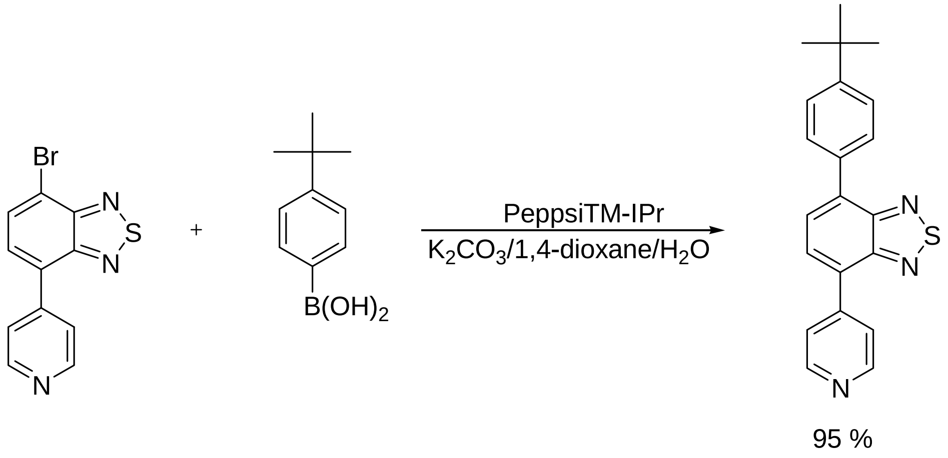
Figure 2. 11 - Ball and stick representation of (L1a) crystal (black = C, blue = N, green = F and grey = H)

The dihedral angle between the planes of the pyridyl ring at the 2-position and the benzimidazole core is approximately 15⁰. The dihedral angle between the planes of the pyridyl ring at the 4-position and the benzimidazole core is approximately 50⁰. The dihedral angle between the planes of the substituted phenyl ring at the 7-position and the benzimidazole core is about 45⁰.

2.5.2 Synthesis of 7-(4- *tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

2.5.2.1. Synthesis of 4-(4- tert-butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (5)

4-(4-*tert*-Butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(5)** was synthesized using a palladium-catalyzed cross-coupling between 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(1)** and 4- *tert*-butyphenylboronic acid (Scheme 2.8). The pure desired compound was obtained by column chromatography using DCM/EtOAc (1:1) mixture. The yield (95%) was high and comparable to that attained at the same stage for the synthesis of **L1**. Table (2.6) shows the major peaks of the ^{1}H NMR spectrum of the compound in $CDCl_3$. ^{13}C NMR data of the product are summarized in section (2.2.2.1).



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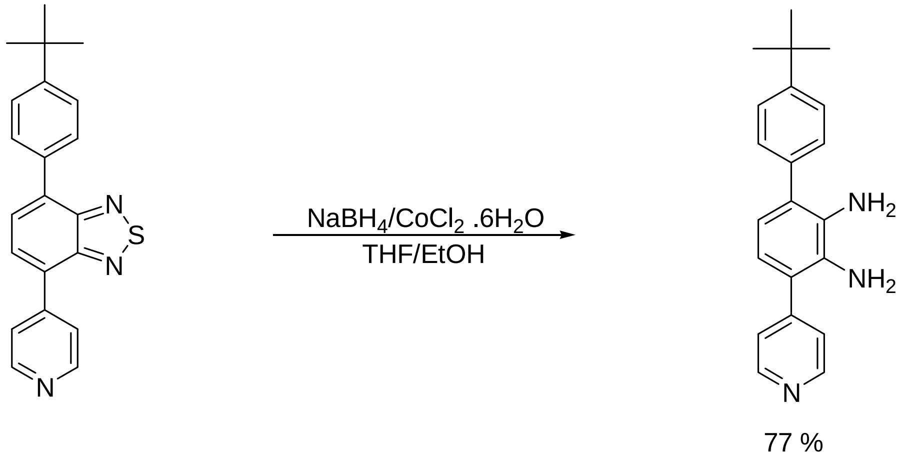
Scheme 2. 8 - Synthesis of 4-(4- *tert*-butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (5)

2.5.2.2. Synthesis of 3-(4-tert-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (6)

3-(4-*tert*-Butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(6)** was synthesized by the reduction of 4-(4-*tert*-butylphenyl)-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(5)** using slightly modified literature method (Scheme 2.9).[45] Cobalt(II) chloride hexahydrate $CoCl_2.6H_2O$ was used as a catalyst, sodium borohydride $NaBH_4$ as a reducing agent and THF/EtOH (1:3) mixture as a solvent. The yield (77%) was lower than that obtained in the synthesis of the 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** (95%) but still in the literature range (71 – 97%; depending on the nature of the **R** groups at the 4 and 7-positions of the benzothiadiazole).[45] 3-(4-*tert*-Butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(6)** was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods. Some of the characterization data for the compound is given in section (2.2.2.2). Table (2.6) shows the major peaks of the ^{1}H NMR spectrum of the compound in $CDCl_3$.



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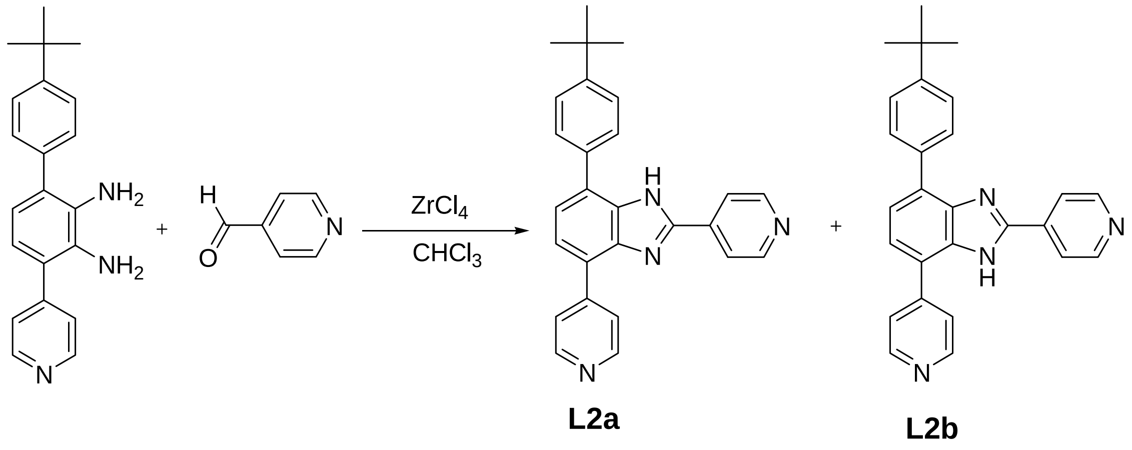
Scheme 2. 9 - Synthesis of 3-(4-*tert*-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine (6)

2.5.2.3. Synthesis of 7-(4-tert-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

Ligand 7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole **(L2)** was synthesized using the condensation reaction between 3-(4-*tert*-butylphenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(6)** and 4-pyridinecarboxaldehyde. The reaction was catalyzed by zirconium tetrachloride.[47] The pure targeted ligand **(L2)** was obtained after a multiple recrystallizations from MeCN. The yield (41%) was comparable to that obtained for the 7-(4-fluorophenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole **(L1)** (48%). Again, the high instability of the diamine and the reaction taking place at RT were probable causes for the low yield. The product was characterized using ^{1}H NMR. Table (2.7) shows the major peaks of the ^1H NMR spectrum of the compound in $CDCl_3$. ^1H NMR spectrum revealed the presence of two isomers **(L2a)** and **(L2b)** of the ligand (Figure 2.12).



Scheme 2. 10 - Synthesis of 7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2)

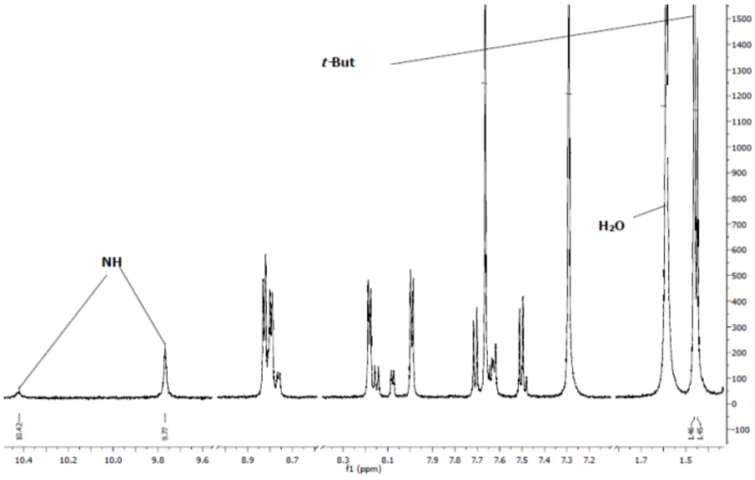


Figure 2. 12 ^1H NMR spectrum of 7-(4-*tert*-butylphenyl)-2,4-di(pyridin-4-yl)-1H-benzimidazole (L2) in $CDCl_3$ showing two isomers

Slow evaporation of a solution of the isomers **(L2a)** and **(L2b)** in a mixture of MeOH and H_2O resulted in the formation of colorless crystals. A single crystal XRD study was performed and the structure obtained was found to be of the **(L2b)** isomer. Some pictures of the crystal structure obtained are given in Figures (2.13) and (2.14) below. Table (2.10) contains the experimental crystal data. Geometric parameters are given in Appendix G.

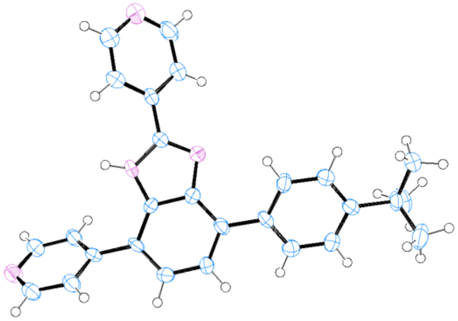


Figure 2. 13 - Crystal structure of (L2b) with 50% ellipsoid probability

Table 2. 10 - Single crystal data of (L2b)

CRYSTAL DATA	
Chemical formula	$C_{27}H_{24}N_4$
M_r	404.50
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	9.1214 (4), 10.5909 (5), 12.0303 (6)
α, β, γ (°)	66.639 (3), 84.961 (3), 81.520 (3)
V (Å^3)	1054.69 (9)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.59
Crystal size (mm)	0.24 x 0.30 x 0.40
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	empirical (SADABS)
Min. and max. transmission	0.6233, 0.7479
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6983, 1296, 1176
R_{int}	0.030
θ_{max} (°)	40.2
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.419
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.107, 1.03
No. of reflections	1296
No. of parameters	307
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.17, -0.15

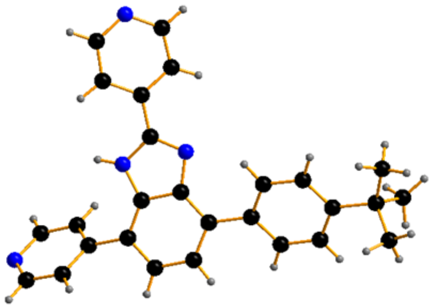


Figure 2. 14 - Ball and stick representation of (L2b) crystal (black = C, blue = N, grey = H)

The dihedral angle between the planes of the pyridyl ring at the 2-position and the benzimidazole core is approximately 27^{o}. The dihedral angle between the planes of the pyridyl ring at the 4-position and the benzimidazole core is approximately 49^{o}. The dihedral angle between the planes of the substituted phenyl ring at the 7-position and the benzimidazole core is about 25^{o}.

Comparing **L1** and **L2** crystal structures, **d**ifferences in dihedral angle values are attributed to the different **R** groups (F for **L1** and ***t*Bu** - which has more steric demand - for **L2**). Bond distances for the two ligands are almost the same and all fall in the typical range. In solid state, both **L1** and **L2** showed H-bonding between the **NH** of one molecule and the pyridine groups in another Figure (2.15).

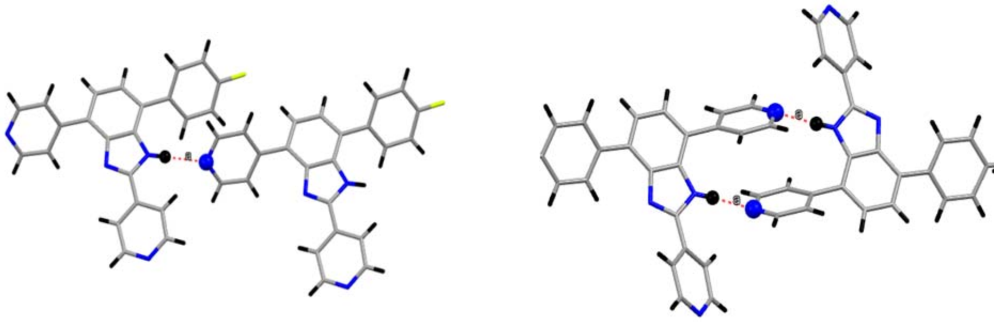
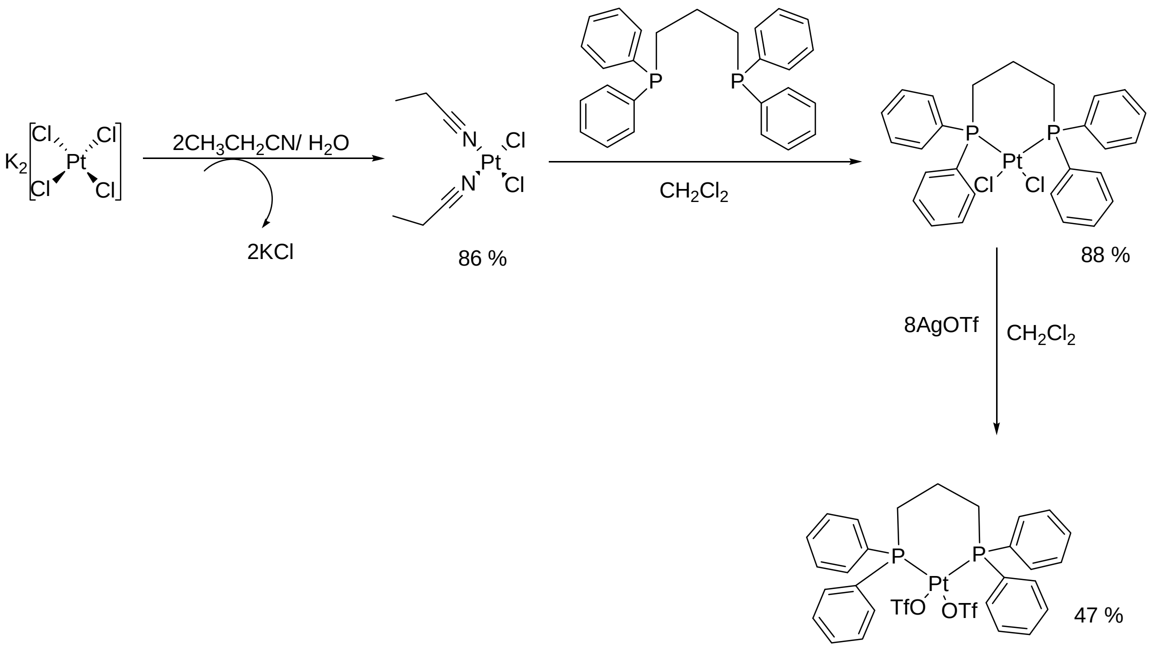


Figure 2. 15 – H-bonding between two molecules: L1 (left) and L2 (right), (*t*Bu groups have been omitted for clarity)

2.5.3. Synthesis of [Pt(dppp)][OTf]$_2$

[Pt(dppp)][OTf]$_2$ was synthesized using literature modified methods (Scheme 2.11).[48] Starting from potassium tetrachloroplatinate(II) (**K_2[PtCl$_4$]**) a series of ligand substitution reactions were performed ending up at the desired *cis*-protected **[Pt(dppp)][OTf]$_2$** metal corner. The final product was characterized using ^{1}H (Figure 2.16) and ^{31}P NMR spectroscopy as well as ^{19}F NMR (Figure 2.22) spectroscopic methods. In addition to being rich in fluorine, which allowed use of ^{19}F NMR spectroscopy, **OTf** was chosen because of being a good leaving group. All reactions were carried out smoothly at ambient temperature.



Scheme 2. 11 - Synthesis of [Pt(dppp)][OTf]$_2$

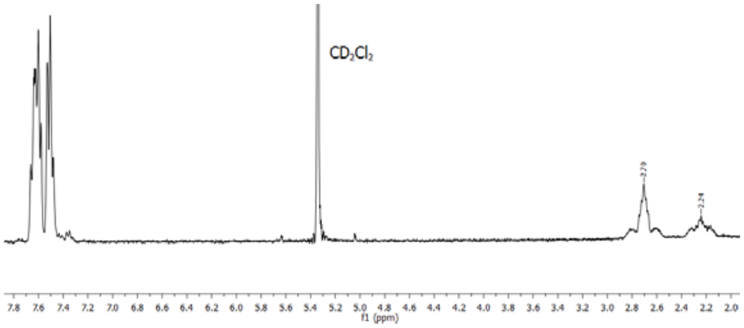


Figure 2. 16 - ^{1}H NMR spectrum of [Pt(dppp][OTf]$_2$

2.5.4 Synthesis of [Pt(dppp)(L1)]$_4$[OTf]$_8$

[Pt(dppp)(L1)]$_4$[OTf]$_8$ was synthesized by simply mixing **(L1)** and the *cis*-protected **[Pt(dppp)][OTf]$_2$** metal corner. Coordination took place at temperatures between 60 and 70 ^{o}C. No reaction was observed at RT. The resulting complex (Figure 2.28) was characterised using 1D ^{1}H NMR, 2D ^{1}H NMR, ^{19}F NMR and ^{31}P NMR spectroscopic methods. 1D ^{1}H NMR spectrum showed a 1:1 (metal:ligand) ratio (Figures 2.17). **Dppp** protons were shifted downfield confirming that coordination took place (Figures 2.18).

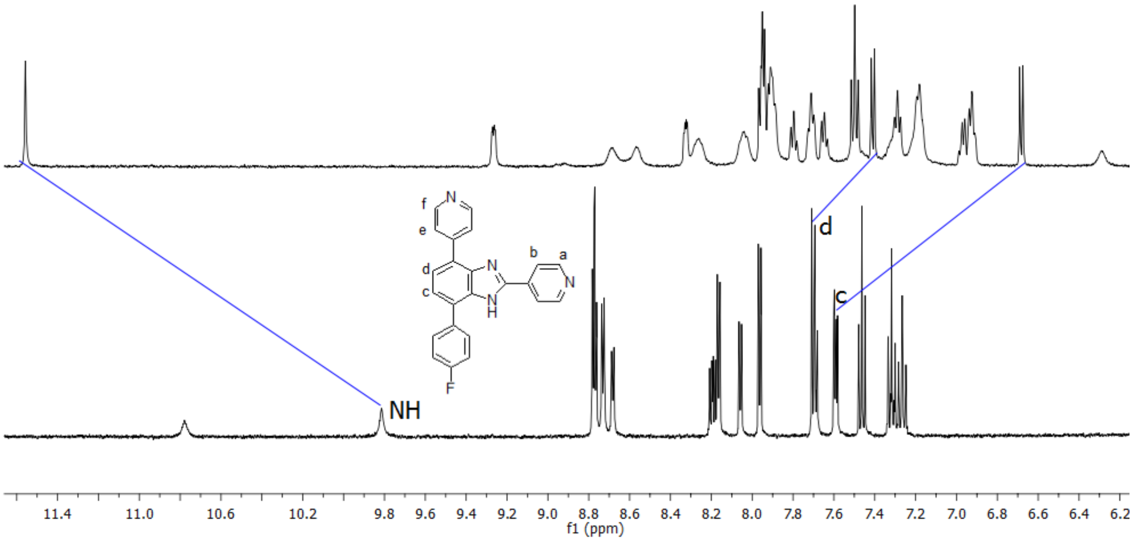


Figure 2. 17 - Partial ^{1}H NMR: L1 (Bottom) and [Pt(dppp)(L1)]$_4$(OTf)$_8$ (Top)

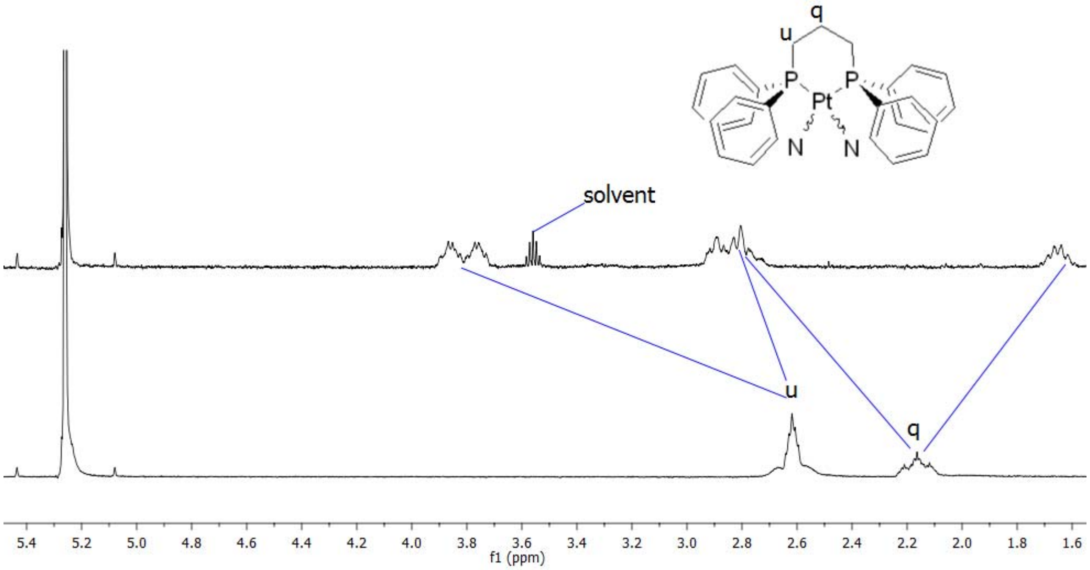


Figure 2. 18 - Partial ^{1}H NMR (CD_2Cl_2): [Pt(dppp)(L1)]$_4$(OTf)$_8$ (Top) and [Pt(dppp)][OTf]$_2$ (Bottom)

DOSY experiments showed that only one species was present in solution (Figures 2.19). ^{19}F NMR spectra showed only two sharp singlets - one of which was the characteristic peak for the **OTf** anions – indicating that the resulting complex had only one F-atom environment due to the ligand (Figure 2.20), whereas ^{31}P NMR spectra showed two separate resonances with a coupling constant indicative of two P-atom environments with a *cis*-geometry (Figures 2.21). This is consistent with the fact that **L1** has two different pyridine donors and suggested that **L1** units were coordinated to the **Pt(II)** ions in a head-to-tail arrangement.

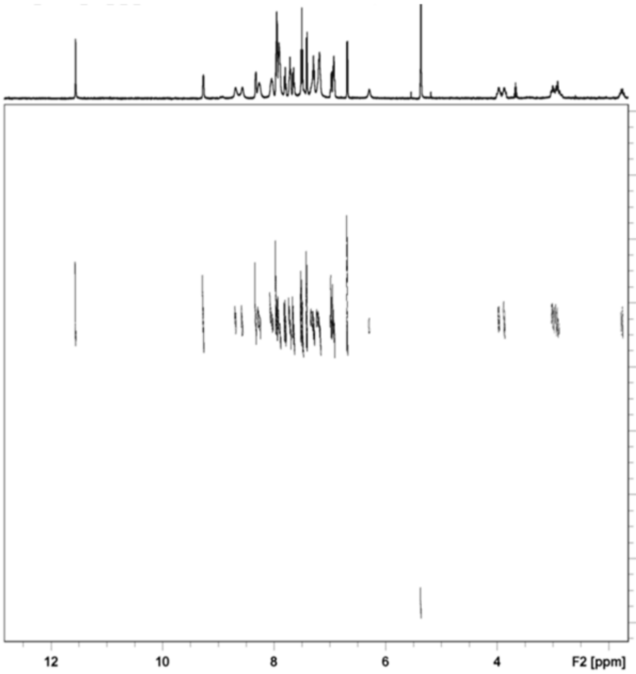


Figure 2. 19 - DOSY spectrum of $[Pt(dppp)(L1)]_4[OTf]_8$ in CD_2Cl_2

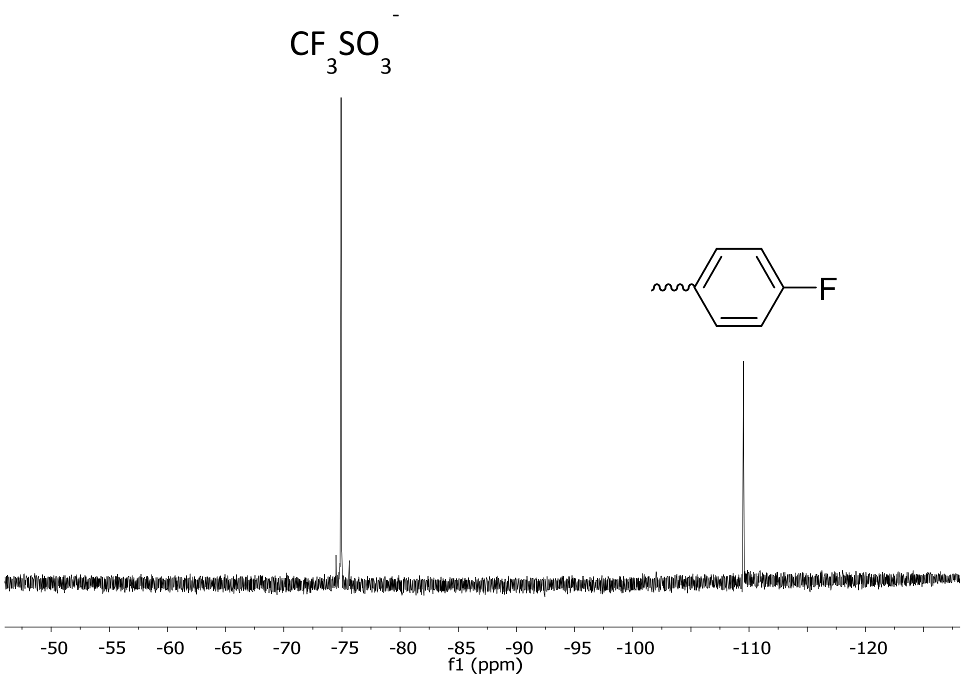


Figure 2. 20 - ^{19}F NMR spectrum of $[Pt(dppp)(L1)]_4[OTf]_8$ in CD_2Cl_2

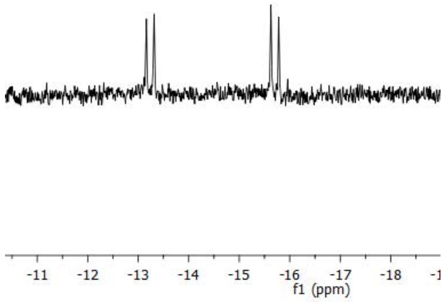


Figure 2. 21 - ^{31}P NMR spectrum of $[Pt(dppp)(L1)]_4[OTf]_8$ in CD_2Cl_2

Monitored by ^{19}F NMR spectroscopy, fluorine atoms were found to be shielded increasingly starting from 4-fluorophenylboronic acid and reaching maximum shield for **L1** fluorine atoms. In **[Pt(dppp)(L1)]$_4$[OTf]$_8$**, the fluorine atoms were slightly deshielded presumably due to the high positive charge exerted by the **Pt(II)** ions. Figure (2.22) show the ^{19}F NMR spectra for all fluorinated compounds except 3-(4-fluorophenyl)-6-(pyridin-4-yl)benzene-1,2-diamine **(4)** which is relatively unstable.

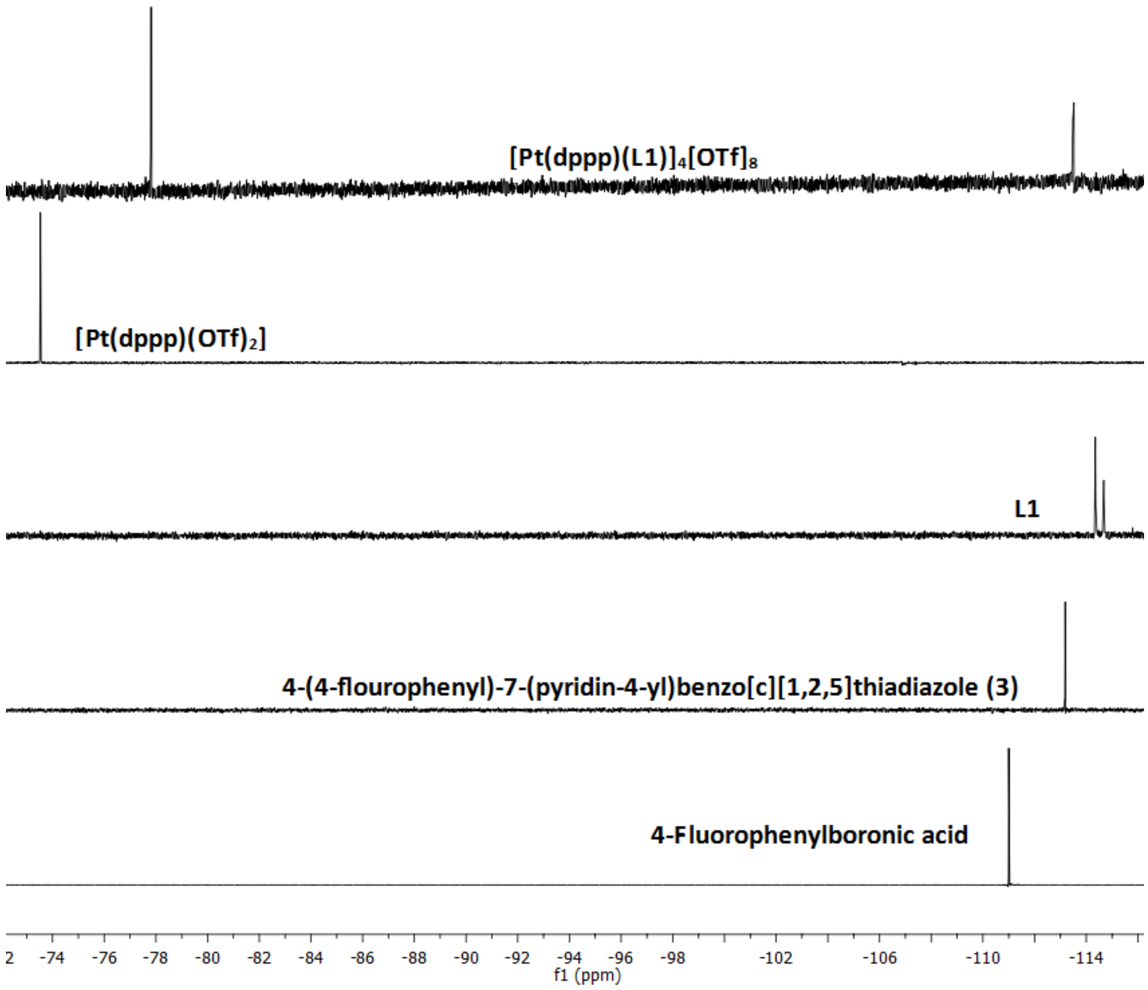


Figure 2. 22 - ^{19}F NMR spectra of fluorinated compounds in DMSO

A single crystal X-ray diffraction experiment was also performed to identify the structure of the complex in the solid state. Figures (2.23) and (2.24) show pictures of the crystal structure of **$[Pt(dppp)(L1)]_4^{8+}$**. Single crystal experimental data are given in table (2.11). Geometric parameters are given in Appendix H.

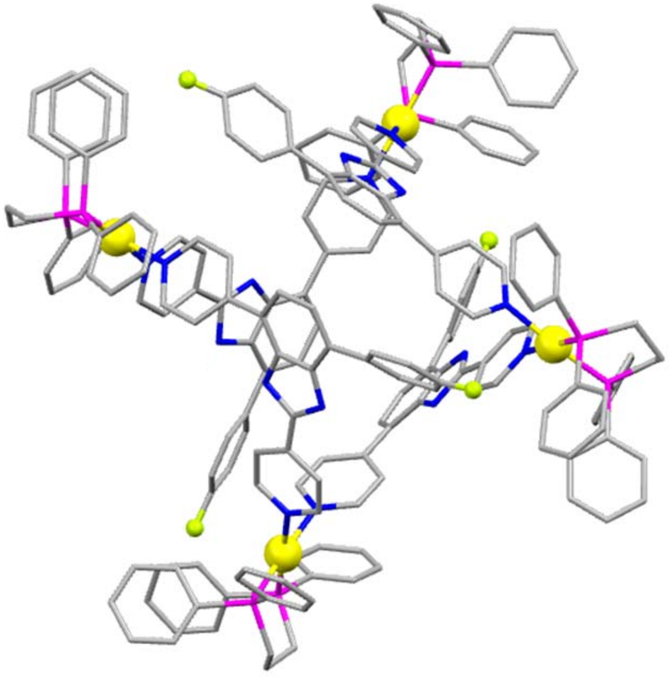


Figure 2. 23 – Capped sticks representation of $[Pt(dppp)(L1)]_4^{8+}$
(Pt and F shown as yellow and lemon green balls respectively; grey = C, blue = N and magenta = P; H atoms have been omitted for clarity)

Pt-Pt average distance is 12.80 Å. **Pt-P** and **Pt-N** average bond distances are 2.25 Å and 2.10 Å respectively. Average bond angles around the **Pt(II)** ions are as follows: **N-Pt-N** = 86°, **P-Pt-P** = 91° and **P-Pt-N** = 92°. Inner void = **350 $Å^3$.**

Table 2. 11 - Single crystal data of $[Pt(dppp)(L1)]_4[OTf]_8$

CRYSTAL DATA	
Chemical formula	$C_{238}H_{240}Cl_{76}F_{28}N_{16}O_{24}P_8Pt_4S_8$
M_r	8219.24
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	23.492 (8), 23.764 (8), 27.348 (10)
α, β, γ (°)	80.079 (4), 79.153 (4), 88.711 (4)
V (Å^3)	14769 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.76
Crystal size (mm)	0.18 x 0.22 x 0.34
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	Empirical (SADABS)
Min. and max. transmission	0.4814, 0.6456
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	106206, 36047, 20300
R_{int}	0.150
θ_{max} (°)	22.0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.526
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.165, 0.412, 1.06
No. of reflections	36047
No. of parameters	1282
No. of restraints	1940
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0971P)^2 + 1127.4922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	3.04, -3.69

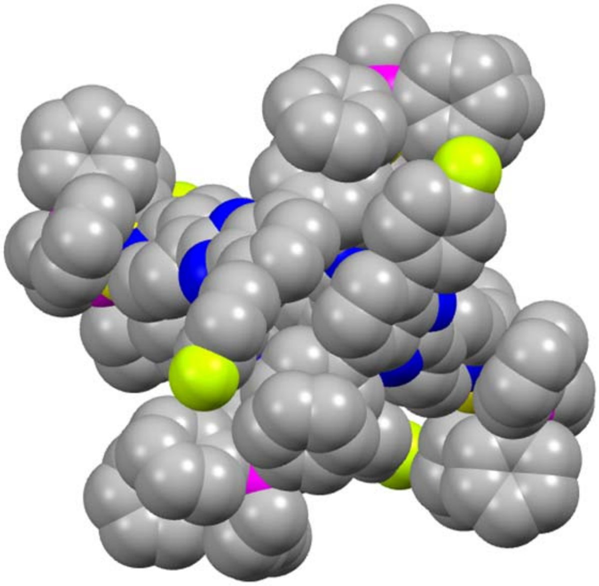


Figure 2. 24 – Single crystal structure (space filling) of $[Pt(dppp)(L1)]_4^{8+}$ (yellow = Pt and lemon green = F; grey = C, blue = N and magenta = P; H atoms have been omitted for clarity)

2.5.5 Synthesis of $[Pt(dppp)(L2)]_4[OTf]_8$

$[Pt(dppp)(L2)]_4[OTf]_8$ was synthesized by stirring a mixture of **(L2)** and the *cis*-protected **$[Pt(dppp)][OTf]_2$** metal corner for 2 h at 70 °C. Attempts at characterization by NMR spectroscopy were unsuccessful as spectra were very broad. However, a single crystal X-ray diffraction experiment was performed and the structure obtained revealed the formation of a tetramer similar to the one shown above for **(L1)**. Some pictures of the tetramer are given in Figures (2.25) and (2.26). Single crystal experimental data are given in table (2.12). Geometric parameters are given in Appendix I.

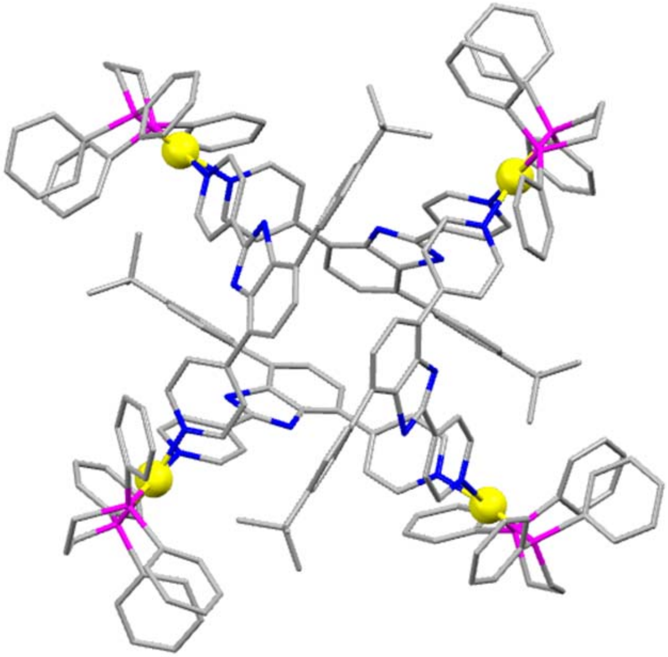


Figure 2. 25 – Capped sticks representation of [Pt(dppp)(L2)]$_4^{8+}$

(Pt shown as yellow balls; grey = C, blue = N and magenta = P; H atoms have been omitted for clarity)

Pt-Pt average distance is 12.99 Å. **Pt-P** and **Pt-N** average bond distances are 2.35 Å and 2.17 Å respectively. Average bond angles around the **Pt(II)** ions are as follows: **N-Pt-N** = 87^{o}, **P-Pt-P** = 87^{o} and **P-Pt-N** = 93^{o}. Inner void = **350 Å^{3}.**

Table 2. 12 - Single crystal data of $[Pt(dppp)(L2)]_4[OTf]_8$

CRYSTAL DATA	
Chemical formula	$C_{251}H_{254}Cl_{54}F_{24}N_{16}O_{24}P_8Pt_4S_8$
M_r	7533.59
Crystal system, space group	Tetragonal, $I\bar{4}$
Temperature (K)	173
a, c (Å)	23.007 (8), 54.844 (19)
V (Å^3)	29030 (22)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.60
Crystal size (mm)	0.28 x 0.30 x 0.32
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	empirical (SADABS)
Min. and max. transmission	0.3749, 0.7449
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	82520, 17731, 8630
R_{int}	0.282
θ_{max} (°)	22.0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.526
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.188, 0.460, 1.06
No. of reflections	17731
No. of parameters	649
No. of restraints	1227
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 5930.9692P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.98, -1.76

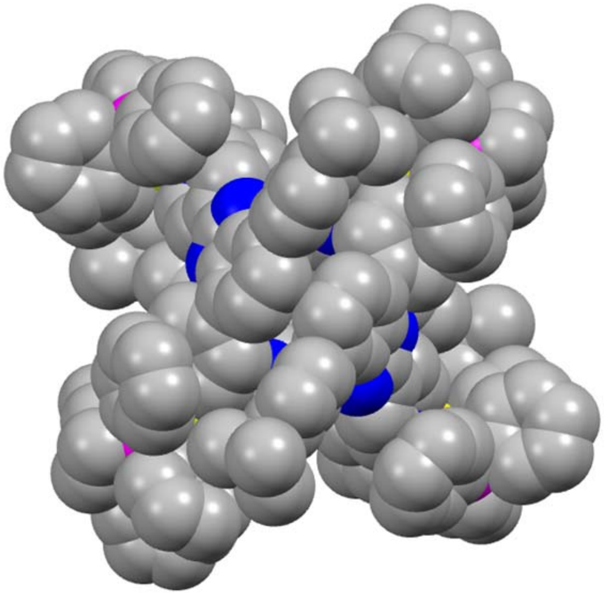


Figure 2. 26 – Single crystal structure (space filling) of $[Pt(dppp)(L2)]_4^{8+}$ (yellow = Pt, grey = C, blue = N and magenta = P; H atoms have been omitted for clarity)

In the solid state the cage openings are blocked by **OTf** anions positioned above and below the **Pt(II)** square plane presumably to maximize the electrostatic interactions with the **Pt(II)** ions (Figure 2.27).

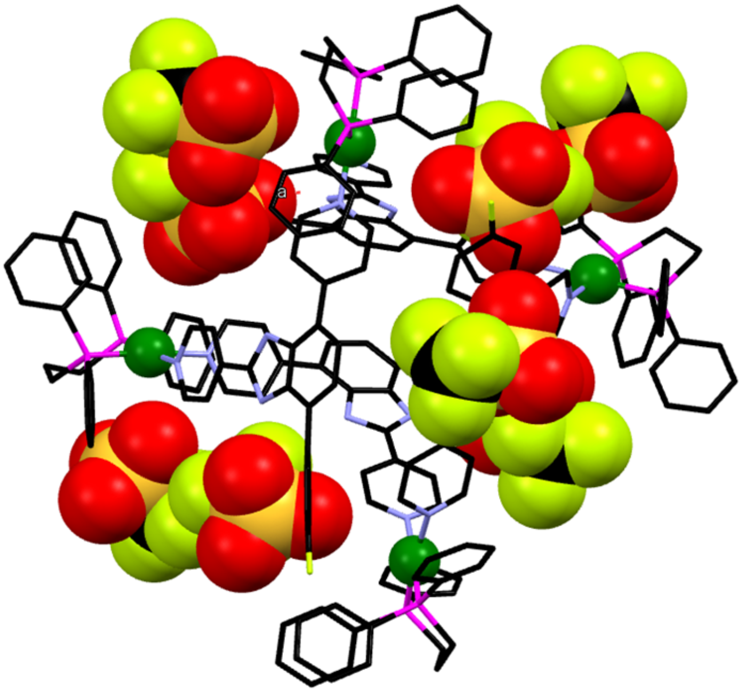


Figure 2. 27 – OTf anions (space-filling) blocking cage (M_4L_4) openings

The **OTf** anions are also interacting with the NH groups via hydrogen bonding which is also playing a role in determining their orientation.

2.6 CONCLUSIONS

Two T-shaped ligands (**L1** and **L2**) were synthesized. The ligands are built on a benzimidazole scaffold with two pyridyl donor groups at 90^{0} rigid angles. The two ligands were characterized using various NMR methods and single crystal X-ray crystallography to confirm structures. **L1** and **L2** showed many similarities in all preparation steps as well as when combined with **[Pd(dppp)]$^{2+}$** *cis*-protected metal corner. NMR spectra showed that both ligands have two isomeric structures (**L1a** and

L1b; L2a and **L2b).** DFT [*] calculations identified the tautomers **L1a** and **L2a** as being of slightly lower energy. Single X-ray crystal structures of **L1** and **L2** revealed that **L1** crystallizes as the more favourable tautomer **L1a** while **L2** as the less favourable tautomer **L2b**. The energy differences are, however, quite small.

The benzimidazole framework proved to be very useful and can be theoretically used in the preparation of a variety of pyridyl ligands using the same simple reactions. Although not reported in this thesis, because of being beyond the scope of this study, some attempts were made to prepare 3-pyridyl substituted compounds. The results are very promising and higher yields were even attained in some reactions.

Two **M_4L_4**-type tetrahedral coordination cages were obtained from the equimolar reactions of each of **L1** and **L2** with **$[Pt(dppp)][OTf]_2$** in CH_3OH solution. A cartoon representation of the two cages **$[Pt(dppp)(L1)]_4^{8+}$** and **$[Pt(dppp)(L2)]_4^{8+}$** showing how the right-angled ligands fold into a tetrahedral shape is displayed in Figure (2.28) below.

Single crystal X-ray structure analysis also showed these **M_4L_4** cages have fairly sizable internal voids of approximately **350 $Å^3$** which is large enough to accommodate four CH_2Cl_2 molecules.

Usually, tetrahedral cages are obtained from metals being at the apices and ligands constructing the edges or the faces of the tetrahedron as described in Chapter one. Surprisingly, the **M_4L_4** cages observed for **$[Pt(dppp)(L1)]_4^{8+}$** and **$[Pt(dppp)(L2)]_4^{8+}$** result,

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[*] DFT study was performed by Dr. Hazem Amarne

not from paneling of ligands, but from the propagation of single cyclic strands of head-to-tail linked ligands such that they are neatly folded to give the tetrahedral shape.

Nature routinely creates three-dimensional shapes by folding strings of organic units such as polypeptides into functional entities. This new ligand set with a right-angle allows for this concept of folded structures to be manifest in a simple metal ligand system and provides a potentially useful design principle that may be applied to the creation of more sophisticated cages and containers.

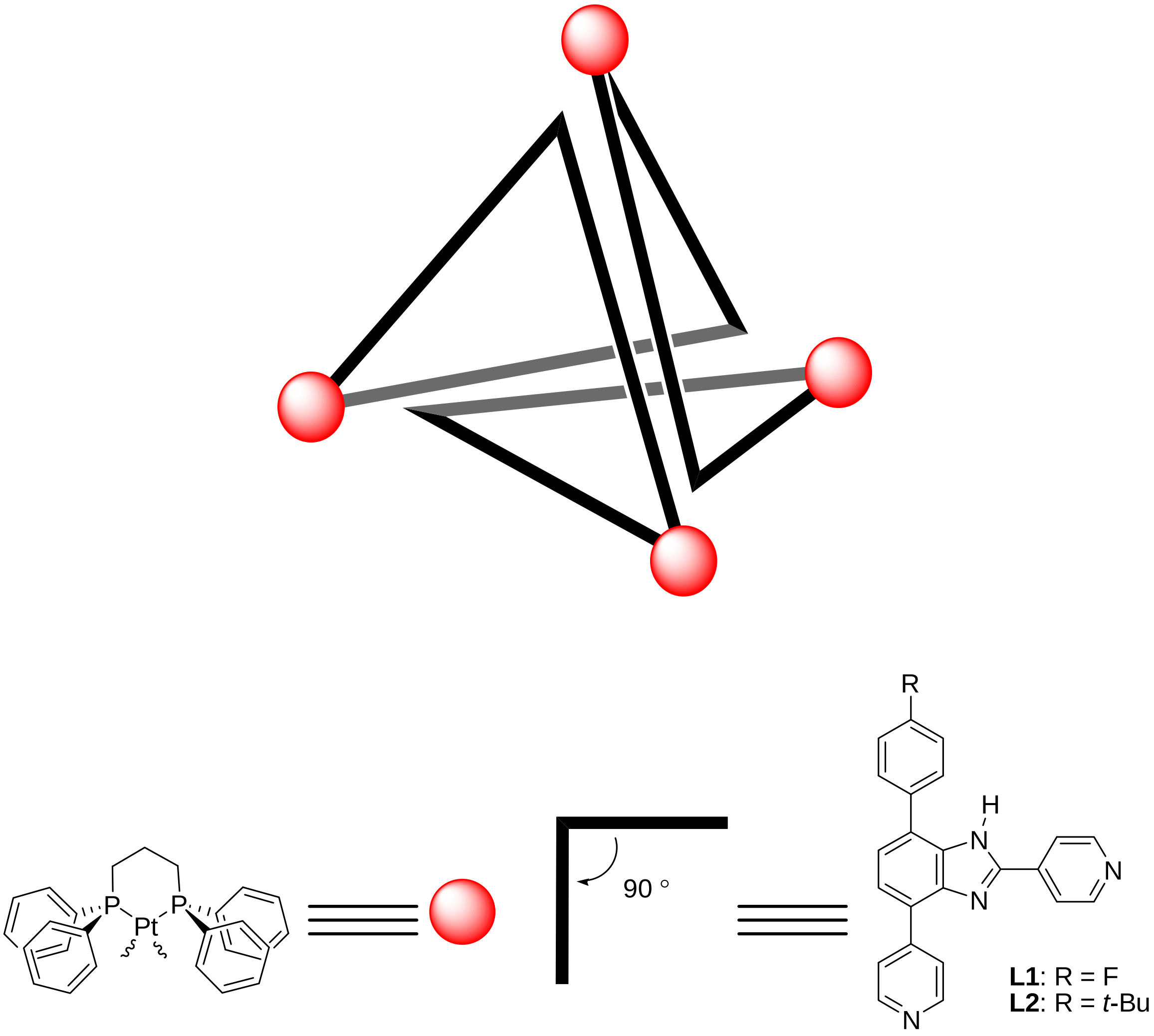

Figure 2. 28 – Cartoon representation of [Pt(dppp)(L1)]$_4^{8+}$ and [Pt(dppp)(L2)]$_4^{8+}$

Chapter 3: ASSEMBLY OF A M_6L_4 CLUSTER

3.1 INTRODUCTION

The last two decades have witnessed a growing understanding of supramolecular chemistry and the intermolecular interactions leading to large three-dimensional self-assemblies. Nowadays, self-assemblies are designed, controlled and invented rather than just being discovered serendipitously. A variety of three-dimensional molecules have been synthesized by connecting smaller molecules via non-covalent bonds such as $\pi-\pi$ interactions, hydrogen bonds and labile metal-ligand interactions. This has led to a new concept/methodology called "*non-covalent synthesis*".[24] Non-covalent synthesis is increasingly attracting chemists and has become a reliable and easy way for preparing both organic and inorganic clusters of various architectures. A considerable number of chemists are now using the non-covalent approach instead of the traditional synthesis.

Fujita *et al* have used a tridentate pyridyl ligand to prepare an **M_6L_4** octahedral coordination cage (Figure 3.1).[24] They used the palladium *cis*-protected metal corner **$[Pd(en)]^{2+}$** - which affords a right angle – and were able to use 2D ligands to efficiently construct 3D cages. Fujita called this approach "*molecular paneling*". The cage was found to be thermodynamically stable because the formation of the product was not affected by the presence of an excess of the metal corner. The same group has used this **M_6L_4** complex in some practical chemical applications.[49]

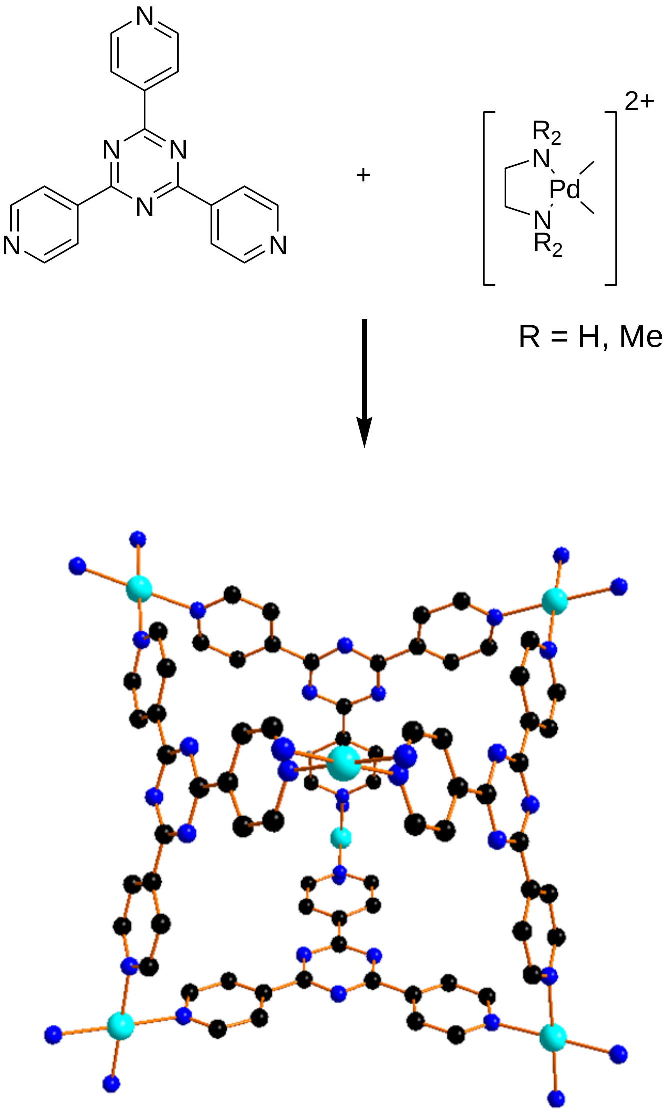

Figure 3. 1 - Fujita's original M_6L_4 cage
(Turquoise = Pd, black = C and blue = N; H atoms and some C atoms - at the metal corner - have been omitted for clarity)

This chapter describes the preparation and characterization of a new tris(pyridine) ligand **(L3)** built on a benzimidazole platform that contains a rigid right angle, which is rare in the literature for an organic compound. Different spectroscopic methods as well as a single crystal X-ray experiment were performed to characterize the new T-shaped tridentate ligand.

A coordination study was also performed. When mixed with **$[Pt(dppp)]^{2+}$** (3:2 metal-ligand ratio) (**L3**) yielded an **M_6L_4** , **$[Pt_6(dppp)_6(L3)_4][OTf]_{12}$**, cluster somewhat similar to Fujita's. A single crystal X-ray study was performed and the results are described in this chapter.

3.2 EXPERIMENTAL: LIGAND SYNTHESIS

3.2.1 Synthesis of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

3.2.1.1 Synthesis of 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (2)

4,7-Dibromo-2,1,3-benzothiadiazole (0.500 g, 1.70 mmol, MW = 293.97 g/mol), 4-pyridylboronic acid (0.439 g, 3.57 mmol, MW = 122.92 g/mol), PEPPSI^{TM}-IPr catalyst ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II)dichloride) (0.046 g, 0.07 mmol. MW = 679.46 g/mol), and potassium carbonate (K_2CO_3) (1.173 g, 8.50 mmol, MW = 138 g/mol) were added to a Schlenk flask. N_2 was blown into the flask for 5 min and water and 1,4-dioxane mixture (1:1) (40 mL) was added to the solids. The mixture was stirred and refluxed under N_2 at 90 □C for 24 h and then cooled to RT. The resulting product was extracted using $CHCl_3$, dried with anhydrous $MgSO_4$ and filtered. Solvent was evaporated and the resulting brown solid **(2)** was recrystallized from MeCN. **Yield**: 0.474 g, 96%, **MW** = 290.34 g/mol. **MP:** 248 □C. **IR** (ATR) (ν/cm^{-1}) = 3051, 3028, 2170, 1593, 1582, 1538, 1471, 1408, 1337, 1306, 1261, 1216, 1120, 1092, 1070, 993, 943, 886, 855, 828,814, 791,756, 712, 667, 624, 593, 551, 519, 508, 454. **EA (CHN) (%):** calculated: C = 66.19; H = 3.47; N = 19.30; found: C = 64.08; H = 3.51; N = 18.63.

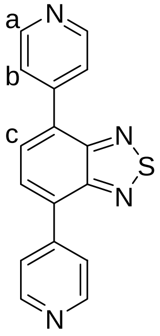

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Table 3. 1 - ^{1}H NMR (500 MHz, CDCl$_3$) data of 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (2)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*d*	*8.80*	*4*	$^3J_{ab} = 6.1$
b, c	*m*	*7.95 – 7.90*	*6*	-

3.2.1.2 Synthesis of 3,6-di(pyridin-4-yl)benzene-1,2-diamine (9)

4,7-Di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(2)** (0.282 g, 0.97 mmol, MW = 290.34 g/mol) was transferred to a round-bottom flask using EtOH (45 mL) and THF (15 mL). Cobalt(II) chloride hexahydrate (0.006 g, 0.02 mmol, MW = 236.9 g/mol) and sodium borohydride (NaBH$_4$) (0.056 g, 1.47 mmol, MW = 38 g/mol) were added. The resulting mixture was refluxed (70 ^{o}C), and the progress of the reaction monitored by TLC using DCM/EtOAc (2:1). More sodium borohydride (NaBH$_4$) (0.056 g, 1.47 mmol, MW = 38 g/mol) was added every 1 h until the reaction was complete (4 h) and then the flask was cooled to RT. The product was extracted with Et_2O filtered under N_2 and the solvent removed using a rotary evaporator. The resulting pale yellow product **(9)** was stored under N_2 for use in the next step. **Yield**: 0.243 g, 96%, MW = 262.31 g/mol. **MP:** 100 ^{o}C (decomposed). **IR** (ATR) (v/cm-1) = 3422, 3330, 3199, 3022, 2961, 2923, 2852, 1941, 1661, 1594, 1540, 1474, 1445, 1402, 1318, 1259, 1211, 1086, 1065, 1014, 992, 876, 795, 752, 707, 677, 661, 643, 597, 580, 529, 475.

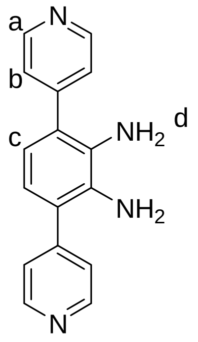

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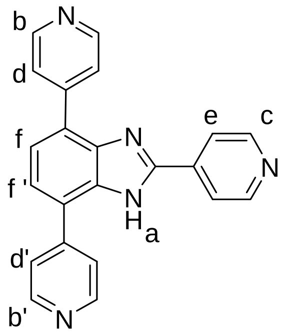
Table 3. 2 - ^{1}H NMR (500 MHz, CD_2Cl_2) data of 3,6-di(pyridin-4-yl)benzene-1,2-diamine (9)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*m*	*8.84 – 8.42*	*4*	-
b	*m*	*7.49 – 6.97*	*4*	-
c	*s*	*6.78*	*2*	-
d	*s*	*3.69*	*4*	-

3.2.1.3 Synthesis of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

4-Pyridinealdehyde (0.082 g, 0.77 mmol, MW = 107.11 g/mol) was weighed into a small vial, diluted with chloroform (10 mL) and added to the 3,6-di(pyridin-4-yl)benzene-1,2-diamine **(9)** (0.200 g, 0.76 mmol MW = 262.31 g/mol) in a round bottom flask. Zirconium tetrachloride ($ZrCl_4$) (0.002 g, 0.01 mmol, MW = 233.6 g/mol) was added and the mixture was stirred overnight at RT. Solvent was removed using a rotary evaporator. The resulting solid was dissolved in THF and filtered. THF was evaporated from the filtrate. The resulting yellow product **(10)** was recrystallized twice from MeCN. **Yield**: 0.132 g, 50%, **MW** = 349.39 g/mol. **MP:** 263 ^{o}C. **IR** (ATR) (v/cm-1) = 3034, 2962, 1709, 1593, 1538, 1484, 1435, 1415, 1367, 1325, 1288, 1258, 1215, 1094, 1066, 1020, 993, 961, 938, 890, 853, 827, 805, 734, 724, 691, 665, 642, 627, 609, 581, 527, 501, 427.



L3

Table 3. 3 - ^{1}H NMR (500 MHz, CD_2Cl_2) data of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

Proton	Multiplicity	δ (ppm)	# of protons	*J* (Hz)
a	*s*	*13.21*	*1*	*-*
b,b',c	*d*	*8.76*	*6*	-
d,d'	*dd*	*8.28*	*4*	$^3J_{d',b'} = 6.1$
e,f	*m*	*7.82 – 7.77*	*3*	-
f'	*d*	*7.54*	*1*	$^3J_{f,f'} = 7.8$

3.3 EXPERIMENTAL: Synthesis of $[Pt_6(dppp)_6(L2)_4]$ $[OTf]_{12}$

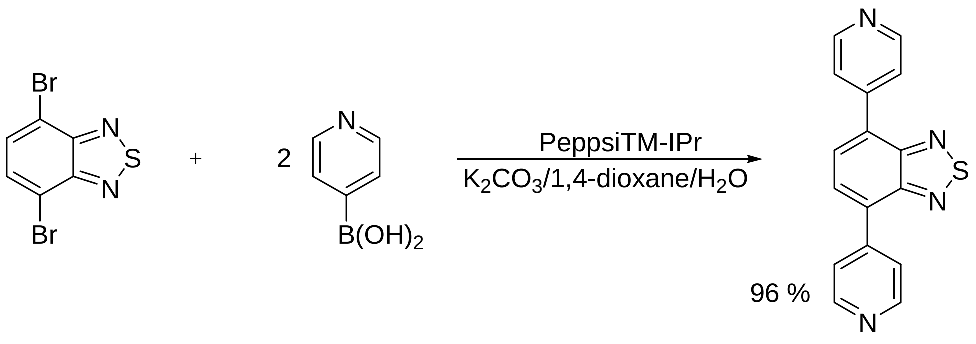
2,4,7-*Tri*(pyridin-4-yl)-1H-benzimidazole (**L3)** (0.010 g, 0.029 mmol, MW = 349.39 g/mol) and **[Pt(dppp)][OTf]$_2$** (0.039 g, 0.043 mmol, MW = 905.66 g/mol) were dissolved in a MeOH/$MeNO_2$ mixture (1:1, 10 mL). The mixture was stirred at 70 ^{o}C for 2 h and cooled to RT. The solvent was slowly evaporated at RT. A couple of days later a yellow powder precipitated from the solution. The mixture was decanted to obtain a clear solution. Slow evaporation of solvent from this solution resulted in small colorless crystals. Theses crystals were collected, dried and dissolved again in MeOH. Larger, better formed crystals were obtained by slow diffusion of diisopropyl ether into a MeOH solution of the compound. **MW** = 6831.57 g/mol. **MP**: 250 ^{o}C. **IR** (ATR) (ν/cm-1) = 3374, 3059, 2925, 1620, 1589, 1484, 1436, 1251, 1223, 1152, 1103, 1028, 998, 975, 918, 840, 793, 747, 707, 690, 634, 572, 511, 482, 439, 425.

3.4 RESULTS AND DISCUSSION

3.4.1 Synthesis of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

3.4.1.1 Synthesis of 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (2)

The 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(2)** was synthesized using a palladium-catalyzed cross-coupling using 4,7-dibromo-2,1,3-benzothiadiazole and an excess of 4-pyridylboronic acid (Scheme 3.1). The reaction proceeded smoothly and the desired product was purified by recrystallization from MeCN. Cross-coupling occurred at the 4 and 7-positions of the benzothiadiazole as planned and desired; the yield (96%) was high. This compound was also obtained as a by-product when synthesizing the 4-bromo-7-(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(1)** (*see section 2.2.1.2)*. The product was characterized by ^{1}H NMR spectroscopy. Table (3.1) lists the major peaks of the ^{1}H NMR spectrum in $CDCl_3$.



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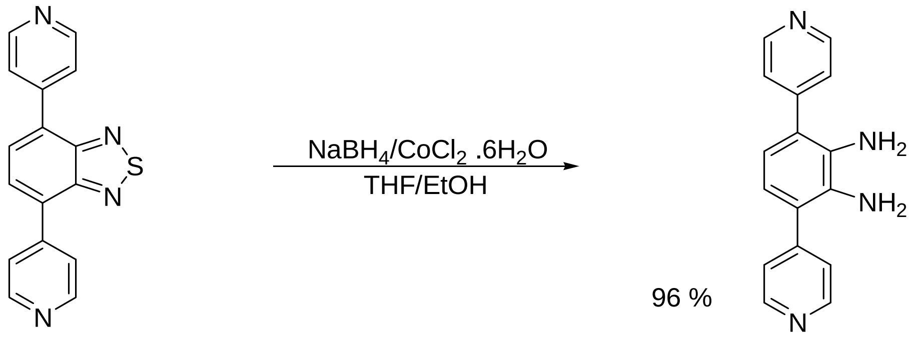
Scheme 3. 1 - Synthesis of 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole (2)

3.4.1.2 Synthesis of 3,6-di(pyridin-4-yl)benzene-1,2-diamine (9)

3,6-Di(pyridin-4-yl)benzene-1,2-diamine **(9)** was synthesized by the reduction of 4,7-di(pyridin-4-yl)benzo[C][1,2,5]thiadiazole **(2)** using slightly modified literature method (Scheme 3.2). [45] The reaction was catalyzed by $CoCl_2.6H_2O$. Sodium borohydride $NaBH_4$ was used as a reducing agent and THF/EtOH (1:3) mixture as the solvent. The yield (96%) was high compared with the literature values (71 - 97%; depending on the nature of the **R** groups at the 4 and 7-positions of the benzothiadiazole).[45] 3,6-*Di*(pyridin-4-yl)benzene-1,2-diamine **(9)** was characterized using IR and ^{1}H NMR spectroscopic methods. The diamine characteristic peak (3350 – 3310 cm^{-1}) was clearly visible at 3330 cm^{-1} in the IR spectrum. Some of the characterization data for the compound is given in section (3.2.1.2**).** Table (3.2) shows the major peaks of the ^{1}H NMR spectrum of the compound in CD_2Cl_2.



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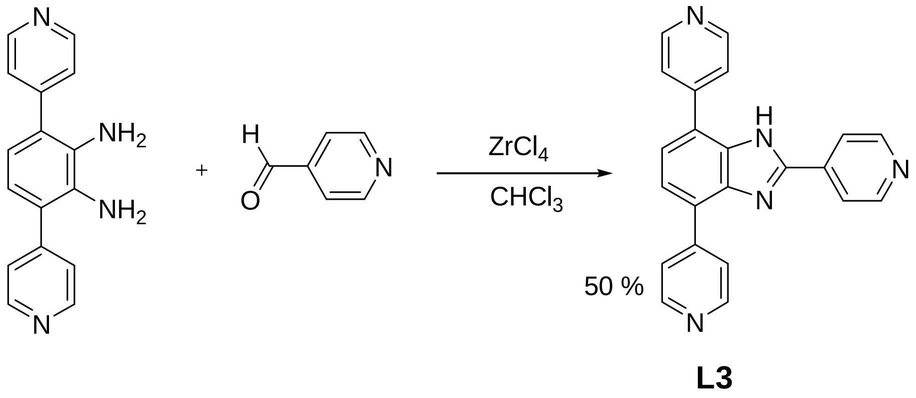
Scheme 3. 2 - Synthesis of 3,6-di(pyridin-4-yl)benzene-1,2-diamine (9)

3.4.1.3 Synthesis of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

The new ligand 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole **(L3)** was synthesized using the condensation reaction of the 3,6-di(pyridin-4-yl)benzene-1,2-diamine **(9)** and 4-pyridinecarboxaldehyde (Scheme 3.3). The reaction was catalyzed by zirconium tetrachloride. The pure targeted ligand **(L3)** was obtained after a couple of recrystallizations from MeCN. The yield (50%) was comparable to that obtained for **(L1)** (48%) and **(L2)** (41%). Again the high instability of the diamine and the reaction taking place at RT were probably causing the low yield. The product was characterized using ^{1}H NMR. Table (3.3) shows the major peaks of the ^{1}H NMR spectrum of the compound in DMSO. Reddish brown crystals of **(L3)** were obtained by a slow evaporation of the ligand solution in MeOH. A single crystal X-ray experiment was performed to confirm the ligand structure. Figures (3.2) and (3.4) show some pictures of the crystal structure. Table (3.4) contains the experimental crystal data. Geometrical parameters are given in Appendix J.



Scheme 3. 3 - Synthesis of 2,4,7-tri(pyridin-4-yl)-1H-benzimidazole (L3)

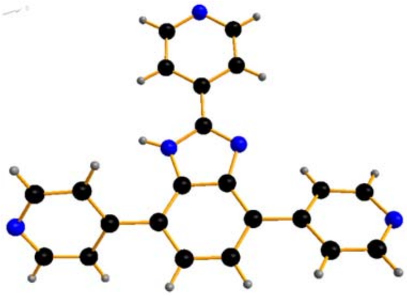


Figure 3. 2 – Ball and stick representation of (L3)
(Black = C, blue = N and grey = H)

The dihedral angle between the planes of the pyridyl ring at the 2-position and the benzimidazole core is approximately 0°. The dihedral angle between the planes of the pyridyl ring at the 4-position and the benzimidazole core is approximately 23°. The dihedral angle between the planes of the pyridyl ring at the 7-position and the benzimidazole core is about 49°. All bond distances for the ligand (**L3**) fall in the typical range. In solid state, **L3** showed H-bonding between the **NH** of one molecule and the pyridine groups in another (Figure 3.3) repeating the same fashion observed for **L1** and **L2** as described in Chapter 2.

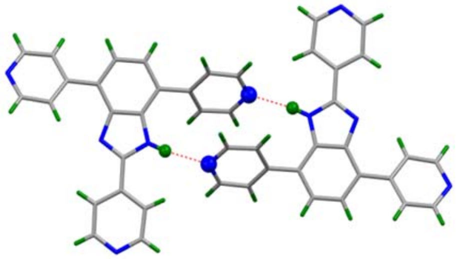


Figure 3. 3 – H-bonding between two molecules of L3

Table 3. 4 - Single crystal data of L3

CRYSTAL DATA	
Chemical formula	$C_{22}H_{15}N_5$
M_r	349.39
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	273
a, *b*, *c* (Å)	7.2957 (12), 10.6767 (17), 11.4249 (19)
α, β, γ (°)	88.4780 (17), 79.4437 (18), 72.7735 (17)
V (Å^3)	835.3 (2)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.22 x 0.28 x 0.34
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	empirical (SADABS)
min. and max. transmission	0.6272, 0.7454
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8118, 2943, 2538
R_{int}	0.024
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.122, 1.08
No. of reflections	2943
No. of parameters	244
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.44, -0.21

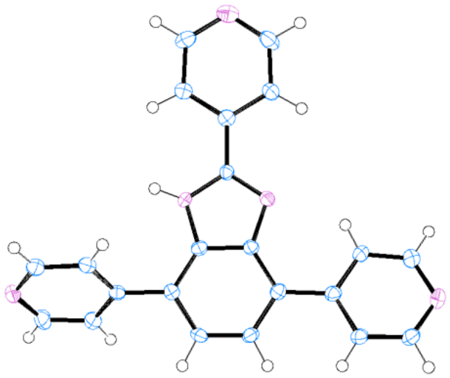


Figure 3. 4 - Crystal structure of (L3) with 50% ellipsoid probability

3.4.2 Synthesis of [Pt$_6$(dppp)$_6$(L3)$_4$] [OTf]$_{12}$

[Pt$_6$(dppp)$_6$(L3)$_4$][OTf]$_{12}$ was synthesized by simply mixing **(L3)** and the *cis*-protected **[Pt(dppp)][OTf]$_2$** metal corner. Coordination took place at temperatures between 60 and 70 ^{O}C. The resulting **M$_6$L$_4$** complex, **[Pt$_6$(dppp)$_6$(L3)$_4$][OTf]$_{12}$** (Figure 3.9), was characterised using 1D ^{1}H NMR spectroscopy. A single crystal X-ray diffraction experiment was performed. Some pictures of the octahedral cluster are given in Figures (3.5) and (3.6). Table (3.5) contains the experimental crystal data. Geometric parameters are shown in appendix K.

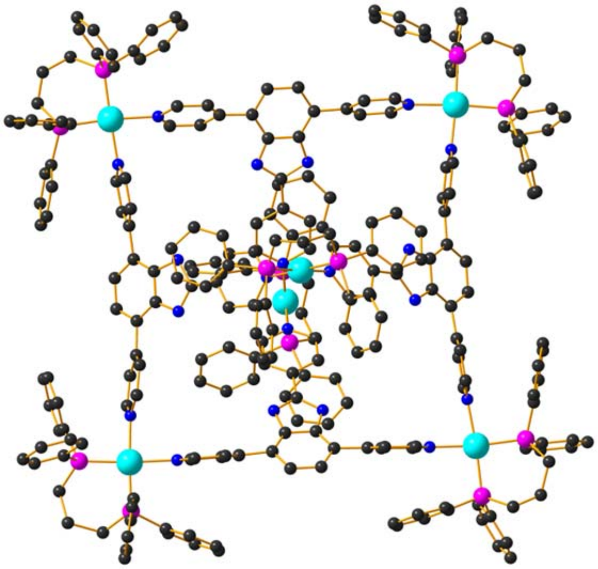


Figure 3. 5 - Ball and stick representation of $[Pt_6(dppp)_6(L3)_4]^{12+}$ (Turquoise = Pt, black = C, pink = P and blue = N; H atoms are omitted for clarity)

To give the detailed picture of the cage geometries, we need to consider the octahedral nature of the cluster with four **Pt(II)** ions constructing a square base and the other two positioned at the apices above and below this square. The overall **Pt-Pt** average distance is 13.29 Å. If the four square **Pt(II)** ions are assigned the letter **S** and the two apical **Pt(II)** ions are assigned the letter **A**, the average **Pt-Pt** distances are: **S-S** = 15.51 Å, **A-A** = 12.02 Å and **A-S** = 12.50 Å. In the same way, the average **Pt-N** bond distance is 2.10 Å, **S-N** = 2.11 and **A-N** = 2.09 Å. Average **Pt-P** bond distance = 2.26 Å, **S-P** = 2.24 Å and **A-P** = 2.28 Å. The overall average **N-Pt-N** angle equals 85°, **N-S-N** = 84° and **N-A-N** = 87°. The overall average **P-Pt-P** is approximately 91°, **P-S-P** = 90°and **P-A-P** = 91°. The overall average **N-Pt-P** angle is approximately 91.5°, **N-S-P** = 92 and **N-A-P** = 91°. Inner void = 1**35 $Å^3$.**

Table 3. 5 - Single crystal data of $[Pt_6(dppp)_6(L3)_4]^{12+}$

CRYSTAL DATA	
Chemical formula	$Pt_{12}P_{24}N_{40}C_{566}H_{424}S_{24}O_{72}F_{72}$
M_r	14159.60
Crystal system, space group	Triclinic, P-1
Temperature (K)	150 K
a, b, c (Å)	24.9930 (12) , 25.7973 (13), 30.8052 (16)
α, β, γ (°)	98.380 (3), 92.778 (3), 110.843 (3)
V (Å^3)	18255.3 (16)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.007
Crystal size (mm)	0.24 x 0.24 x 0.34
DATA COLLECTION	
Diffractometer	Bruker D8 Venture
Absorption correction	Empirical (SADABS)
Min. and max. transmission	0.3851, 0.7516
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	108453, 36945, 19461
R_{int}	0.1010
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	67.68
REFINEMENT	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.1888, 0.2863
No. of reflections	36945
No. of parameters	2977/2934
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.648, 0.218

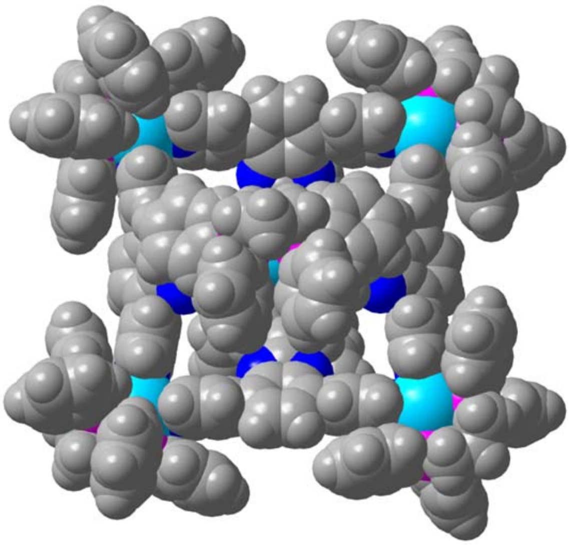


Figure 3. 6 - Single crystal structure (space filling) of $[Pt_6(dppp)_6(L3)_4]^{12+}$ (Turquoise = Pt, black = C, pink = P and blue = N; H atoms are omitted for clarity)

In the solid state, the openings of the cage (four faces) are blocked by **OTf** anions positioned exactly above and below the **Pt(II)** square plane (Figure 3.7) repeating the same pattern observed for the **M_4L_4** cages of **L1** and **L2** (Figure 2.27).

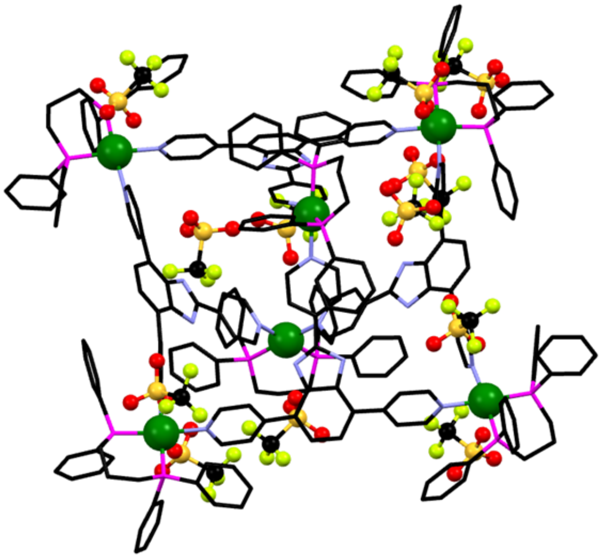


Figure 3. 7 – OTf anions (ball and stick) blocking cage (M_6L_4) openings (Pt(II) ions shown as green balls)

3.5 CONCLUSIONS

A third pyridyl ligand was synthesized which has the same T-shape of **L1** and **L2** but being tridentate rather than bidentate with two pyridyl groups at the 4- and 7- positions of the benzimidazole framework and each of them is at a right angle to a third pyridyl group at the 2-position. Compared to **L1** and **L2, L3** had the best coupling reaction yield, clearly because of being symmetrical which is also very good in avoiding the isomerism obstacle we faced with **L1** and **L2**. However, its solubility was the worst among the three ligands and it lacks the substituent groups that are useful for NMR spectroscopic characterization.

The reaction of **L3** with **$[Pt(dppp)][OTf]_2$** in CH_3OH solution resulted in an octahedral **M_6L_4-type** coordination cage **$[Pt_6(dppp)_6(L3)_4]^{12+}$**. A cartoon representation of the structure of **$[Pt_6(dppp)_6(L3)_4]^{12+}$** is displayed in Figure (3.9) below.

$[Pt_6(dppp)_6(L3)_4]^{12+}$, like the **$M_6L_4$** paneling product prepared by Fujita et al. (Section 3.1), has an octahedral shape and has a cavity size of about **135 Å** which is enough to accommodate three to four methanol molecules. It is expected that this cage might be capable of showing molecular recognition for neutral organic molecules, in aqueous media, and could be used for trapping organic molecules of comparable sizes.

Usually in **M_6L_4** paneling octahedra, like Fujita's, ligands only cover the faces of the octahedron with the edges remaining hypothetical (Figure 3.1). In **$[Pt_6(dppp)_6(L3)_4]^{12+}$**, four **Pt(II)** ions are positioned at the four corners of an ideal square and the remaining two **Pt(II)** ions are located at the apical points above and below the square to complete a typical octahedron. The four ligands are covering four face of the octahedron. The longer pyridyl parts of the ligands are constructing real edges of the square base of the octahedron giving the cage its novelty (Figure 3.8).

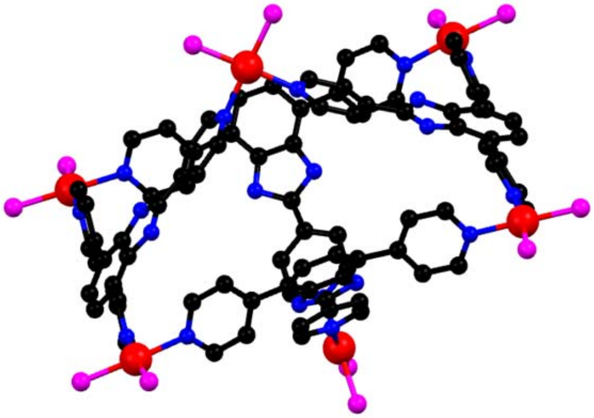


Figure 3. 8 – $[Pt_6(dppp)_6(L3)_4]^{12+}$ octahedron
(red = Pt, black = C, blue = N and pink = P)

(H atom and dppp C atoms are removed for clarity)

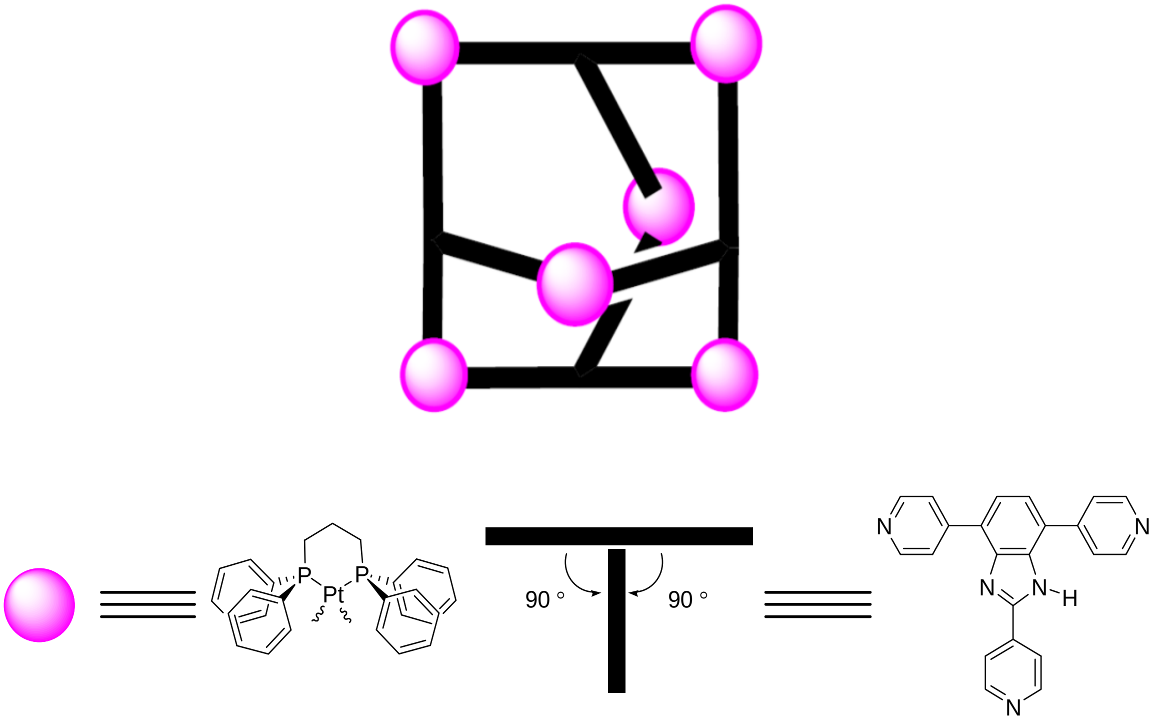


Figure 3. 9 - Cartoon representation of $[Pt_6(dppp)_6(L3)_4][OTf]_{12}$

Chapter 4: SUMMARY AND FUTURE CONSIDERATIONS

4.1 LIGANDS

Bidentate and tridentate benzimidazole-based T-shaped ligands (**L1**, **L2** and **L3**) were successfully synthesized. Starting from 2,1,3-benzothiadiazole the ligands were constructed in four steps using simple reactions. Preceded by the bromination of 2,1,3-benzothiadiazole, a Suzuki coupling reaction was first used to attach the desired groups to the 4- and 7- positions of the benzimidazole framework, followed by a sulfur extrusion reaction yielding the corresponding diamines which were finally converted to the desired ligands via cyclization condensation reaction. The ligands have, in common, 4-pyridyl donor groups and 90^o rigid angles.

As mentioned previously, the benzimidazole framework proved to be very useful and can be theoretically used in the preparation of a variety of pyridyl ligands (Figure 4.1) using the same simple reactions. 3-Pyridyl substituted compounds could be used instead of the 4-pyridyl ones to synthesize similar bidentate or tridentate ligands.

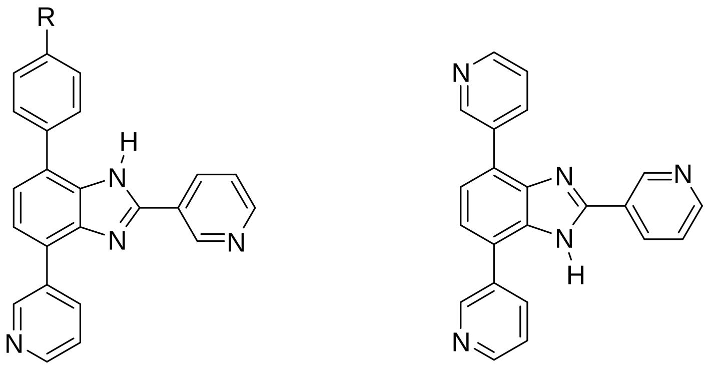


Figure 4. 1 – 3-Pyridyl ligands

The synthesis of ligands having both 3- and 4-pyridyl donor sites is also possible.

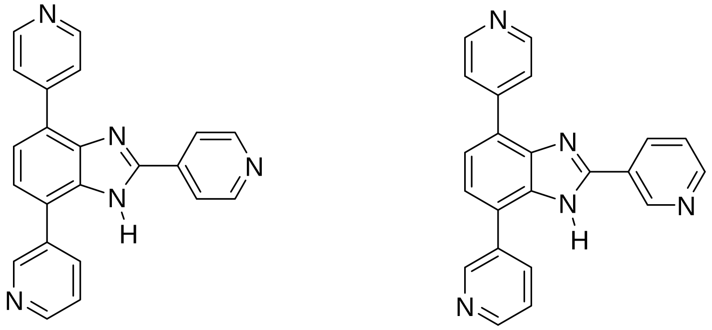


Figure 4. 2 – Ligands containing both 3- and 4-pyridyl donor groups

The denticity of the ligands could be increased and the ligands shape could be modified. Preparation of H-shaped benzimidazole-based tetradentate ligands with 4-pyridyl, 3-pyridyl or both is a good example of theoretically possible amendments.

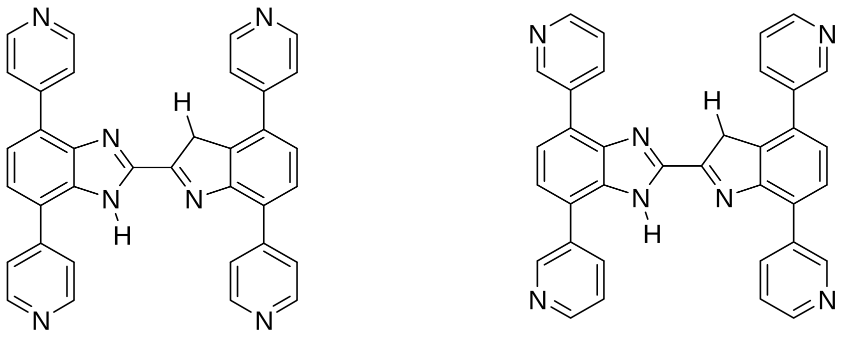
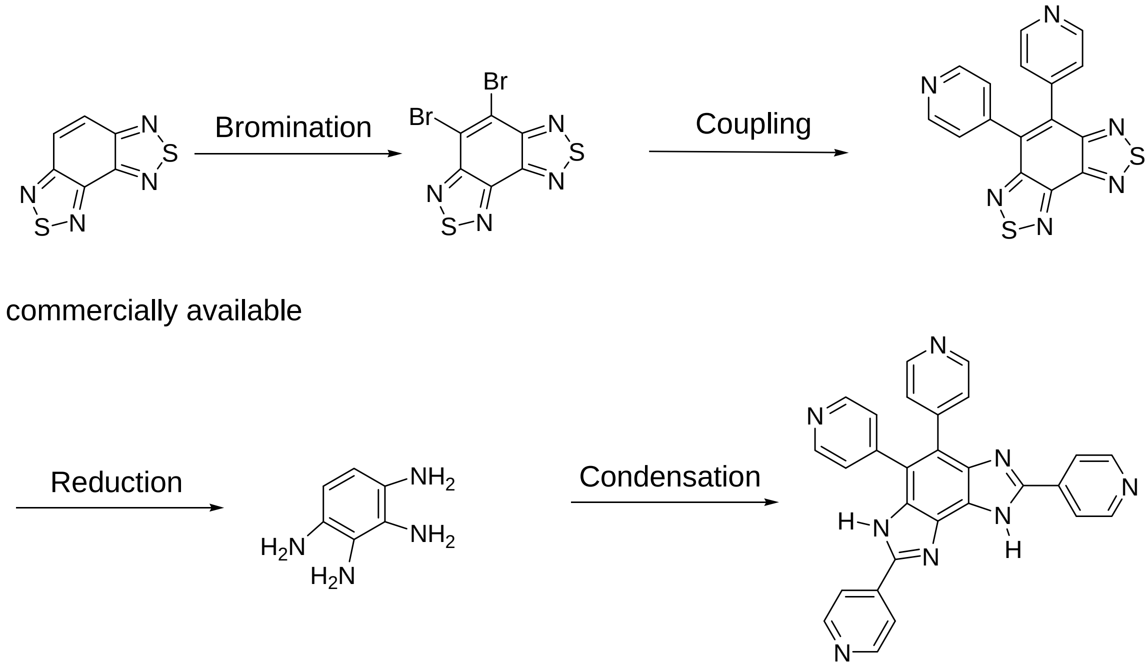


Figure 4. 3 – H-shaped benzimidazole-based ligands

A scissors-like ligand with two right angles (Scheme 4.1), which was a part of our plan, could be synthesized using the same reactions. The starting material is commercially available and the ligand is expected to undergo very interesting coordination reactions probably leading to polymeric nano-tubes.



Scheme 4. 1 – Preparation of scissors-like benzimidazole-based ligand

4.2 CLUSTERS

Two novel **M_4L_4-type** tetrahedral coordination cages were obtained from the equimolar reactions of each of **L1** and **L2** with **$[Pt(dppp)][OTf]_2$** in CH_3OH solution.

The reaction of **L3** with **$[Pt(dppp)][OTf]_2$** in CH_3OH solution resulted in a novel octahedral **M_6L_4-type** coordination cage.

L1, **L2** and **L3** are expected to have the same chemistry with metal ions which have the same square geometry (eg. **Pd(II)**). Although there might be steric clashes, exploring the chemistry of these ligands with cheaper tetrahedral metal ions such as **Cu(II)** is not a bad idea. Projects described in this thesis could also be expanded by using free **Pt(II)** or **Pd(II)** ions rather than using the *cis*-protected complexes.

Replacing the **R** groups (**F** for **L1** and ***t*-But** for **L2**) with long alkyl threads (changing aspect ratio) might result in mesogenic coordination species which may be used as liquid crystal displays.

Coordination self-assemblies having a cage nature and suitable cavity sizes have recently been used in some practical applications.[50] Insertion of spacers to **L1**, **L2** and **L3** would perhaps result in cages that have larger cavities. Cavity-directed chemical transformations[51, 52] chemical storage and crystal-free crystallography[53] are important features of three-dimensional hosts and could be tried with our systems.

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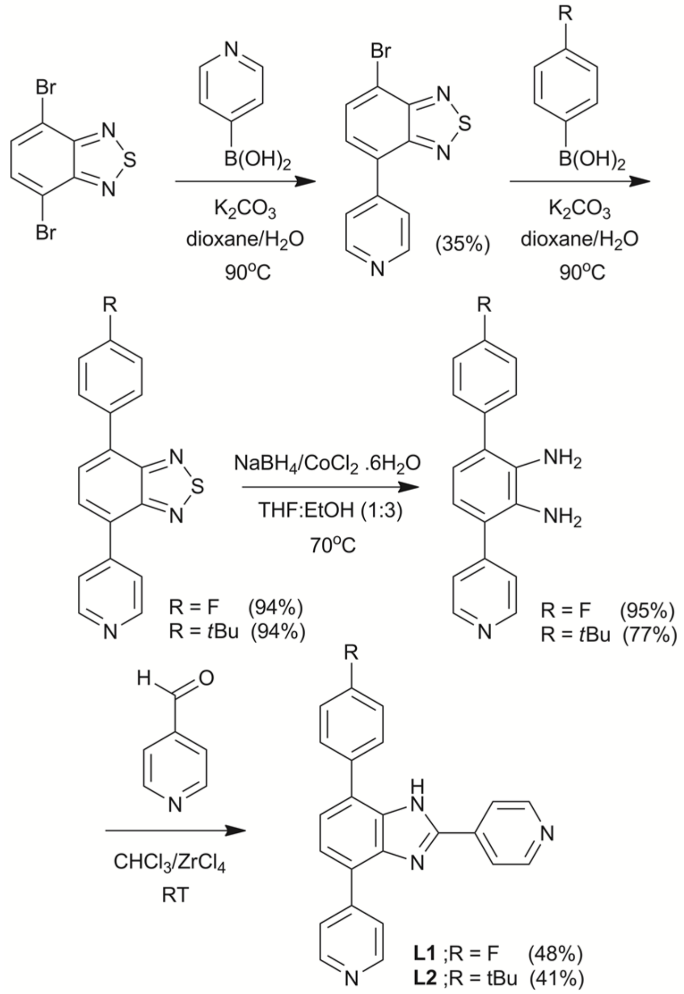
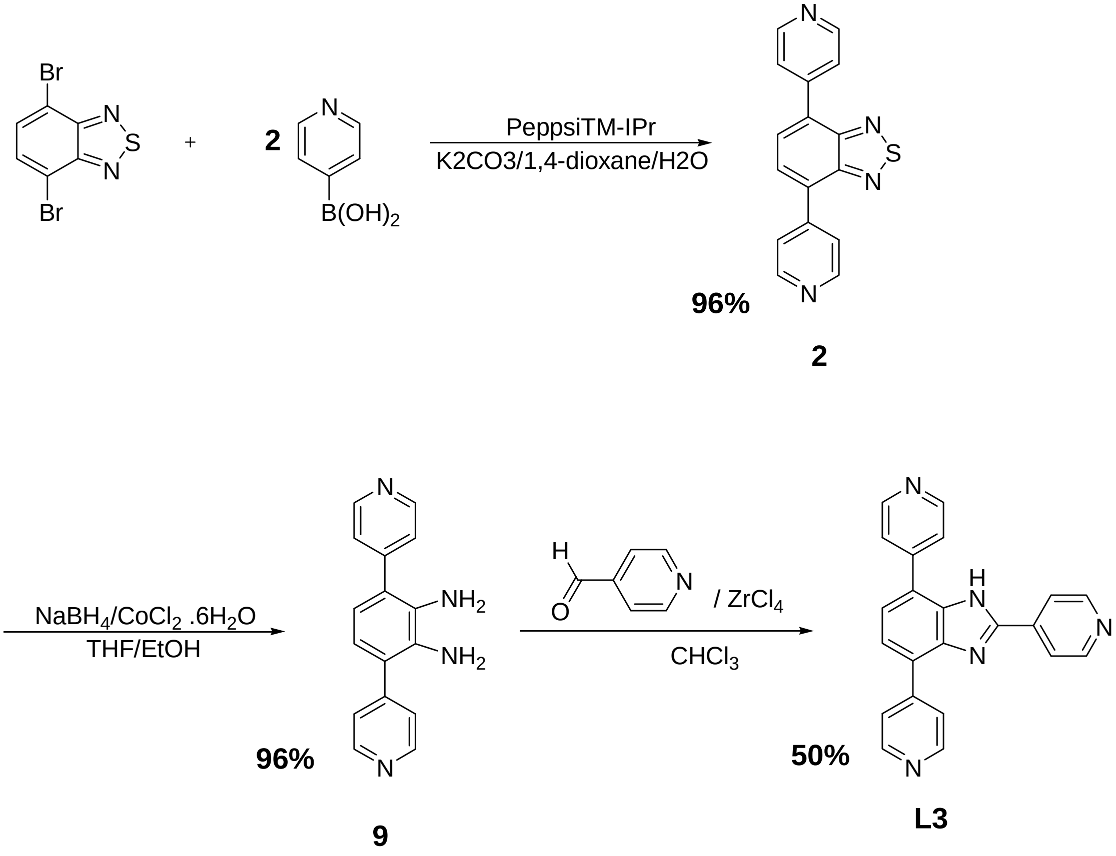
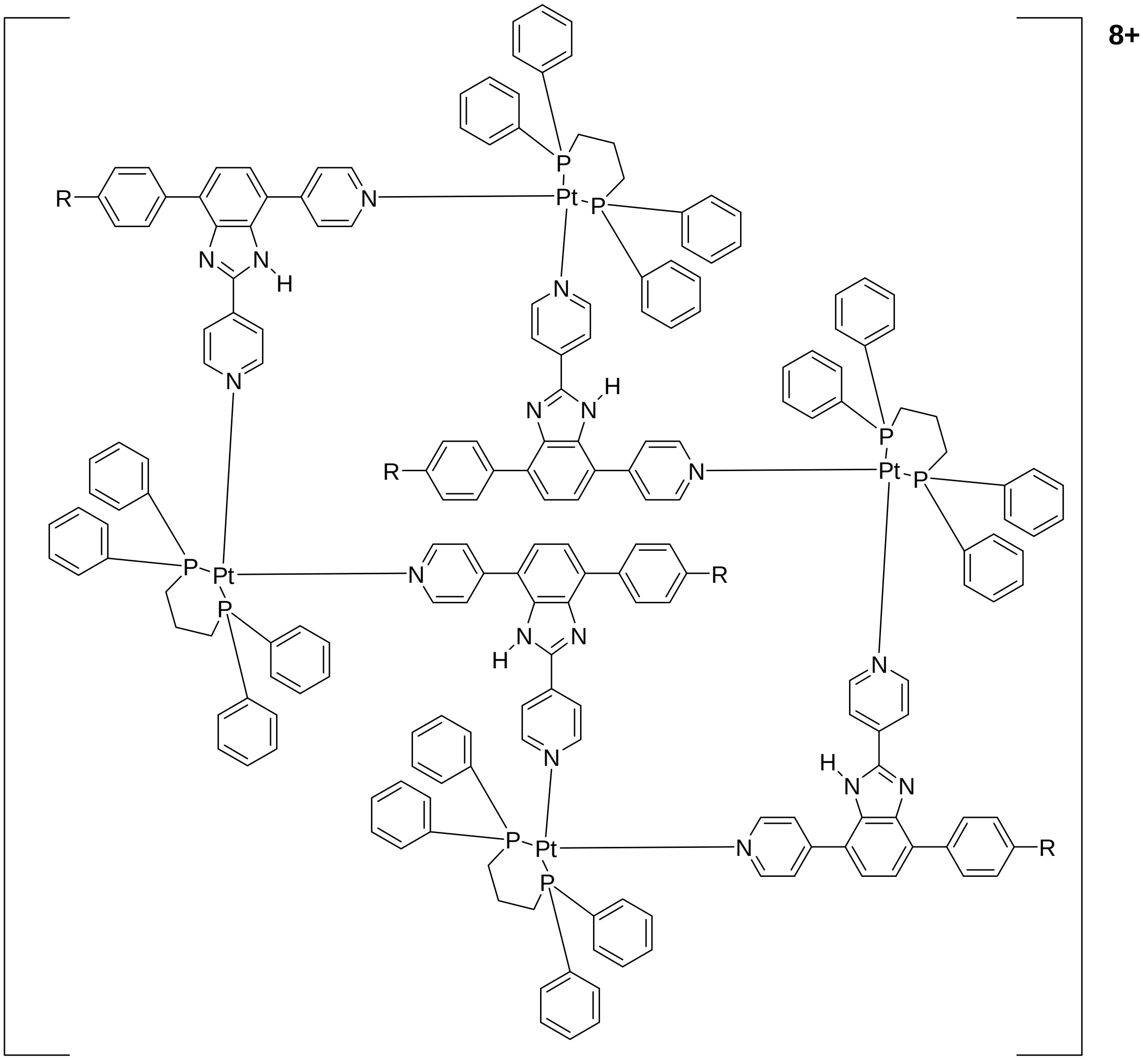
Appendix A - Summary of L1 and L2 synthesis



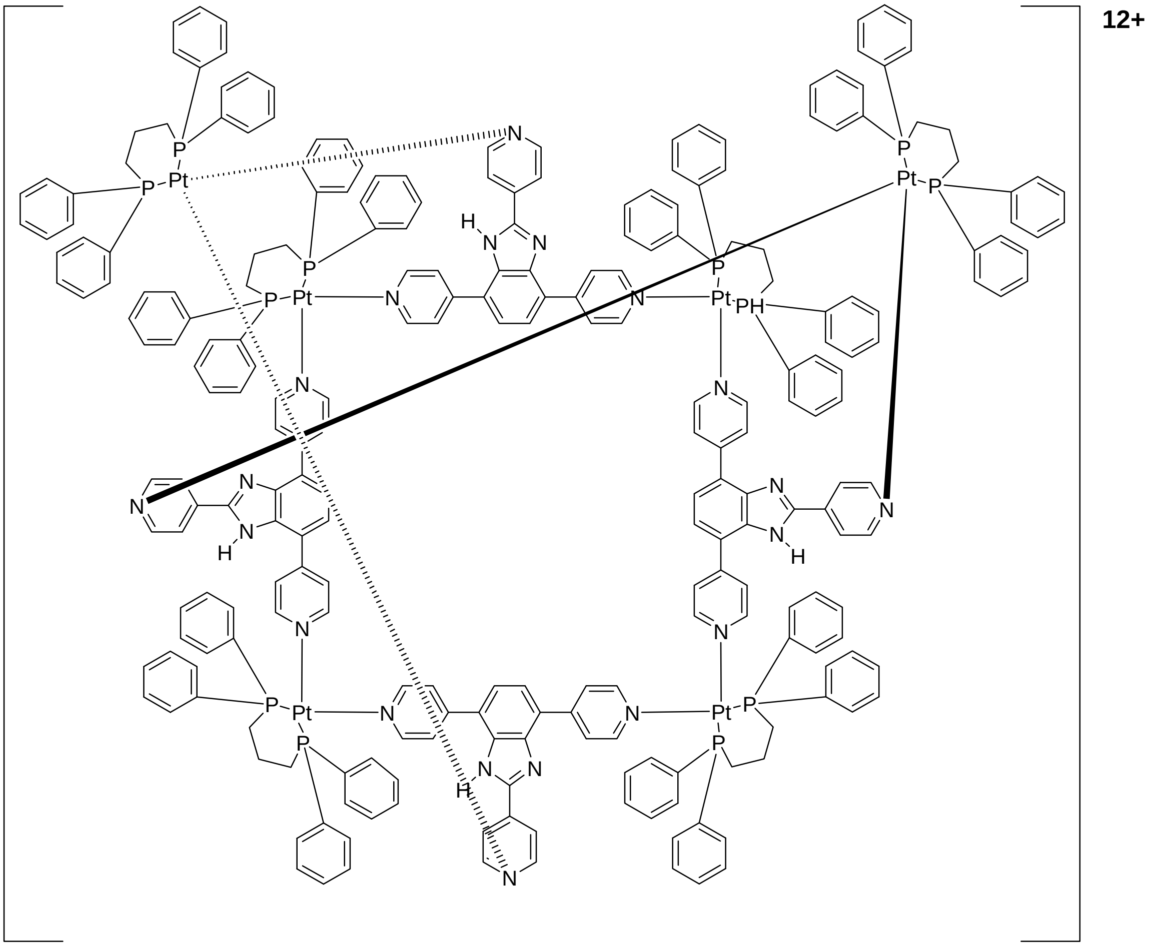
Appendix B - Summary of L3 synthesis



Appendix C - Diagram of [Pt(dppp)(L1)]$_4^{8+}$ (R = F), and [Pt(dppp)(L2)]$_4^{8+}$ (R = *t*Bu)



Appendix D - Diagram of $[Pt_6(dppp)_6(L3)_4]^{12+}$



Appendix E - Geometric parameters (Å, °) of (L1a)

F1—C1	1.364 (3)	C5—C6	1.386 (4)
N1—C15	1.343 (4)	C7—C12	1.392 (4)
N1—C16	1.336 (3)	C7—C8	1.404 (4)
N2—C18	1.370 (3)	C8—C9	1.410 (3)
N2—C8	1.383 (3)	C9—C10	1.404 (3)
N3—C18	1.319 (3)	C10—C11	1.388 (4)
N3—C9	1.384 (3)	C10—C13	1.478 (3)
N4—C21	1.330 (4)	C11—C12	1.394 (4)
N4—C22	1.333 (4)	C13—C14	1.391 (4)
C1S—Cl3	1.758 (3)	C13—C17	1.394 (4)
C1S—Cl2	1.755 (3)	C14—C15	1.383 (4)
C1S—Cl1	1.757 (3)	C16—C17	1.382 (4)
C1—C2	1.365 (4)	C18—C19	1.462 (3)
C1—C6	1.371 (4)	C19—C23	1.389 (4)
C2—C3	1.387 (4)	C19—C20	1.388 (4)
C3—C4	1.392 (4)	C20—C21	1.382 (4)
C4—C5	1.394 (4)	C22—C23	1.380 (4)
C4—C7	1.480 (4)		
C15—N1—C16	116.5 (2)	N3—C9—C8	110.2 (2)
C18—N2—C8	106.79 (19)	C10—C9—C8	121.3 (2)
C18—N3—C9	104.8 (2)	C11—C10—C9	116.2 (2)
C21—N4—C22	116.4 (2)	C11—C10—C13	120.9 (2)
Cl3—C1S—Cl2	110.58 (15)	C9—C10—C13	122.9 (2)
Cl3—C1S—Cl1	109.35 (15)	C10—C11—C12	121.9 (2)
Cl2—C1S—Cl1	110.50 (15)	C7—C12—C11	123.2 (2)
C2—C1—F1	118.3 (3)	C14—C13—C17	116.7 (2)
C2—C1—C6	123.4 (3)	C14—C13—C10	123.2 (2)
F1—C1—C6	118.3 (3)	C17—C13—C10	120.1 (2)
C1—C2—C3	118.1 (2)	C15—C14—C13	119.4 (2)
C2—C3—C4	121.2 (2)	N1—C15—C14	123.9 (2)
C5—C4—C3	118.2 (2)	N1—C16—C17	123.5 (2)
C5—C4—C7	119.9 (2)	C16—C17—C13	120.0 (2)
C3—C4—C7	121.9 (2)	N3—C18—N2	113.2 (2)
C4—C5—C6	121.4 (3)	N3—C18—C19	123.0 (2)
C1—C6—C5	117.7 (3)	N2—C18—C19	123.8 (2)

C12—C7—C8	115.0 (2)	C23—C19—C20	117.5 (2)
C12—C7—C4	120.6 (2)	C23—C19—C18	118.9 (2)
C8—C7—C4	124.3 (2)	C20—C19—C18	123.5 (2)
N2—C8—C7	132.8 (2)	C21—C20—C19	118.7 (2)
N2—C8—C9	105.0 (2)	N4—C21—C20	124.3 (3)
C7—C8—C9	122.3 (2)	N4—C22—C23	123.8 (3)
N3—C9—C10	128.5 (2)	C22—C23—C19	119.2 (2)

Appendix F - Geometric parameters (Å, º) of (L2b)

N1—C20	1.331 (4)	C6—C7	1.388 (5)
N1—C19	1.337 (4)	C6—H6A	0.9500
N2—C22	1.314 (4)	C7—C8	1.388 (5)
N2—C12	1.398 (4)	C7—H7A	0.9500
N3—C22	1.370 (4)	C8—C9	1.389 (5)
N3—C13	1.384 (4)	C8—C11	1.486 (5)
N3—H3A	0.8800	C9—C10	1.382 (5)
N4—C26	1.321 (5)	C9—H9A	0.9500
N4—C25	1.332 (5)	C10—H10A	0.9500
C1A—C4	1.512 (10)	C11—C16	1.389 (5)
C1A—H1AA	0.9800	C11—C12	1.404 (5)
C1A—H1AB	0.9800	C12—C13	1.413 (5)
C1A—H1AC	0.9800	C13—C14	1.390 (5)
C2A—C4	1.465 (10)	C14—C15	1.386 (4)
C2A—H2AA	0.9800	C14—C17	1.481 (5)
C2A—H2AB	0.9800	C15—C16	1.392 (4)
C2A—H2AC	0.9800	C15—H15A	0.9500
C3A—C4	1.522 (10)	C16—H16A	0.9500
C3A—H3AA	0.9800	C17—C21	1.385 (4)
C3A—H3AB	0.9800	C17—C18	1.394 (5)
C3A—H3AC	0.9800	C18—C19	1.374 (4)
C1B—C4	1.545 (9)	C18—H18A	0.9500
C1B—H1BA	0.9800	C19—H19A	0.9500
C1B—H1BB	0.9800	C20—C21	1.386 (4)
C1B—H1BC	0.9800	C20—H20A	0.9500
C2B—C4	1.518 (9)	C21—H21A	0.9500
C2B—H2BA	0.9800	C22—C23	1.461 (5)

C2B—H2BB	0.9800	C23—C24	1.379 (5)
C2B—H2BC	0.9800	C23—C27	1.391 (5)
C3B—C4	1.501 (9)	C24—C25	1.388 (5)
C3B—H3BA	0.9800	C24—H24A	0.9500
C3B—H3BB	0.9800	C25—H25A	0.9500
C3B—H3BC	0.9800	C26—C27	1.380 (5)
C4—C5	1.524 (5)	C26—H26A	0.9500
C5—C6	1.385 (5)	C27—H27A	0.9500
C5—C10	1.393 (5)		
C20—N1—C19	116.1 (3)	C8—C7—H7A	119.3
C22—N2—C12	104.6 (3)	C7—C8—C9	116.3 (4)
C22—N3—C13	107.2 (3)	C7—C8—C11	122.0 (4)
C22—N3—H3A	126.4	C9—C8—C11	121.7 (4)
C13—N3—H3A	126.4	C10—C9—C8	121.7 (3)
C26—N4—C25	116.0 (3)	C10—C9—H9A	119.2
C4—C1A—H1AA	109.5	C8—C9—H9A	119.2
C4—C1A—H1AB	109.5	C9—C10—C5	122.5 (3)
H1AA—C1A—H1AB	109.5	C9—C10—H10A	118.7
C4—C1A—H1AC	109.5	C5—C10—H10A	118.7
H1AA—C1A—H1AC	109.5	C16—C11—C12	115.0 (4)
H1AB—C1A—H1AC	109.5	C16—C11—C8	120.4 (4)
C4—C2A—H2AA	109.5	C12—C11—C8	124.6 (4)
C4—C2A—H2AB	109.5	N2—C12—C11	129.5 (5)
H2AA—C2A—H2AB	109.5	N2—C12—C13	110.2 (4)
C4—C2A—H2AC	109.5	C11—C12—C13	120.3 (4)
H2AA—C2A—H2AC	109.5	N3—C13—C14	131.6 (4)
H2AB—C2A—H2AC	109.5	N3—C13—C12	104.6 (4)
C4—C3A—H3AA	109.5	C14—C13—C12	123.8 (4)
C4—C3A—H3AB	109.5	C15—C14—C13	115.0 (3)
H3AA—C3A—H3AB	109.5	C15—C14—C17	121.8 (4)
C4—C3A—H3AC	109.5	C13—C14—C17	123.0 (4)
H3AA—C3A—H3AC	109.5	C14—C15—C16	121.6 (3)
H3AB—C3A—H3AC	109.5	C14—C15—H15A	119.2
C4—C1B—H1BA	109.5	C16—C15—H15A	119.2
C4—C1B—H1BB	109.5	C15—C16—C11	124.0 (3)
H1BA—C1B—H1BB	109.5	C15—C16—H16A	118.0

C4—C1B—H1BC	109.5	C11—C16—H16A	118.0
H1BA—C1B—H1BC	109.5	C21—C17—C18	116.9 (3)
H1BB—C1B—H1BC	109.5	C21—C17—C14	121.8 (4)
C4—C2B—H2BA	109.5	C18—C17—C14	121.2 (4)
C4—C2B—H2BB	109.5	C19—C18—C17	119.6 (3)
H2BA—C2B—H2BB	109.5	C19—C18—H18A	120.2
C4—C2B—H2BC	109.5	C17—C18—H18A	120.2
H2BA—C2B—H2BC	109.5	N1—C19—C18	124.0 (3)
H2BB—C2B—H2BC	109.5	N1—C19—H19A	118.0
C4—C3B—H3BA	109.5	C18—C19—H19A	118.0
C4—C3B—H3BB	109.5	N1—C20—C21	124.2 (3)
H3BA—C3B—H3BB	109.5	N1—C20—H20A	117.9
C4—C3B—H3BC	109.5	C21—C20—H20A	117.9
H3BA—C3B—H3BC	109.5	C17—C21—C20	119.2 (3)
H3BB—C3B—H3BC	109.5	C17—C21—H21A	120.4
C2A—C4—C1A	108.5 (8)	C20—C21—H21A	120.4
C3B—C4—C2B	108.9 (6)	N2—C22—N3	113.4 (3)
C2A—C4—C3A	106.7 (9)	N2—C22—C23	123.6 (5)
C1A—C4—C3A	112.3 (9)	N3—C22—C23	123.0 (5)
C2A—C4—C5	113.3 (4)	C24—C23—C27	116.9 (4)
C3B—C4—C5	113.4 (4)	C24—C23—C22	120.7 (5)
C1A—C4—C5	110.2 (5)	C27—C23—C22	122.3 (4)
C2B—C4—C5	109.6 (4)	C23—C24—C25	119.2 (4)
C3A—C4—C5	105.8 (4)	C23—C24—H24A	120.4
C3B—C4—C1B	109.0 (6)	C25—C24—H24A	120.4
C2B—C4—C1B	108.1 (7)	N4—C25—C24	124.2 (3)
C5—C4—C1B	107.9 (4)	N4—C25—H25A	117.9
C6—C5—C10	115.3 (3)	C24—C25—H25A	117.9
C6—C5—C4	123.2 (4)	N4—C26—C27	124.4 (4)
C10—C5—C4	121.5 (4)	N4—C26—H26A	117.8
C5—C6—C7	122.7 (3)	C27—C26—H26A	117.8
C5—C6—H6A	118.7	C26—C27—C23	119.3 (4)
C7—C6—H6A	118.7	C26—C27—H27A	120.3
C6—C7—C8	121.4 (3)	C23—C27—H27A	120.3
C6—C7—H7A	119.3		

Appendix G - Geometric parameters (Å, º) of $[Pt(dppp)(L1)]_4[OTf]_8$

Pt1—N101	2.067 (11)	C263—H26C	0.9500
Pt1—N404	2.116 (12)	C265—C266	1.3900
Pt1—P102	2.232 (8)	C265—H26D	0.9500
Pt1—P101	2.259 (8)	C266—H26E	0.9500
Pt2—N104	2.041 (13)	N301—C301	1.3900
Pt2—N201	2.126 (17)	N301—C305	1.3900
Pt2—P201	2.239 (11)	C301—C302	1.3900
Pt2—P202	2.309 (13)	C301—H30A	0.9500
Pt3—N204	2.089 (14)	C302—C303	1.3900
Pt3—N301	2.104 (13)	C302—H30B	0.9500
Pt3—P302	2.251 (9)	C303—C304	1.3900
Pt3—P301	2.272 (10)	C303—C306	1.487 (17)
Pt4—N401	2.071 (13)	C304—C305	1.3900
Pt4—N304	2.098 (13)	C304—H30C	0.9500
Pt4—P402	2.219 (10)	C305—H30D	0.9500
Pt4—P401	2.242 (10)	C306—C307	1.3900
P101—C131	1.820 (15)	C306—C311	1.3900
P101—C141	1.828 (13)	C307—C308	1.3900
P101—C124	1.838 (17)	C308—C309	1.3900
P102—C151	1.831 (13)	C309—C310	1.3900
P102—C126	1.842 (16)	C309—C312	1.518 (15)
P102—C161	1.842 (15)	C310—C311	1.3900
P201—C231	1.837 (18)	C310—H31A	0.9500
P201—C241	1.841 (17)	C311—H31B	0.9500
P201—C224	1.860 (19)	C312—C313	1.3900
P202—C251	1.816 (15)	C312—C317	1.3900
P202—C226	1.838 (18)	C313—C314	1.3900
P202—C261	1.871 (16)	C313—H31C	0.9500
P301—C331	1.792 (14)	C314—C315	1.3900
P301—C324	1.840 (17)	C314—H31D	0.9500
P301—C341	1.848 (15)	C315—C316	1.3900
P302—C361	1.820 (14)	C316—C317	1.3900
P302—C351	1.830 (16)	C316—H31E	0.9500
P302—C326	1.849 (17)	C317—H31F	0.9500
P401—C441	1.824 (15)	C318—C319	1.47 (3)
P401—C424	1.836 (18)	C319—C320	1.3900

P401—C431	1.839 (15)	C319—C323	1.3900
P402—C451	1.835 (15)	C320—C321	1.3900
P402—C461	1.841 (16)	C320—H32G	0.9500
P402—C426	1.846 (18)	C321—N304	1.3900
N102—C118	1.27 (4)	C321—H32H	0.9500
N102—C107	1.30 (2)	N304—C322	1.3900
N103—C108	1.37 (3)	C322—C323	1.3900
N103—C118	1.42 (4)	C322—H32I	0.9500
N103—H10E	0.8800	C323—H32J	0.9500
N202—C207	1.33 (3)	C324—C325	1.50 (4)
N202—C218	1.40 (5)	C324—H32A	0.9900
N203—C208	1.38 (4)	C324—H32B	0.9900
N203—C218	1.42 (5)	C325—C326	1.41 (4)
N203—H20E	0.8800	C325—H32C	0.9900
N302—C307	1.37 (2)	C325—H32D	0.9900
N302—C318	1.38 (3)	C326—H32E	0.9900
N303—C318	1.30 (3)	C326—H32F	0.9900
N303—C308	1.36 (2)	C331—C332	1.3900
N303—H30E	0.8800	C331—C336	1.3900
N402—C418	1.32 (4)	C332—C333	1.3900
N402—C407	1.43 (3)	C332—H33A	0.9500
N403—C408	1.33 (3)	C333—C334	1.3900
N403—C418	1.39 (4)	C333—H33B	0.9500
N403—H40E	0.8800	C334—C335	1.3900
F101—C115	1.328 (9)	C334—H33C	0.9500
F201—C215	1.332 (10)	C335—C336	1.3900
F301—C315	1.330 (9)	C335—H33D	0.9500
F401—C415	1.334 (10)	C336—H33E	0.9500
N101—C101	1.3900	C341—C342	1.3900
N101—C105	1.3900	C341—C346	1.3900
C101—C102	1.3900	C342—C343	1.3900
C101—H10A	0.9500	C342—H34A	0.9500
C102—C103	1.3900	C343—C344	1.3900
C102—H10B	0.9500	C343—H34B	0.9500
C103—C104	1.3900	C344—C345	1.3900
C103—C106	1.561 (16)	C344—H34C	0.9500
C104—C105	1.3900	C345—C346	1.3900

C104—H10C	0.9500	C345—H34D	0.9500
C105—H10D	0.9500	C346—H34E	0.9500
C106—C107	1.3900	C351—C352	1.3900
C106—C111	1.3900	C351—C356	1.3900
C107—C108	1.3900	C352—C353	1.3900
C108—C109	1.3900	C352—H35A	0.9500
C109—C110	1.3900	C353—C354	1.3900
C109—C112	1.548 (17)	C353—H35B	0.9500
C110—C111	1.3900	C354—C355	1.3900
C110—H11A	0.9500	C354—H35C	0.9500
C111—H11B	0.9500	C355—C356	1.3900
C112—C113	1.3900	C355—H35D	0.9500
C112—C117	1.3900	C356—H35E	0.9500
C113—C114	1.3900	C361—C362	1.3900
C113—H11C	0.9500	C361—C366	1.3900
C114—C115	1.3900	C362—C363	1.3900
C114—H11D	0.9500	C362—H36A	0.9500
C115—C116	1.3900	C363—C364	1.3900
C116—C117	1.3900	C363—H36B	0.9500
C116—H11E	0.9500	C364—C365	1.3900
C117—H11F	0.9500	C364—H36C	0.9500
C118—C119	1.50 (4)	C365—C366	1.3900
C119—C120	1.3900	C365—H36D	0.9500
C119—C123	1.3900	C366—H36E	0.9500
C120—C121	1.3900	N401—C401	1.3900
C120—H12G	0.9500	N401—C405	1.3900
C121—N104	1.3900	C401—C402	1.3900
C121—H12H	0.9500	C401—H40A	0.9500
N104—C122	1.3900	C402—C403	1.3900
C122—C123	1.3900	C402—H40B	0.9500
C122—H12I	0.9500	C403—C404	1.3900
C123—H12J	0.9500	C403—C406	1.60 (2)
C124—C125	1.56 (4)	C404—C405	1.3900
C124—H12A	0.9900	C404—H40C	0.9500
C124—H12B	0.9900	C405—H40D	0.9500
C125—C126	1.47 (4)	C406—C407	1.3900
C125—H12C	0.9900	C406—C411	1.3900

C125—H12D	0.9900	C407—C408	1.3900
C126—H12E	0.9900	C408—C409	1.3900
C126—H12F	0.9900	C409—C410	1.3900
C131—C132	1.3900	C409—C412	1.53 (3)
C131—C136	1.3900	C410—C411	1.3900
C132—C133	1.3900	C410—H41A	0.9500
C132—H13A	0.9500	C411—H41B	0.9500
C133—C134	1.3900	C412—C413	1.3900
C133—H13B	0.9500	C412—C417	1.3900
C134—C135	1.3900	C413—C414	1.3900
C134—H13C	0.9500	C413—H41C	0.9500
C135—C136	1.3900	C414—C415	1.3900
C135—H13D	0.9500	C414—H41D	0.9500
C136—H13E	0.9500	C415—C416	1.3900
C141—C142	1.3900	C416—C417	1.3900
C141—C146	1.3900	C416—H41E	0.9500
C142—C143	1.3900	C417—H41F	0.9500
C142—H14A	0.9500	C418—C419	1.48 (3)
C143—C144	1.3900	C419—C420	1.3900
C143—H14B	0.9500	C419—C423	1.3900
C144—C145	1.3900	C420—C421	1.3900
C144—H14C	0.9500	C420—H42G	0.9500
C145—C146	1.3900	C421—N404	1.3900
C145—H14D	0.9500	C421—H42H	0.9500
C146—H14E	0.9500	N404—C422	1.3900
C151—C152	1.3900	C422—C423	1.3900
C151—C156	1.3900	C422—H42I	0.9500
C152—C153	1.3900	C423—H42J	0.9500
C152—H15A	0.9500	C424—C425	1.46 (6)
C153—C154	1.3900	C424—H42A	0.9900
C153—H15B	0.9500	C424—H42B	0.9900
C154—C155	1.3900	C425—C426	1.61 (6)
C154—H15C	0.9500	C425—H42C	0.9900
C155—C156	1.3900	C425—H42D	0.9900
C155—H15D	0.9500	C426—H42E	0.9900
C156—H15E	0.9500	C426—H42F	0.9900
C161—C162	1.3900	C431—C432	1.3900

C161—C166	1.3900	C431—C436	1.3900
C162—C163	1.3900	C432—C433	1.3900
C162—H16A	0.9500	C432—H43A	0.9500
C163—C164	1.3900	C433—C434	1.3900
C163—H16B	0.9500	C433—H43B	0.9500
C164—C165	1.3900	C434—C435	1.3900
C164—H16C	0.9500	C434—H43C	0.9500
C165—C166	1.3900	C435—C436	1.3900
C165—H16D	0.9500	C435—H43D	0.9500
C166—H16E	0.9500	C436—H43E	0.9500
N201—C201	1.3900	C441—C442	1.3900
N201—C205	1.3900	C441—C446	1.3900
C201—C202	1.3900	C442—C443	1.3900
C201—H20A	0.9500	C442—H44A	0.9500
C202—C203	1.3900	C443—C444	1.3900
C202—H20B	0.9500	C443—H44B	0.9500
C203—C204	1.3900	C444—C445	1.3900
C203—C206	1.49 (3)	C444—H44C	0.9500
C204—C205	1.3900	C445—C446	1.3900
C204—H20C	0.9500	C445—H44D	0.9500
C205—H20D	0.9500	C446—H44E	0.9500
C206—C207	1.3900	C451—C452	1.3900
C206—C211	1.3900	C451—C456	1.3900
C207—C208	1.3900	C452—C453	1.3900
C208—C209	1.3900	C452—H45A	0.9500
C209—C210	1.3900	C453—C454	1.3900
C209—C212	1.59 (3)	C453—H45B	0.9500
C210—C211	1.3900	C454—C455	1.3900
C210—H21A	0.9500	C454—H45C	0.9500
C211—H21B	0.9500	C455—C456	1.3900
C212—C213	1.3900	C455—H45D	0.9500
C212—C217	1.3900	C456—H45E	0.9500
C213—C214	1.3900	C461—C462	1.3900
C213—H21C	0.9500	C461—C466	1.3900
C214—C215	1.3900	C462—C463	1.3900
C214—H21D	0.9500	C462—H46A	0.9500
C215—C216	1.3900	C463—C464	1.3900

C216—C217	1.3900	C463—H46B	0.9500
C216—H21E	0.9500	C464—C465	1.3900
C217—H21F	0.9500	C464—H46C	0.9500
C218—C219	1.39 (4)	C465—C466	1.3900
C219—C220	1.3900	C465—H46D	0.9500
C219—C223	1.3900	C466—H46E	0.9500
C220—C221	1.3900	S1—O11	1.437 (9)
C220—H22G	0.9500	S1—O12	1.449 (9)
C221—N204	1.3900	S1—O13	1.456 (9)
C221—H22H	0.9500	S1—C1T	1.821 (9)
N204—C222	1.3900	C1T—F13	1.320 (10)
C222—C223	1.3900	C1T—F12	1.322 (10)
C222—H22I	0.9500	C1T—F11	1.324 (10)
C223—H22J	0.9500	S2—O21	1.436 (9)
C224—C225	1.44 (5)	S2—O23	1.447 (9)
C224—H22A	0.9900	S2—O22	1.458 (9)
C224—H22B	0.9900	S2—C2T	1.817 (10)
C225—C226	1.48 (5)	C2T—F21	1.317 (10)
C225—H22C	0.9900	C2T—F22	1.319 (10)
C225—H22D	0.9900	C2T—F23	1.319 (10)
C226—H22E	0.9900	S3—O31	1.447 (9)
C226—H22F	0.9900	S3—O32	1.448 (9)
C231—C232	1.3900	S3—O33	1.452 (9)
C231—C236	1.3900	S3—C3T	1.817 (10)
C232—C233	1.3900	C3T—F31	1.317 (10)
C232—H23A	0.9500	C3T—F32	1.319 (10)
C233—C234	1.3900	C3T—F33	1.322 (10)
C233—H23B	0.9500	S4—O42	1.443 (10)
C234—C235	1.3900	S4—O41	1.448 (10)
C234—H23C	0.9500	S4—O43	1.454 (10)
C235—C236	1.3900	S4—C4T	1.813 (10)
C235—H23D	0.9500	C4T—F41	1.318 (10)
C236—H23E	0.9500	C4T—F42	1.318 (10)
C241—C242	1.3900	C4T—F43	1.320 (10)
C241—C246	1.3900	S5—O51	1.433 (9)
C242—C243	1.3900	S5—O52	1.459 (9)
C242—H24A	0.9500	S5—O53	1.463 (9)

C243—C244	1.3900	S5—C5T	1.816 (9)
C243—H24B	0.9500	C5T—F53	1.319 (10)
C244—C245	1.3900	C5T—F52	1.322 (10)
C244—H24C	0.9500	C5T—F51	1.333 (10)
C245—C246	1.3900	S6—O62	1.429 (9)
C245—H24D	0.9500	S6—O63	1.461 (9)
C246—H24E	0.9500	S6—O61	1.466 (9)
C251—C252	1.3900	S6—C6T	1.832 (9)
C251—C256	1.3900	C6T—F63	1.322 (10)
C252—C253	1.3900	C6T—F61	1.328 (10)
C252—H25A	0.9500	C6T—F62	1.337 (10)
C253—C254	1.3900	S7—O71	1.442 (10)
C253—H25B	0.9500	S7—O73	1.450 (10)
C254—C255	1.3900	S7—O72	1.457 (10)
C254—H25C	0.9500	S7—C7T	1.817 (10)
C255—C256	1.3900	C7T—F73	1.319 (10)
C255—H25D	0.9500	C7T—F71	1.319 (10)
C256—H25E	0.9500	C7T—F72	1.319 (10)
C261—C262	1.3900	S8—O83	1.445 (9)
C261—C266	1.3900	S8—O82	1.448 (9)
C262—C264	1.3900	S8—O81	1.449 (10)
C262—H26A	0.9500	S8—C8T	1.821 (10)
C264—C263	1.3900	C8T—F83	1.318 (10)
C264—H26B	0.9500	C8T—F82	1.321 (10)
C263—C265	1.3900	C8T—F81	1.322 (10)
N101—Pt1—N404	86.5 (6)	N301—C301—H30A	120.0
N101—Pt1—P102	91.5 (5)	C302—C301—H30A	120.0
N404—Pt1—P102	177.9 (5)	C303—C302—C301	120.0
N101—Pt1—P101	176.9 (5)	C303—C302—H30B	120.0
N404—Pt1—P101	90.7 (5)	C301—C302—H30B	120.0
P102—Pt1—P101	91.3 (3)	C302—C303—C304	120.0
N104—Pt2—N201	84.6 (8)	C302—C303—C306	120.5 (14)
N104—Pt2—P201	177.0 (6)	C304—C303—C306	119.5 (14)
N201—Pt2—P201	93.1 (8)	C303—C304—C305	120.0
N104—Pt2—P202	91.1 (6)	C303—C304—H30C	120.0
N201—Pt2—P202	175.5 (7)	C305—C304—H30C	120.0

P201—Pt2—P202	91.1 (6)	C304—C305—N301	120.0
N204—Pt3—N301	85.8 (7)	C304—C305—H30D	120.0
N204—Pt3—P302	91.3 (6)	N301—C305—H30D	120.0
N301—Pt3—P302	175.0 (6)	C307—C306—C311	120.0
N204—Pt3—P301	176.8 (5)	C307—C306—C303	120.5 (13)
N301—Pt3—P301	91.4 (6)	C311—C306—C303	119.2 (13)
P302—Pt3—P301	91.6 (3)	N302—C307—C306	127.1 (15)
N401—Pt4—N304	87.1 (7)	N302—C307—C308	112.7 (15)
N401—Pt4—P402	91.3 (6)	C306—C307—C308	120.0
N304—Pt4—P402	175.6 (6)	N303—C308—C307	104.2 (15)
N401—Pt4—P401	174.6 (6)	N303—C308—C309	135.7 (15)
N304—Pt4—P401	92.1 (5)	C307—C308—C309	120.0
P402—Pt4—P401	89.9 (4)	C308—C309—C310	120.0
C131—P101—C141	106.1 (12)	C308—C309—C312	123.5 (12)
C131—P101—C124	100.9 (13)	C310—C309—C312	116.2 (12)
C141—P101—C124	105.6 (12)	C311—C310—C309	120.0
C131—P101—Pt1	112.9 (9)	C311—C310—H31A	120.0
C141—P101—Pt1	116.0 (8)	C309—C310—H31A	120.0
C124—P101—Pt1	113.9 (10)	C310—C311—C306	120.0
C151—P102—C126	104.0 (12)	C310—C311—H31B	120.0
C151—P102—C161	106.8 (11)	C306—C311—H31B	120.0
C126—P102—C161	105.4 (13)	C313—C312—C317	120.0
C151—P102—Pt1	115.3 (8)	C313—C312—C309	120.7 (12)
C126—P102—Pt1	115.8 (10)	C317—C312—C309	119.2 (12)
C161—P102—Pt1	108.8 (9)	C314—C313—C312	120.0
C231—P201—C241	107 (2)	C314—C313—H31C	120.0
C231—P201—C224	109 (2)	C312—C313—H31C	120.0
C241—P201—C224	101 (2)	C313—C314—C315	120.0
C231—P201—Pt2	112.8 (16)	C313—C314—H31D	120.0
C241—P201—Pt2	115.0 (13)	C315—C314—H31D	120.0
C224—P201—Pt2	111.5 (16)	F301—C315—C316	118.3 (14)
C251—P202—C226	104.5 (17)	F301—C315—C314	121.7 (14)
C251—P202—C261	102.5 (14)	C316—C315—C314	120.0
C226—P202—C261	100.8 (17)	C315—C316—C317	120.0
C251—P202—Pt2	116.3 (11)	C315—C316—H31E	120.0
C226—P202—Pt2	119.3 (15)	C317—C316—H31E	120.0
C261—P202—Pt2	111.2 (11)	C316—C317—C312	120.0

C331—P301—C324	107.7 (14)	C316—C317—H31F	120.0
C331—P301—C341	105.0 (12)	C312—C317—H31F	120.0
C324—P301—C341	104.9 (13)	N303—C318—N302	115 (2)
C331—P301—Pt3	113.4 (9)	N303—C318—C319	128 (2)
C324—P301—Pt3	112.8 (12)	N302—C318—C319	117 (2)
C341—P301—Pt3	112.3 (9)	C320—C319—C323	120.0
C361—P302—C351	108.5 (15)	C320—C319—C318	116.5 (16)
C361—P302—C326	103.7 (14)	C323—C319—C318	123.4 (16)
C351—P302—C326	104.1 (16)	C319—C320—C321	120.0
C361—P302—Pt3	116.5 (9)	C319—C320—H32G	120.0
C351—P302—Pt3	112.7 (11)	C321—C320—H32G	120.0
C326—P302—Pt3	110.2 (12)	N304—C321—C320	120.0
C441—P401—C424	110.8 (17)	N304—C321—H32H	120.0
C441—P401—C431	100.3 (13)	C320—C321—H32H	120.0
C424—P401—C431	101.5 (17)	C322—N304—C321	120.0
C441—P401—Pt4	116.8 (9)	C322—N304—Pt4	121.4 (9)
C424—P401—Pt4	113.2 (15)	C321—N304—Pt4	118.6 (9)
C431—P401—Pt4	112.5 (9)	N304—C322—C323	120.0
C451—P402—C461	106.6 (14)	N304—C322—H32I	120.0
C451—P402—C426	102.7 (16)	C323—C322—H32I	120.0
C461—P402—C426	105.4 (17)	C322—C323—C319	120.0
C451—P402—Pt4	111.2 (11)	C322—C323—H32J	120.0
C461—P402—Pt4	116.5 (11)	C319—C323—H32J	120.0
C426—P402—Pt4	113.3 (14)	C325—C324—P301	110 (2)
C118—N102—C107	106 (2)	C325—C324—H32A	109.7
C108—N103—C118	102 (2)	P301—C324—H32A	109.7
C108—N103—H10E	128.8	C325—C324—H32B	109.7
C118—N103—H10E	128.8	P301—C324—H32B	109.7
C207—N202—C218	109 (3)	H32A—C324—H32B	108.2
C208—N203—C218	107 (3)	C326—C325—C324	116 (3)
C208—N203—H20E	126.5	C326—C325—H32C	108.3
C218—N203—H20E	126.5	C324—C325—H32C	108.3
C307—N302—C318	100 (2)	C326—C325—H32D	108.3
C318—N303—C308	108 (2)	C324—C325—H32D	108.3
C318—N303—H30E	126.1	H32C—C325—H32D	107.4
C308—N303—H30E	126.1	C325—C326—P302	120 (2)
C418—N402—C407	100 (2)	C325—C326—H32E	107.4

C408—N403—C418	105 (2)	P302—C326—H32E	107.4
C408—N403—H40E	127.5	C325—C326—H32F	107.4
C418—N403—H40E	127.5	P302—C326—H32F	107.4
C101—N101—C105	120.0	H32E—C326—H32F	106.9
C101—N101—Pt1	120.5 (9)	C332—C331—C336	120.0
C105—N101—Pt1	119.5 (9)	C332—C331—P301	119.0 (14)
C102—C101—N101	120.0	C336—C331—P301	121.0 (14)
C102—C101—H10A	120.0	C331—C332—C333	120.0
N101—C101—H10A	120.0	C331—C332—H33A	120.0
C103—C102—C101	120.0	C333—C332—H33A	120.0
C103—C102—H10B	120.0	C334—C333—C332	120.0
C101—C102—H10B	120.0	C334—C333—H33B	120.0
C102—C103—C104	120.0	C332—C333—H33B	120.0
C102—C103—C106	121.1 (12)	C335—C334—C333	120.0
C104—C103—C106	118.8 (12)	C335—C334—H33C	120.0
C105—C104—C103	120.0	C333—C334—H33C	120.0
C105—C104—H10C	120.0	C334—C335—C336	120.0
C103—C104—H10C	120.0	C334—C335—H33D	120.0
C104—C105—N101	120.0	C336—C335—H33D	120.0
C104—C105—H10D	120.0	C335—C336—C331	120.0
N101—C105—H10D	120.0	C335—C336—H33E	120.0
C107—C106—C111	120.0	C331—C336—H33E	120.0
C107—C106—C103	120.4 (12)	C342—C341—C346	120.0
C111—C106—C103	119.5 (12)	C342—C341—P301	119.2 (15)
N102—C107—C108	111.5 (15)	C346—C341—P301	120.8 (15)
N102—C107—C106	128.5 (15)	C341—C342—C343	120.0
C108—C107—C106	120.0	C341—C342—H34A	120.0
N103—C108—C107	106.0 (15)	C343—C342—H34A	120.0
N103—C108—C109	134.0 (15)	C342—C343—C344	120.0
C107—C108—C109	120.0	C342—C343—H34B	120.0
C110—C109—C108	120.0	C344—C343—H34B	120.0
C110—C109—C112	118.1 (13)	C345—C344—C343	120.0
C108—C109—C112	121.9 (13)	C345—C344—H34C	120.0
C109—C110—C111	120.0	C343—C344—H34C	120.0
C109—C110—H11A	120.0	C346—C345—C344	120.0
C111—C110—H11A	120.0	C346—C345—H34D	120.0
C110—C111—C106	120.0	C344—C345—H34D	120.0

C110—C111—H11B	120.0	C345—C346—C341	120.0
C106—C111—H11B	120.0	C345—C346—H34E	120.0
C113—C112—C117	120.0	C341—C346—H34E	120.0
C113—C112—C109	123.9 (14)	C352—C351—C356	120.0
C117—C112—C109	116.1 (14)	C352—C351—P302	126 (2)
C112—C113—C114	120.0	C356—C351—P302	114 (2)
C112—C113—H11C	120.0	C351—C352—C353	120.0
C114—C113—H11C	120.0	C351—C352—H35A	120.0
C115—C114—C113	120.0	C353—C352—H35A	120.0
C115—C114—H11D	120.0	C354—C353—C352	120.0
C113—C114—H11D	120.0	C354—C353—H35B	120.0
F101—C115—C116	123 (2)	C352—C353—H35B	120.0
F101—C115—C114	117 (2)	C353—C354—C355	120.0
C116—C115—C114	120.0	C353—C354—H35C	120.0
C115—C116—C117	120.0	C355—C354—H35C	120.0
C115—C116—H11E	120.0	C354—C355—C356	120.0
C117—C116—H11E	120.0	C354—C355—H35D	120.0
C116—C117—C112	120.0	C356—C355—H35D	120.0
C116—C117—H11F	120.0	C355—C356—C351	120.0
C112—C117—H11F	120.0	C355—C356—H35E	120.0
N102—C118—N103	114 (3)	C351—C356—H35E	120.0
N102—C118—C119	124 (3)	C362—C361—C366	120.0
N103—C118—C119	121 (3)	C362—C361—P302	114.2 (14)
C120—C119—C123	120.0	C366—C361—P302	125.7 (14)
C120—C119—C118	117.9 (18)	C361—C362—C363	120.0
C123—C119—C118	122.1 (18)	C361—C362—H36A	120.0
C121—C120—C119	120.0	C363—C362—H36A	120.0
C121—C120—H12G	120.0	C364—C363—C362	120.0
C119—C120—H12G	120.0	C364—C363—H36B	120.0
N104—C121—C120	120.0	C362—C363—H36B	120.0
N104—C121—H12H	120.0	C363—C364—C365	120.0
C120—C121—H12H	120.0	C363—C364—H36C	120.0
C122—N104—C121	120.0	C365—C364—H36C	120.0
C122—N104—Pt2	126.7 (10)	C366—C365—C364	120.0
C121—N104—Pt2	113.3 (10)	C366—C365—H36D	120.0
N104—C122—C123	120.0	C364—C365—H36D	120.0
N104—C122—H12I	120.0	C365—C366—C361	120.0

C123—C122—H12I	120.0	C365—C366—H36E	120.0
C122—C123—C119	120.0	C361—C366—H36E	120.0
C122—C123—H12J	120.0	C401—N401—C405	120.0
C119—C123—H12J	120.0	C401—N401—Pt4	116.9 (10)
C125—C124—P101	111.4 (18)	C405—N401—Pt4	122.1 (10)
C125—C124—H12A	109.3	C402—C401—N401	120.0
P101—C124—H12A	109.3	C402—C401—H40A	120.0
C125—C124—H12B	109.3	N401—C401—H40A	120.0
P101—C124—H12B	109.3	C401—C402—C403	120.0
H12A—C124—H12B	108.0	C401—C402—H40B	120.0
C126—C125—C124	116 (2)	C403—C402—H40B	120.0
C126—C125—H12C	108.2	C404—C403—C402	120.0
C124—C125—H12C	108.2	C404—C403—C406	121.4 (15)
C126—C125—H12D	108.2	C402—C403—C406	117.9 (15)
C124—C125—H12D	108.2	C405—C404—C403	120.0
H12C—C125—H12D	107.3	C405—C404—H40C	120.0
C125—C126—P102	114.1 (19)	C403—C404—H40C	120.0
C125—C126—H12E	108.7	C404—C405—N401	120.0
P102—C126—H12E	108.7	C404—C405—H40D	120.0
C125—C126—H12F	108.7	N401—C405—H40D	120.0
P102—C126—H12F	108.7	C407—C406—C411	120.0
H12E—C126—H12F	107.6	C407—C406—C403	119.5 (16)
C132—C131—C136	120.0	C411—C406—C403	119.6 (16)
C132—C131—P101	117.5 (19)	C408—C407—C406	120.0
C136—C131—P101	122.4 (19)	C408—C407—N402	111.7 (18)
C131—C132—C133	120.0	C406—C407—N402	128.2 (18)
C131—C132—H13A	120.0	N403—C408—C407	107.0 (18)
C133—C132—H13A	120.0	N403—C408—C409	133.0 (18)
C132—C133—C134	120.0	C407—C408—C409	120.0
C132—C133—H13B	120.0	C410—C409—C408	120.0
C134—C133—H13B	120.0	C410—C409—C412	116.5 (19)
C133—C134—C135	120.0	C408—C409—C412	123 (2)
C133—C134—H13C	120.0	C409—C410—C411	120.0
C135—C134—H13C	120.0	C409—C410—H41A	120.0
C136—C135—C134	120.0	C411—C410—H41A	120.0
C136—C135—H13D	120.0	C410—C411—C406	120.0
C134—C135—H13D	120.0	C410—C411—H41B	120.0

C135—C136—C131	120.0	C406—C411—H41B	120.0
C135—C136—H13E	120.0	C413—C412—C417	120.0
C131—C136—H13E	120.0	C413—C412—C409	123 (3)
C142—C141—C146	120.0	C417—C412—C409	117 (3)
C142—C141—P101	118.7 (12)	C412—C413—C414	120.0
C146—C141—P101	121.2 (12)	C412—C413—H41C	120.0
C141—C142—C143	120.0	C414—C413—H41C	120.0
C141—C142—H14A	120.0	C413—C414—C415	120.0
C143—C142—H14A	120.0	C413—C414—H41D	120.0
C144—C143—C142	120.0	C415—C414—H41D	120.0
C144—C143—H14B	120.0	F401—C415—C416	131 (4)
C142—C143—H14B	120.0	F401—C415—C414	109 (4)
C143—C144—C145	120.0	C416—C415—C414	120.0
C143—C144—H14C	120.0	C415—C416—C417	120.0
C145—C144—H14C	120.0	C415—C416—H41E	120.0
C146—C145—C144	120.0	C417—C416—H41E	120.0
C146—C145—H14D	120.0	C416—C417—C412	120.0
C144—C145—H14D	120.0	C416—C417—H41F	120.0
C145—C146—C141	120.0	C412—C417—H41F	120.0
C145—C146—H14E	120.0	N402—C418—N403	117 (3)
C141—C146—H14E	120.0	N402—C418—C419	118 (3)
C152—C151—C156	120.0	N403—C418—C419	126 (3)
C152—C151—P102	122.8 (12)	C420—C419—C423	120.0
C156—C151—P102	117.2 (12)	C420—C419—C418	118.3 (18)
C153—C152—C151	120.0	C423—C419—C418	121.7 (18)
C153—C152—H15A	120.0	C419—C420—C421	120.0
C151—C152—H15A	120.0	C419—C420—H42G	120.0
C152—C153—C154	120.0	C421—C420—H42G	120.0
C152—C153—H15B	120.0	C420—C421—N404	120.0
C154—C153—H15B	120.0	C420—C421—H42H	120.0
C153—C154—C155	120.0	N404—C421—H42H	120.0
C153—C154—H15C	120.0	C422—N404—C421	120.0
C155—C154—H15C	120.0	C422—N404—Pt1	122.5 (9)
C156—C155—C154	120.0	C421—N404—Pt1	117.4 (9)
C156—C155—H15D	120.0	N404—C422—C423	120.0
C154—C155—H15D	120.0	N404—C422—H42I	120.0
C155—C156—C151	120.0	C423—C422—H42I	120.0

C155—C156—H15E	120.0	C422—C423—C419	120.0
C151—C156—H15E	120.0	C422—C423—H42J	120.0
C162—C161—C166	120.0	C419—C423—H42J	120.0
C162—C161—P102	123.8 (15)	C425—C424—P401	109 (3)
C166—C161—P102	115.1 (15)	C425—C424—H42A	109.8
C163—C162—C161	120.0	P401—C424—H42A	109.8
C163—C162—H16A	120.0	C425—C424—H42B	109.8
C161—C162—H16A	120.0	P401—C424—H42B	109.8
C164—C163—C162	120.0	H42A—C424—H42B	108.3
C164—C163—H16B	120.0	C424—C425—C426	116 (4)
C162—C163—H16B	120.0	C424—C425—H42C	108.3
C163—C164—C165	120.0	C426—C425—H42C	108.3
C163—C164—H16C	120.0	C424—C425—H42D	108.3
C165—C164—H16C	120.0	C426—C425—H42D	108.3
C166—C165—C164	120.0	H42C—C425—H42D	107.4
C166—C165—H16D	120.0	C425—C426—P402	109 (3)
C164—C165—H16D	120.0	C425—C426—H42E	109.8
C165—C166—C161	120.0	P402—C426—H42E	109.8
C165—C166—H16E	120.0	C425—C426—H42F	109.8
C161—C166—H16E	120.0	P402—C426—H42F	109.8
C201—N201—C205	120.0	H42E—C426—H42F	108.2
C201—N201—Pt2	118.3 (13)	C432—C431—C436	120.0
C205—N201—Pt2	121.7 (13)	C432—C431—P401	120.5 (18)
N201—C201—C202	120.0	C436—C431—P401	119.3 (19)
N201—C201—H20A	120.0	C433—C432—C431	120.0
C202—C201—H20A	120.0	C433—C432—H43A	120.0
C201—C202—C203	120.0	C431—C432—H43A	120.0
C201—C202—H20B	120.0	C434—C433—C432	120.0
C203—C202—H20B	120.0	C434—C433—H43B	120.0
C204—C203—C202	120.0	C432—C433—H43B	120.0
C204—C203—C206	117 (2)	C433—C434—C435	120.0
C202—C203—C206	123 (2)	C433—C434—H43C	120.0
C203—C204—C205	120.0	C435—C434—H43C	120.0
C203—C204—H20C	120.0	C436—C435—C434	120.0
C205—C204—H20C	120.0	C436—C435—H43D	120.0
C204—C205—N201	120.0	C434—C435—H43D	120.0
C204—C205—H20D	120.0	C435—C436—C431	120.0

N201—C205—H20D	120.0	C435—C436—H43E	120.0
C207—C206—C211	120.0	C431—C436—H43E	120.0
C207—C206—C203	118 (2)	C442—C441—C446	120.0
C211—C206—C203	122 (2)	C442—C441—P401	119.3 (16)
N202—C207—C206	131 (3)	C446—C441—P401	120.7 (16)
N202—C207—C208	109 (3)	C441—C442—C443	120.0
C206—C207—C208	120.0	C441—C442—H44A	120.0
N203—C208—C207	108 (3)	C443—C442—H44A	120.0
N203—C208—C209	132 (3)	C442—C443—C444	120.0
C207—C208—C209	120.0	C442—C443—H44B	120.0
C210—C209—C208	120.0	C444—C443—H44B	120.0
C210—C209—C212	114 (3)	C445—C444—C443	120.0
C208—C209—C212	126 (3)	C445—C444—H44C	120.0
C211—C210—C209	120.0	C443—C444—H44C	120.0
C211—C210—H21A	120.0	C444—C445—C446	120.0
C209—C210—H21A	120.0	C444—C445—H44D	120.0
C210—C211—C206	120.0	C446—C445—H44D	120.0
C210—C211—H21B	120.0	C445—C446—C441	120.0
C206—C211—H21B	120.0	C445—C446—H44E	120.0
C213—C212—C217	120.0	C441—C446—H44E	120.0
C213—C212—C209	114 (3)	C452—C451—C456	120.0
C217—C212—C209	126 (3)	C452—C451—P402	115.3 (18)
C212—C213—C214	120.0	C456—C451—P402	124.6 (18)
C212—C213—H21C	120.0	C453—C452—C451	120.0
C214—C213—H21C	120.0	C453—C452—H45A	120.0
C215—C214—C213	120.0	C451—C452—H45A	120.0
C215—C214—H21D	120.0	C454—C453—C452	120.0
C213—C214—H21D	120.0	C454—C453—H45B	120.0
F201—C215—C214	128 (3)	C452—C453—H45B	120.0
F201—C215—C216	112 (3)	C453—C454—C455	120.0
C214—C215—C216	120.0	C453—C454—H45C	120.0
C215—C216—C217	120.0	C455—C454—H45C	120.0
C215—C216—H21E	120.0	C454—C455—C456	120.0
C217—C216—H21E	120.0	C454—C455—H45D	120.0
C216—C217—C212	120.0	C456—C455—H45D	120.0
C216—C217—H21F	120.0	C455—C456—C451	120.0
C212—C217—H21F	120.0	C455—C456—H45E	120.0

C219—C218—N202	122 (3)	C451—C456—H45E	120.0
C219—C218—N203	131 (4)	C462—C461—C466	120.0
N202—C218—N203	106 (3)	C462—C461—P402	123 (2)
C218—C219—C220	122 (2)	C466—C461—P402	117 (2)
C218—C219—C223	117 (2)	C461—C462—C463	120.0
C220—C219—C223	120.0	C461—C462—H46A	120.0
C219—C220—C221	120.0	C463—C462—H46A	120.0
C219—C220—H22G	120.0	C464—C463—C462	120.0
C221—C220—H22G	120.0	C464—C463—H46B	120.0
C220—C221—N204	120.0	C462—C463—H46B	120.0
C220—C221—H22H	120.0	C463—C464—C465	120.0
N204—C221—H22H	120.0	C463—C464—H46C	120.0
C222—N204—C221	120.0	C465—C464—H46C	120.0
C222—N204—Pt3	128.0 (10)	C466—C465—C464	120.0
C221—N204—Pt3	111.8 (10)	C466—C465—H46D	120.0
N204—C222—C223	120.0	C464—C465—H46D	120.0
N204—C222—H22I	120.0	C465—C466—C461	120.0
C223—C222—H22I	120.0	C465—C466—H46E	120.0
C222—C223—C219	120.0	C461—C466—H46E	120.0
C222—C223—H22J	120.0	O11—S1—O12	114.9 (9)
C219—C223—H22J	120.0	O11—S1—O13	113.4 (8)
C225—C224—P201	117 (3)	O12—S1—O13	112.6 (9)
C225—C224—H22A	108.0	O11—S1—C1T	103.7 (10)
P201—C224—H22A	108.0	O12—S1—C1T	106.4 (9)
C225—C224—H22B	108.0	O13—S1—C1T	104.6 (9)
P201—C224—H22B	108.0	F13—C1T—F12	108.6 (11)
H22A—C224—H22B	107.3	F13—C1T—F11	108.3 (11)
C224—C225—C226	134 (4)	F12—C1T—F11	109.0 (11)
C224—C225—H22C	103.8	F13—C1T—S1	108.4 (11)
C226—C225—H22C	103.8	F12—C1T—S1	112.6 (12)
C224—C225—H22D	103.8	F11—C1T—S1	109.9 (12)
C226—C225—H22D	103.8	O21—S2—O23	115.2 (10)
H22C—C225—H22D	105.4	O21—S2—O22	114.5 (10)
C225—C226—P202	101 (3)	O23—S2—O22	114.5 (10)
C225—C226—H22E	111.5	O21—S2—C2T	99.7 (15)
P202—C226—H22E	111.5	O23—S2—C2T	106.2 (14)
C225—C226—H22F	111.5	O22—S2—C2T	104.6 (14)

P202—C226—H22F	111.5	F21—C2T—F22	108.5 (14)
H22E—C226—H22F	109.3	F21—C2T—F23	108.7 (14)
C232—C231—C236	120.0	F22—C2T—F23	108.8 (13)
C232—C231—P201	112 (4)	F21—C2T—S2	109.2 (17)
C236—C231—P201	127 (4)	F22—C2T—S2	110.4 (17)
C233—C232—C231	120.0	F23—C2T—S2	111.2 (18)
C233—C232—H23A	120.0	O31—S3—O32	116.3 (10)
C231—C232—H23A	120.0	O31—S3—O33	115.9 (10)
C232—C233—C234	120.0	O32—S3—O33	115.9 (10)
C232—C233—H23B	120.0	O31—S3—C3T	98.9 (12)
C234—C233—H23B	120.0	O32—S3—C3T	102.8 (13)
C233—C234—C235	120.0	O33—S3—C3T	103.2 (13)
C233—C234—H23C	120.0	F31—C3T—F32	110.6 (13)
C235—C234—H23C	120.0	F31—C3T—F33	109.5 (12)
C236—C235—C234	120.0	F32—C3T—F33	108.2 (12)
C236—C235—H23D	120.0	F31—C3T—S3	108.4 (16)
C234—C235—H23D	120.0	F32—C3T—S3	111.3 (14)
C235—C236—C231	120.0	F33—C3T—S3	108.8 (13)
C235—C236—H23E	120.0	O42—S4—O41	115.8 (11)
C231—C236—H23E	120.0	O42—S4—O43	115.6 (13)
C242—C241—C246	120.0	O41—S4—O43	114.6 (12)
C242—C241—P201	120 (3)	O42—S4—C4T	103.5 (18)
C246—C241—P201	119 (3)	O41—S4—C4T	103 (2)
C241—C242—C243	120.0	O43—S4—C4T	101.9 (19)
C241—C242—H24A	120.0	F41—C4T—F42	106.5 (16)
C243—C242—H24A	120.0	F41—C4T—F43	105.8 (16)
C244—C243—C242	120.0	F42—C4T—F43	106.1 (16)
C244—C243—H24B	120.0	F41—C4T—S4	120 (3)
C242—C243—H24B	120.0	F42—C4T—S4	109 (2)
C245—C244—C243	120.0	F43—C4T—S4	108.6 (18)
C245—C244—H24C	120.0	O51—S5—O52	116.5 (10)
C243—C244—H24C	120.0	O51—S5—O53	115.1 (10)
C244—C245—C246	120.0	O52—S5—O53	113.0 (9)
C244—C245—H24D	120.0	O51—S5—C5T	104.8 (7)
C246—C245—H24D	120.0	O52—S5—C5T	102.4 (7)
C245—C246—C241	120.0	O53—S5—C5T	102.7 (7)
C245—C246—H24E	120.0	F53—C5T—F52	109.6 (12)

C241—C246—H24E	120.0	F53—C5T—F51	108.4 (11)
C252—C251—C256	120.0	F52—C5T—F51	107.8 (11)
C252—C251—P202	116.5 (17)	F53—C5T—S5	111.1 (9)
C256—C251—P202	123.4 (17)	F52—C5T—S5	110.1 (9)
C251—C252—C253	120.0	F51—C5T—S5	109.7 (9)
C251—C252—H25A	120.0	O62—S6—O63	115.4 (9)
C253—C252—H25A	120.0	O62—S6—O61	117.1 (10)
C254—C253—C252	120.0	O63—S6—O61	114.4 (9)
C254—C253—H25B	120.0	O62—S6—C6T	104.0 (7)
C252—C253—H25B	120.0	O63—S6—C6T	101.5 (7)
C255—C254—C253	120.0	O61—S6—C6T	101.0 (7)
C255—C254—H25C	120.0	F63—C6T—F61	111.6 (12)
C253—C254—H25C	120.0	F63—C6T—F62	110.7 (11)
C256—C255—C254	120.0	F61—C6T—F62	108.0 (11)
C256—C255—H25D	120.0	F63—C6T—S6	108.8 (9)
C254—C255—H25D	120.0	F61—C6T—S6	109.1 (9)
C255—C256—C251	120.0	F62—C6T—S6	108.6 (9)
C255—C256—H25E	120.0	O71—S7—O73	114.6 (14)
C251—C256—H25E	120.0	O71—S7—O72	113.2 (13)
C262—C261—C266	120.0	O73—S7—O72	112.7 (14)
C262—C261—P202	121 (2)	O71—S7—C7T	106 (2)
C266—C261—P202	119 (2)	O73—S7—C7T	108 (2)
C261—C262—C264	120.0	O72—S7—C7T	101 (2)
C261—C262—H26A	120.0	F73—C7T—F71	115.3 (14)
C264—C262—H26A	120.0	F73—C7T—F72	116.0 (14)
C262—C264—C263	120.0	F71—C7T—F72	115.4 (14)
C262—C264—H26B	120.0	F73—C7T—S7	106 (2)
C263—C264—H26B	120.0	F71—C7T—S7	104 (2)
C265—C263—C264	120.0	F72—C7T—S7	97 (2)
C265—C263—H26C	120.0	O83—S8—O82	114.3 (11)
C264—C263—H26C	120.0	O83—S8—O81	113.7 (11)
C263—C265—C266	120.0	O82—S8—O81	114.6 (11)
C263—C265—H26D	120.0	O83—S8—C8T	105.2 (15)
C266—C265—H26D	120.0	O82—S8—C8T	105.1 (14)
C265—C266—C261	120.0	O81—S8—C8T	102.3 (18)
C265—C266—H26E	120.0	F83—C8T—F82	106.9 (14)
C261—C266—H26E	120.0	F83—C8T—F81	106.7 (14)

C301—N301—C305	120.0	F82—C8T—F81	106.8 (14)
C301—N301—Pt3	117.0 (9)	F83—C8T—S8	111.1 (18)
C305—N301—Pt3	122.7 (9)	F82—C8T—S8	109.0 (18)
N301—C301—C302	120.0	F81—C8T—S8	116 (2)

Appendix H - Geometric parameters (Å, °) of [Pt(dppp)(L2)]$_4$[OTf]$_8$

Pt1—N104^{i}	2.09 (12)	C203—C204	1.3900
Pt1—N101	2.18 (2)	C203—C206	1.61 (6)
Pt1—P101	2.220 (18)	C204—C205	1.3900
Pt1—P102	2.25 (2)	C206—C207	1.3900
P101—C128	1.85 (3)	C206—C211	1.3900
P101—C141	1.86 (3)	C207—C208	1.3900
P101—C131	1.87 (3)	C207—N202	1.42 (7)
P101—C142	2.08 (15)	C208—C209	1.3900
P102—C130	1.85 (3)	C208—N203	1.70 (11)
P102—C151	1.85 (2)	C208—C222	1.99 (10)
P102—C161	1.88 (3)	C209—C210	1.3900
N101—C101	1.3900	C209—C212	1.66 (6)
N101—C105	1.3900	C210—C211	1.3900
C101—C102	1.3900	C212—C213	1.3900
C102—C103	1.3900	C212—C217	1.3900
C103—C104	1.3900	C213—C214	1.3900
C103—C106	1.57 (4)	C214—C215	1.3900
C104—C105	1.3900	C215—C216	1.3900
C106—C107	1.3900	C215—C218	1.53 (3)
C106—C111	1.3900	C216—C217	1.3900
C107—C108	1.3900	C218—C219	1.54 (2)
C107—N102	1.45 (6)	C218—C220	1.54 (2)
C108—N103	1.23 (4)	C218—C221	1.55 (2)
C108—C109	1.3900	N202—C222	1.31 (10)
C109—C110	1.3900	N203—C222	1.21 (12)
C109—C112	1.55 (5)	C222—C223	1.54 (9)
C110—C111	1.3900	C223—C224	1.3900
C112—C113	1.3900	C223—C227	1.3900
C112—C117	1.3900	C224—C225	1.3900
C113—C114	1.3900	C225—N204	1.3900
C114—C115	1.3900	N204—C226	1.3900

C115—C116	1.3900	N204—Pt2^{iv}	2.30 (4)
C115—C118	1.53 (3)	C226—C227	1.3900
C116—C117	1.3900	C228—C229	1.57 (3)
C118—C120	1.54 (2)	C229—C230	1.54 (3)
C118—C119	1.54 (2)	C231—C232	1.3900
C118—C121	1.55 (2)	C231—C236	1.3900
N102—C122	1.15 (7)	C232—C233	1.3900
N103—C122	1.50 (7)	C233—C234	1.3900
C122—C123	1.44 (6)	C234—C235	1.3900
C123—C124	1.3900	C235—C236	1.3900
C123—C127	1.3900	C241—C242	1.3900
C124—C125	1.3900	C241—C246	1.3900
C125—N104	1.3900	C242—C243	1.3900
N104—C126	1.3900	C243—C244	1.3900
N104—Pt1^{ii}	2.086 (19)	C244—C245	1.3900
C126—C127	1.3900	C245—C246	1.3900
C128—C129	1.60 (3)	C251—C252	1.3900
C129—C130	1.56 (3)	C251—C256	1.3900
C131—C132	1.3900	C252—C253	1.3900
C131—C136	1.3900	C253—C254	1.3900
C132—C133	1.3900	C254—C255	1.3900
C133—C134	1.3900	C255—C256	1.3900
C134—C135	1.3900	C261—C262	1.3900
C135—C136	1.3900	C261—C266	1.3900
C141—C142	1.3900	C262—C263	1.3900
C141—C146	1.3900	C263—C264	1.3900
C142—C143	1.3900	C264—C265	1.3900
C143—C144	1.3900	C265—C266	1.3900
C144—C145	1.3900	S1—O1	1.447 (14)
C145—C146	1.3900	S1—O3	1.447 (14)
C151—C152	1.3900	S1—O2	1.456 (14)
C151—C156	1.3900	S1—C1T	1.824 (14)
C152—C153	1.3900	C1T—F3	1.317 (14)
C153—C154	1.3900	C1T—F2	1.318 (14)
C154—C155	1.3900	C1T—F1	1.321 (14)
C155—C156	1.3900	S2—O5	1.448 (14)
C161—C162	1.3900	S2—O4	1.451 (14)

C161—C166	1.3900	S2—O6	1.458 (14)
C162—C163	1.3900	S2—C2T	1.822 (14)
C163—C164	1.3900	C2T—F6	1.320 (14)
C164—C165	1.3900	C2T—F5	1.321 (14)
C165—C166	1.3900	C2T—F4	1.322 (14)
Pt2—N201	2.05 (5)	S3—O8	1.443 (14)
Pt2—P202	2.30 (3)	S3—O9	1.448 (14)
Pt2—N204^{iii}	2.3 (3)	S3—O7	1.455 (14)
Pt2—P201	2.40 (3)	S3—C3T	1.822 (14)
P201—C231	1.80 (3)	C3T—F9	1.321 (14)
P201—C241	1.87 (2)	C3T—F7	1.323 (14)
P201—C228	1.90 (3)	C3T—F8	1.326 (14)
P202—C230	1.85 (3)	S4—O12	1.446 (14)
P202—C251	1.85 (3)	S4—O11	1.450 (14)
P202—C261	1.85 (3)	S4—O10	1.454 (14)
N201—C201	1.3900	S4—C4T	1.820 (14)
N201—C205	1.3900	C4T—F10	1.320 (15)
C201—C202	1.3900	C4T—F12	1.321 (14)
C202—C203	1.3900	C4T—F11	1.323 (14)
N104^{i}—Pt1—N101	86 (4)	C202—C203—C206	122 (5)
N104^{i}—Pt1—P101	96 (4)	C204—C203—C206	118 (5)
N101—Pt1—P101	177.3 (10)	C205—C204—C203	120.0
N104^{i}—Pt1—P102	176 (3)	C204—C205—N201	120.0
N101—Pt1—P102	90.2 (10)	C207—C206—C211	120.0
P101—Pt1—P102	87.2 (7)	C207—C206—C203	109 (5)
C128—P101—C141	130 (4)	C211—C206—C203	131 (5)
C128—P101—C131	103 (3)	C206—C207—C208	120.0
C141—P101—C131	102 (4)	C206—C207—N202	133 (5)
C128—P101—C142	92 (3)	C208—C207—N202	107 (5)
C141—P101—C142	41 (2)	C209—C208—C207	120.0
C131—P101—C142	101 (4)	C209—C208—N203	131 (6)
C128—P101—Pt1	132.6 (16)	C207—C208—N203	109 (6)
C141—P101—Pt1	81 (4)	C209—C208—C222	168 (4)
C131—P101—Pt1	103 (2)	C207—C208—C222	72 (4)
C142—P101—Pt1	120 (2)	N203—C208—C222	37 (4)
C130—P102—C151	109 (3)	C208—C209—C210	120.0

C130—P102—C161	103 (4)	C208—C209—C212	125 (5)
C151—P102—C161	96 (3)	C210—C209—C212	114 (5)
C130—P102—Pt1	118 (3)	C211—C210—C209	120.0
C151—P102—Pt1	110 (2)	C210—C211—C206	120.0
C161—P102—Pt1	119 (3)	C213—C212—C217	120.0
C101—N101—C105	120.0	C213—C212—C209	122 (6)
C101—N101—Pt1	129.0 (16)	C217—C212—C209	118 (6)
C105—N101—Pt1	111.0 (16)	C214—C213—C212	120.0
C102—C101—N101	120.0	C215—C214—C213	120.0
C103—C102—C101	120.0	C214—C215—C216	120.0
C102—C103—C104	120.0	C214—C215—C218	127 (6)
C102—C103—C106	116 (3)	C216—C215—C218	113 (6)
C104—C103—C106	124 (3)	C215—C216—C217	120.0
C105—C104—C103	120.0	C216—C217—C212	120.0
C104—C105—N101	120.0	C215—C218—C219	115 (7)
C107—C106—C111	120.0	C215—C218—C220	106 (6)
C107—C106—C103	119 (3)	C219—C218—C220	109 (2)
C111—C106—C103	121 (3)	C215—C218—C221	111 (7)
C108—C107—C106	120.0	C219—C218—C221	108 (2)
C108—C107—N102	104 (3)	C220—C218—C221	108 (2)
C106—C107—N102	136 (3)	C222—N202—C207	97 (6)
N103—C108—C107	110 (3)	C222—N203—C208	84 (8)
N103—C108—C109	130 (3)	N203—C222—N202	142 (10)
C107—C108—C109	120.0	N203—C222—C223	101 (9)
C108—C109—C110	120.0	N202—C222—C223	117 (8)
C108—C109—C112	126 (3)	N203—C222—C208	58 (7)
C110—C109—C112	113 (3)	N202—C222—C208	84 (5)
C111—C110—C109	120.0	C223—C222—C208	159 (7)
C110—C111—C106	120.0	C224—C223—C227	120.0
C113—C112—C117	120.0	C224—C223—C222	117 (6)
C113—C112—C109	112 (4)	C227—C223—C222	123 (6)
C117—C112—C109	127 (4)	C225—C224—C223	120.0
C112—C113—C114	120.0	C224—C225—N204	120.0
C115—C114—C113	120.0	C226—N204—C225	120.0
C114—C115—C116	120.0	C226—N204—Pt2$^{\mathrm{iv}}$	132 (3)
C114—C115—C118	117 (5)	C225—N204—Pt2$^{\mathrm{iv}}$	108 (3)
C116—C115—C118	122 (5)	N204—C226—C227	120.0

C117—C116—C115	120.0	C226—C227—C223	120.0
C116—C117—C112	120.0	C229—C228—P201	137 (5)
C115—C118—C120	115 (8)	C230—C229—C228	119 (8)
C115—C118—C119	116 (9)	C229—C230—P202	103 (5)
C120—C118—C119	103 (4)	C232—C231—C236	120.0
C115—C118—C121	116 (7)	C232—C231—P201	127 (4)
C120—C118—C121	103 (4)	C236—C231—P201	110 (4)
C119—C118—C121	103 (4)	C231—C232—C233	120.0
C122—N102—C107	109 (5)	C234—C233—C232	120.0
C108—N103—C122	106 (4)	C233—C234—C235	120.0
N102—C122—C123	124 (5)	C236—C235—C234	120.0
N102—C122—N103	110 (5)	C235—C236—C231	120.0
C123—C122—N103	126 (4)	C242—C241—C246	120.0
C124—C123—C127	120.0	C242—C241—P201	110 (3)
C124—C123—C122	116 (3)	C246—C241—P201	128 (3)
C127—C123—C122	124 (3)	C241—C242—C243	120.0
C123—C124—C125	120.0	C244—C243—C242	120.0
N104—C125—C124	120.0	C245—C244—C243	120.0
C125—N104—C126	120.0	C246—C245—C244	120.0
C125—N104—Pt1^{ii}	117.4 (14)	C245—C246—C241	120.0
C126—N104—Pt1^{ii}	122.6 (14)	C252—C251—C256	120.0
C127—C126—N104	120.0	C252—C251—P202	117 (6)
C126—C127—C123	120.0	C256—C251—P202	122 (6)
C129—C128—P101	106 (3)	C253—C252—C251	120.0
C130—C129—C128	126 (5)	C252—C253—C254	120.0
C129—C130—P102	115 (4)	C255—C254—C253	120.0
C132—C131—C136	120.0	C256—C255—C254	120.0
C132—C131—P101	118 (5)	C255—C256—C251	120.0
C136—C131—P101	121 (5)	C262—C261—C266	120.0
C133—C132—C131	120.0	C262—C261—P202	132 (5)
C132—C133—C134	120.0	C266—C261—P202	108 (5)
C135—C134—C133	120.0	C261—C262—C263	120.0
C134—C135—C136	120.0	C264—C263—C262	120.0
C135—C136—C131	120.0	C265—C264—C263	120.0
C142—C141—C146	120.00 (7)	C264—C265—C266	120.0
C142—C141—P101	78 (7)	C265—C266—C261	120.0
C146—C141—P101	161 (7)	O1—S1—O3	120.4 (15)

C141—C142—C143	120.00 (6)	O1—S1—O2	119.8 (15)
C141—C142—P101	61 (5)	O3—S1—O2	119.1 (15)
C143—C142—P101	175 (6)	O1—S1—C1T	97 (3)
C142—C143—C144	120.00 (5)	O3—S1—C1T	82 (3)
C145—C144—C143	120.00 (7)	O2—S1—C1T	99 (3)
C144—C145—C146	120.00 (5)	F3—C1T—F2	106 (3)
C145—C146—C141	120.00 (5)	F3—C1T—F1	107 (3)
C152—C151—C156	120.0	F2—C1T—F1	105 (3)
C152—C151—P102	111 (3)	F3—C1T—S1	101 (4)
C156—C151—P102	129 (3)	F2—C1T—S1	130 (4)
C151—C152—C153	120.0	F1—C1T—S1	106 (3)
C154—C153—C152	120.0	O5—S2—O4	118.1 (18)
C155—C154—C153	120.0	O5—S2—O6	117.2 (17)
C156—C155—C154	120.0	O4—S2—O6	116.3 (17)
C155—C156—C151	120.0	O5—S2—C2T	103 (3)
C162—C161—C166	120.0	O4—S2—C2T	104 (3)
C162—C161—P102	118 (5)	O6—S2—C2T	92 (3)
C166—C161—P102	120 (4)	F6—C2T—F5	112 (2)
C163—C162—C161	120.0	F6—C2T—F4	112 (2)
C162—C163—C164	120.0	F5—C2T—F4	112 (2)
C165—C164—C163	120.0	F6—C2T—S2	106 (3)
C164—C165—C166	120.0	F5—C2T—S2	107 (4)
C165—C166—C161	120.0	F4—C2T—S2	108 (4)
N201—Pt2—P202	101.2 (19)	O8—S3—O9	114 (3)
N201—Pt2—N204^{iii}	79 (8)	O8—S3—O7	113 (3)
P202—Pt2—N204^{iii}	180 (6)	O9—S3—O7	111 (3)
N201—Pt2—P201	160.7 (19)	O8—S3—C3T	105 (4)
P202—Pt2—P201	96.5 (11)	O9—S3—C3T	91 (4)
N204^{iii}—Pt2—P201	84 (7)	O7—S3—C3T	122 (4)
C231—P201—C241	105 (3)	F9—C3T—F7	113 (3)
C231—P201—C228	123 (3)	F9—C3T—F8	113 (3)
C241—P201—C228	94 (3)	F7—C3T—F8	113 (3)
C231—P201—Pt2	121 (2)	F9—C3T—S3	108 (4)
C241—P201—Pt2	108.0 (19)	F7—C3T—S3	104 (5)
C228—P201—Pt2	102 (2)	F8—C3T—S3	106 (4)
C230—P202—C251	94 (4)	O12—S4—O11	116 (2)
C230—P202—C261	110 (6)	O12—S4—O10	116 (2)

C251—P202—C261	112 (4)	O11—S4—O10	115 (2)
C230—P202—Pt2	124 (5)	O12—S4—C4T	111 (5)
C251—P202—Pt2	112 (3)	O11—S4—C4T	109 (5)
C261—P202—Pt2	105 (3)	O10—S4—C4T	86 (4)
C201—N201—C205	120.0	F10—C4T—F12	108 (3)
C201—N201—Pt2	123 (4)	F10—C4T—F11	108 (3)
C205—N201—Pt2	117 (4)	F12—C4T—F11	109 (3)
N201—C201—C202	120.0	F10—C4T—S4	104 (5)
C203—C202—C201	120.0	F12—C4T—S4	120 (5)
C202—C203—C204	120.0	F11—C4T—S4	106 (4)

Appendix I - Geometric parameters (Å, º) of (L3)

N1—C1	1.336 (3)	C8—C9	1.395 (2)
N1—C5	1.337 (2)	C9—C10	1.388 (2)
N2—C15	1.334 (2)	C9—C12	1.479 (2)
N2—C14	1.342 (2)	C10—C11	1.391 (2)
N3—C17	1.315 (2)	C10—H10A	0.9300
N3—C7	1.387 (2)	C11—H11A	0.9300
N4—C17	1.365 (2)	C12—C16	1.388 (3)
N4—C8	1.374 (2)	C12—C13	1.391 (3)
N4—H4B	0.8600	C13—C14	1.380 (2)
N5—C20	1.333 (3)	C13—H13A	0.9300
N5—C21	1.332 (3)	C14—H14A	0.9300
C1—C2	1.383 (3)	C15—C16	1.373 (3)
C1—H1A	0.9300	C15—H15A	0.9300
C2—C3	1.392 (3)	C16—H16A	0.9300
C2—H2A	0.9300	C17—C18	1.466 (2)
C3—C4	1.394 (2)	C18—C22	1.383 (2)
C3—C6	1.482 (2)	C18—C19	1.388 (3)
C4—C5	1.375 (3)	C19—C20	1.379 (3)
C4—H4A	0.9300	C19—H19A	0.9300
C5—H5A	0.9300	C20—H20A	0.9300
C6—C11	1.392 (2)	C21—C22	1.380 (3)
C6—C7	1.407 (2)	C21—H21A	0.9300
C7—C8	1.408 (2)	C22—H22A	0.9300

C1—N1—C5	115.05 (16)	C10—C11—C6	122.79 (16)
C15—N2—C14	115.75 (16)	C10—C11—H11A	118.6
C17—N3—C7	105.06 (14)	C6—C11—H11A	118.6
C17—N4—C8	106.66 (14)	C16—C12—C13	117.15 (16)
C17—N4—H4B	126.7	C16—C12—C9	120.80 (16)
C8—N4—H4B	126.7	C13—C12—C9	122.05 (16)
C20—N5—C21	116.36 (16)	C14—C13—C12	119.04 (17)
N1—C1—C2	124.81 (18)	C14—C13—H13A	120.5
N1—C1—H1A	117.6	C12—C13—H13A	120.5
C2—C1—H1A	117.6	N2—C14—C13	124.15 (17)
C1—C2—C3	119.35 (17)	N2—C14—H14A	117.9
C1—C2—H2A	120.3	C13—C14—H14A	117.9
C3—C2—H2A	120.3	N2—C15—C16	124.47 (18)
C2—C3—C4	116.27 (16)	N2—C15—H15A	117.8
C2—C3—C6	122.67 (16)	C16—C15—H15A	117.8
C4—C3—C6	121.05 (16)	C15—C16—C12	119.40 (17)
C5—C4—C3	119.77 (17)	C15—C16—H16A	120.3
C5—C4—H4A	120.1	C12—C16—H16A	120.3
C3—C4—H4A	120.1	N3—C17—N4	113.25 (15)
N1—C5—C4	124.74 (17)	N3—C17—C18	123.67 (15)
N1—C5—H5A	117.6	N4—C17—C18	123.04 (15)
C4—C5—H5A	117.6	C22—C18—C19	117.22 (17)
C11—C6—C7	115.92 (16)	C22—C18—C17	122.33 (16)
C11—C6—C3	120.85 (15)	C19—C18—C17	120.42 (16)
C7—C6—C3	123.23 (16)	C20—C19—C18	119.20 (17)
N3—C7—C8	109.38 (14)	C20—C19—H19A	120.4
N3—C7—C6	130.11 (16)	C18—C19—H19A	120.4
C8—C7—C6	120.50 (16)	N5—C20—C19	123.94 (18)
N4—C8—C9	131.31 (16)	N5—C20—H20A	118.0
N4—C8—C7	105.60 (15)	C19—C20—H20A	118.0
C9—C8—C7	123.08 (16)	N5—C21—C22	123.88 (18)
C10—C9—C8	115.47 (15)	N5—C21—H21A	118.1
C10—C9—C12	121.59 (16)	C22—C21—H21A	118.1
C8—C9—C12	122.93 (15)	C21—C22—C18	119.37 (17)
C11—C10—C9	122.16 (16)	C21—C22—H22A	120.3
C11—C10—H10A	118.9	C18—C22—H22A	120.3
C9—C10—H10A	118.9		

Appendix J - Geometric parameters (Å, º) of $[Pt_6(dppp)_6(L3)_4]$ $[OTf]_{12}$

Pt1—N11	2.058 (19)	C335—C336	1.3900
Pt1—N42	2.125 (15)	C341—C342	1.3900
Pt1—P11	2.231 (11)	C341—C346	1.3900
Pt1—P12	2.271 (9)	C342—C343	1.3900
Pt2—N21	2.071 (16)	C343—C344	1.3900
Pt2—N12	2.13 (2)	C344—C345	1.3900
Pt2—P21	2.243 (10)	C345—C346	1.3900
Pt2—P22	2.282 (13)	C351—C352	1.3900
Pt3—N31	2.120 (15)	C351—C356	1.3900
Pt3—N22	2.141 (13)	C352—C353	1.3900
Pt3—P31	2.223 (9)	C353—C354	1.3900 (16)
Pt3—P32	2.262 (8)	C354—C355	1.3900 (14)
Pt4—N32	2.051 (15)	C355—C356	1.3900
Pt4—N41	2.146 (16)	C361—C362	1.3900
Pt4—P42	2.234 (10)	C361—C366	1.3900
Pt4—P41	2.268 (8)	C362—C363	1.3900
Pt5—N15	2.04 (3)	C363—C364	1.3900
Pt5—N35	2.10 (2)	C364—C365	1.3900
Pt5—P51	2.286 (13)	C365—C366	1.3900
Pt5—P52	2.296 (12)	N41—C401	1.3900
Pt6—N25	2.117 (18)	N41—C405	1.3900
Pt6—N45	2.146 (16)	C401—C402	1.3900
Pt6—P62	2.263 (11)	C402—C403	1.3900
Pt6—P61	2.261 (9)	C403—C404	1.3900
P11—C123	1.77 (4)	C403—C406	1.50 (2)
P11—C131	1.79 (3)	C404—C405	1.3900
P11—C145	1.81 (4)	C406—C407	1.3900
P12—C151	1.72 (2)	C406—C411	1.3900
P12—C125	1.74 (4)	C407—C408	1.3900
P12—C161	1.83 (3)	C407—N43	1.38 (3)
P21—C241	1.76 (3)	C408—N44	1.37 (3)
P21—C231	1.77 (3)	C408—C409	1.3900
P21—C223	1.80 (5)	C409—C410	1.3900
P22—C251	1.73 (4)	C409—C412	1.47 (2)

P22—C261	1.82 (3)	C410—C411	1.3900
P22—C225	1.82 (4)	C412—C413	1.3900
P31—C323	1.77 (4)	C412—C416	1.3900
P31—C331	1.86 (3)	C413—C414	1.3900
P31—C341	1.85 (3)	C414—N42	1.3900
P32—C351	1.75 (2)	N42—C415	1.3900
P32—C325	1.77 (4)	C415—C416	1.3900
P32—C361	1.85 (2)	N43—C417	1.34 (4)
P41—C423	1.78 (3)	C417—N44	1.38 (4)
P41—C441	1.80 (3)	C417—C418	1.46 (4)
P41—C431	1.82 (2)	C418—C419	1.3900
P42—C461	1.76 (3)	C418—C422	1.3900
P42—C425	1.85 (4)	C419—C420	1.3900
P42—C451	1.91 (3)	C420—N45	1.3900
P51—C523	1.61 (5)	N45—C421	1.3900
P51—C541	1.77 (4)	C421—C422	1.3900
P51—C531	1.92 (3)	C423—C424	1.45 (5)
P52—C525	1.71 (7)	C424—C425	1.49 (5)
P52—C561	1.83 (3)	C431—C432	1.3900
P52—C551	1.75 (3)	C431—C436	1.3900
P61—C623	1.81 (4)	C432—C433	1.3900
P61—C631	1.81 (2)	C433—C434	1.3900
P61—C641	1.83 (2)	C434—C435	1.3900
P62—C651	1.73 (2)	C435—C436	1.3900
P62—C661	1.75 (2)	C441—C442	1.3900
P62—C625	1.81 (4)	C441—C446	1.3900
N11—C101	1.3900	C442—C443	1.3900
N11—C105	1.3900	C443—C444	1.3900 (11)
C101—C102	1.3900	C444—C445	1.3900
C102—C103	1.3900	C445—C446	1.3900
C103—C104	1.3900	C451—C452	1.3900
C103—C106	1.53 (3)	C451—C456	1.3900
C104—C105	1.3900	C452—C453	1.3900
C106—C107	1.3900	C453—C454	1.3900
C106—C111	1.3900	C454—C455	1.3900
C107—N13	1.33 (3)	C455—C456	1.3900
C107—C108	1.3900	C461—C462	1.3900 (16)

C108—N14	1.30 (4)	C461—C466	1.3900
C108—C109	1.3900	C462—C463	1.3900
C109—C110	1.3900	C463—C464	1.3900
C109—C112	1.52 (3)	C464—C465	1.3900 (14)
C110—C111	1.3900	C465—C466	1.3900
C112—C113	1.3900	C523—C524	1.60 (7)
C112—C116	1.3900	C524—C525	1.52 (7)
C113—C114	1.3900	C531—C532	1.3900 (10)
C114—N12	1.3900	C531—C536	1.3900 (15)
N12—C115	1.3900	C532—C533	1.3900
C115—C116	1.3900	C533—C534	1.3900 (16)
N13—C117	1.40 (5)	C534—C535	1.3900 (11)
C117—C118	1.43 (6)	C535—C536	1.3900
C117—N14	1.46 (5)	C541—C542	1.3900
C118—C119	1.3900	C541—C546	1.3900
C118—C122	1.3900	C542—C543	1.3900 (18)
C119—C120	1.3900	C543—C544	1.3900
C120—N15	1.3900	C544—C545	1.3900
N15—C121	1.3900	C545—C546	1.3900 (14)
C121—C122	1.3900	C551—C552	1.3900
C123—C124	1.62 (6)	C551—C556	1.3900 (18)
C124—C125	1.65 (5)	C552—C553	1.3900
C131—C132	1.3900	C553—C554	1.3900 (18)
C131—C136	1.3900	C554—C555	1.3900
C132—C133	1.3900	C555—C556	1.3900
C133—C134	1.3900	C561—C562	1.3900
C134—C135	1.3900	C561—C566	1.3900
C135—C136	1.3900	C562—C563	1.3900
C141—C142	1.3900	C563—C564	1.3900
C141—C146	1.3900	C564—C565	1.3900
C142—C143	1.3900 (11)	C565—C566	1.3900
C143—C144	1.3900	C623—C624	1.53 (5)
C144—C145	1.3900	C624—C625	1.50 (5)
C145—C146	1.3900	C631—C632	1.3900
C151—C152	1.3900	C631—C636	1.3900
C151—C156	1.3900	C632—C633	1.3900
C152—C153	1.3900	C633—C634	1.3900

C153—C154	1.3900 (12)	C634—C635	1.3900
C154—C155	1.3900 (10)	C635—C636	1.3900
C155—C156	1.3900	C641—C642	1.3900
C161—C162	1.3900	C641—C646	1.3900
C161—C166	1.3900	C642—C643	1.3900
C162—C163	1.3900	C643—C644	1.3900
C163—C164	1.3900	C644—C645	1.3900
C164—C165	1.3900	C645—C646	1.3900
C165—C166	1.3900	C651—C652	1.3900
N21—C201	1.3900	C651—C656	1.3900 (14)
N21—C205	1.3900	C652—C653	1.3900
C201—C202	1.3900	C653—C654	1.3900
C202—C203	1.3900	C654—C655	1.3900
C203—C204	1.3900	C655—C656	1.3900
C203—C206	1.54 (2)	C661—C662	1.3900
C204—C205	1.3900	C661—C666	1.3900
C206—C207	1.3900	C662—C663	1.3900
C206—C211	1.3900	C663—C664	1.3900
C207—N23	1.31 (3)	C664—C665	1.3900
C207—C208	1.3900	C665—C666	1.3900
C208—N24	1.41 (3)	S5—O14	1.421 (14)
C208—C209	1.3900	S5—O13	1.429 (14)
C209—C210	1.3900	S5—O15	1.446 (14)
C209—C212	1.49 (2)	S5—C5T	1.821 (12)
C210—C211	1.3900	C5T—F15	1.327 (15)
C212—C213	1.3900	C5T—F13	1.324 (15)
C212—C216	1.3900	C5T—F14	1.337 (15)
C213—C214	1.3900	S1—O2	1.416 (15)
C214—N22	1.3900	S1—O3	1.415 (15)
N22—C215	1.3900	S1—O1	1.456 (15)
C215—C216	1.3900	S1—C1T	1.834 (13)
N23—C217	1.37 (4)	C1T—F2	1.326 (16)
C217—N24	1.26 (4)	C1T—F1	1.331 (16)
C217—C218	1.47 (4)	C1T—F3	1.331 (16)
C218—C219	1.3900	S2—O6	1.409 (15)
C218—C222	1.3900	S2—O5	1.420 (15)
C219—C220	1.3900	S2—O4	1.460 (15)

C220—N25	1.3900	S2—C2T	1.832 (12)
N25—C221	1.3900	C2T—F4	1.320 (16)
C221—C222	1.3900	C2T—F5	1.331 (16)
C223—C224	1.50 (9)	C2T—F6	1.327 (16)
C224—C225	1.51 (6)	S3—O9	1.416 (15)
C231—C232	1.3900	S3—O8	1.423 (15)
C231—C236	1.3900	S3—O7	1.454 (15)
C232—C233	1.3900 (10)	S3—C3T	1.825 (13)
C233—C234	1.3900	C3T—F8	1.335 (15)
C234—C235	1.3900	C3T—F7	1.330 (16)
C235—C236	1.3900	C3T—F9	1.328 (15)
C241—C242	1.3900 (11)	S4—O10	1.416 (15)
C241—C246	1.3900	S4—O11	1.443 (16)
C242—C243	1.3900	S4—O12	1.446 (16)
C243—C244	1.3900	S4—C4T	1.822 (13)
C244—C245	1.3900	C4T—F12	1.328 (16)
C245—C246	1.3900	C4T—F11	1.331 (16)
C251—C252	1.3900	C4T—F10	1.330 (16)
C251—C256	1.3900	S6—O17	1.407 (15)
C252—C253	1.3900	S6—O18	1.426 (15)
C253—C254	1.3900	S6—O16	1.453 (16)
C254—C255	1.3900	S6—C6T	1.816 (12)
C255—C256	1.3900	C6T—F18	1.309 (15)
C261—C262	1.3900	C6T—F17	1.323 (15)
C261—C266	1.3900 (14)	C6T—F16	1.343 (16)
C262—C263	1.3900 (12)	S7—O20	1.424 (15)
C263—C264	1.3900 (18)	S7—O19	1.431 (16)
C264—C265	1.3900	S7—O21	1.438 (15)
C265—C266	1.3900 (13)	S7—C7T	1.830 (13)
N31—C301	1.3900	C7T—F21	1.325 (16)
N31—C305	1.3900	C7T—F19	1.330 (16)
C301—C302	1.3900	C7T—F20	1.324 (16)
C302—C303	1.3900	S8—O24	1.414 (15)
C303—C304	1.3900	S8—O23	1.447 (16)
C303—C306	1.54 (2)	S8—O22	1.444 (16)
C304—C305	1.3900	S8—C8T	1.812 (12)
C306—C307	1.3900	C8T—F24	1.317 (16)

C306—C311	1.3900	C8T—F22	1.331 (16)
C307—C308	1.3900	C8T—F23	1.334 (16)
C307—N33	1.41 (3)	S9—O25	1.417 (16)
C308—C309	1.3900	S9—O26	1.431 (15)
C308—N34	1.43 (3)	S9—O27	1.441 (15)
C309—C310	1.3900	S9—C9T	1.830 (12)
C309—C312	1.53 (2)	C9T—F25	1.323 (16)
C310—C311	1.3900	C9T—F26	1.326 (16)
C312—C313	1.3900	C9T—F27	1.334 (16)
C312—C316	1.3900	S10—O29	1.423 (16)
C313—C314	1.3900	S10—O30	1.434 (16)
C314—N32	1.3900	S10—O28	1.433 (16)
N32—C315	1.3900	S10—C10T	1.835 (13)
C315—C316	1.3900	C10T—F28	1.327 (16)
N33—C317	1.31 (4)	C10T—F29	1.330 (17)
C317—N34	1.42 (4)	C10T—F30	1.328 (16)
C317—C318	1.41 (4)	S11—O31	1.407 (15)
C318—C319	1.3900	S11—O33	1.423 (15)
C318—C322	1.3900	S11—O32	1.445 (15)
C319—C320	1.3900	S11—C11T	1.833 (12)
C320—N35	1.3900	C11T—F33	1.336 (16)
N35—C321	1.3900	C11T—F31	1.330 (16)
C321—C322	1.3900	C11T—F32	1.335 (16)
C323—C324	1.64 (5)	S12—O35	1.428 (15)
C324—C325	1.61 (5)	S12—O34	1.428 (15)
C331—C332	1.3900	S12—O36	1.432 (15)
C331—C336	1.3900	S12—C12T	1.829 (12)
C332—C333	1.3900	C12T—F36	1.320 (16)
C333—C334	1.3900	C12T—F35	1.330 (15)
C334—C335	1.3900	C12T—F34	1.331 (16)
N11—Pt1—N42	84.2 (8)	C332—C331—P31	120 (3)
N11—Pt1—P11	175.4 (7)	C336—C331—P31	120 (3)
N42—Pt1—P11	92.2 (7)	C333—C332—C331	120.0
N11—Pt1—P12	91.7 (6)	C334—C333—C332	120.0
N42—Pt1—P12	175.9 (6)	C335—C334—C333	120.0
P11—Pt1—P12	91.9 (4)	C334—C335—C336	120.00 (8)

N21—Pt2—N12	81.7 (8)	C335—C336—C331	120.0
N21—Pt2—P21	174.2 (8)	C342—C341—C346	120.0
N12—Pt2—P21	92.9 (7)	C342—C341—P31	124 (2)
N21—Pt2—P22	94.7 (6)	C346—C341—P31	116 (2)
N12—Pt2—P22	175.7 (8)	C343—C342—C341	120.00 (7)
P21—Pt2—P22	90.8 (4)	C342—C343—C344	120.00 (7)
N31—Pt3—N22	86.2 (7)	C345—C344—C343	120.0
N31—Pt3—P31	177.4 (5)	C346—C345—C344	120.00 (8)
N22—Pt3—P31	91.2 (5)	C345—C346—C341	120.0
N31—Pt3—P32	90.2 (5)	C352—C351—C356	120.0
N22—Pt3—P32	176.5 (5)	C352—C351—P32	122 (2)
P31—Pt3—P32	92.3 (4)	C356—C351—P32	118 (2)
N32—Pt4—N41	84.0 (7)	C351—C352—C353	120.00 (11)
N32—Pt4—P42	177.9 (7)	C354—C353—C352	120.0
N41—Pt4—P42	94.2 (6)	C353—C354—C355	120.0
N32—Pt4—P41	90.8 (6)	C356—C355—C354	120.00 (7)
N41—Pt4—P41	174.7 (6)	C355—C356—C351	120.00 (5)
P42—Pt4—P41	91.0 (4)	C362—C361—C366	120.0
N15—Pt5—N35	86.5 (9)	C362—C361—P32	119 (2)
N15—Pt5—P51	91.1 (8)	C366—C361—P32	121 (2)
N35—Pt5—P51	177.3 (7)	C361—C362—C363	120.0
N15—Pt5—P52	179.0 (8)	C364—C363—C362	120.0
N35—Pt5—P52	92.5 (7)	C363—C364—C365	120.0
P51—Pt5—P52	90.0 (6)	C366—C365—C364	120.0
N25—Pt6—N45	88.1 (8)	C365—C366—C361	120.0
N25—Pt6—P62	178.8 (6)	C401—N41—C405	120.0
N45—Pt6—P62	90.6 (6)	C401—N41—Pt4	122.9 (15)
N25—Pt6—P61	89.9 (6)	C405—N41—Pt4	117.1 (15)
N45—Pt6—P61	177.4 (7)	C402—C401—N41	120.0
P62—Pt6—P61	91.3 (4)	C401—C402—C403	120.00 (8)
C123—P11—C131	104 (2)	C404—C403—C402	120.00 (5)
C123—P11—C145	114 (2)	C404—C403—C406	118 (2)
C131—P11—C145	105 (2)	C402—C403—C406	122 (2)
C123—P11—Pt1	112.1 (15)	C405—C404—C403	120.0
C131—P11—Pt1	112.9 (14)	C404—C405—N41	120.00 (5)
C145—P11—Pt1	109.6 (13)	C407—C406—C411	120.0
C151—P12—C125	112.4 (18)	C407—C406—C403	124 (2)

C151—P12—C161	103.7 (19)	C411—C406—C403	116 (2)
C125—P12—C161	99 (2)	C406—C407—C408	120.00 (6)
C151—P12—Pt1	114.3 (11)	C406—C407—N43	128 (2)
C125—P12—Pt1	114.7 (12)	C408—C407—N43	112 (2)
C161—P12—Pt1	110.7 (10)	N44—C408—C409	134 (2)
C241—P21—C231	102 (2)	N44—C408—C407	106 (2)
C241—P21—C223	103 (3)	C409—C408—C407	120.0
C231—P21—C223	106 (2)	C408—C409—C410	120.0
C241—P21—Pt2	114.7 (16)	C408—C409—C412	120 (2)
C231—P21—Pt2	108.9 (11)	C410—C409—C412	119 (2)
C223—P21—Pt2	120 (2)	C411—C410—C409	120.00 (6)
C251—P22—C261	112 (2)	C410—C411—C406	120.0
C251—P22—C225	102 (2)	C413—C412—C416	120.0
C261—P22—C225	107 (2)	C413—C412—C409	119 (2)
C251—P22—Pt2	117.2 (15)	C416—C412—C409	121 (2)
C261—P22—Pt2	105.8 (13)	C412—C413—C414	120.0
C225—P22—Pt2	112.3 (17)	C413—C414—N42	120.0
C323—P31—C331	101.6 (18)	C415—N42—C414	120.0
C323—P31—C341	108.0 (19)	C415—N42—Pt1	122.7 (13)
C331—P31—C341	106.4 (17)	C414—N42—Pt1	117.1 (13)
C323—P31—Pt3	116.5 (14)	C416—C415—N42	120.0
C331—P31—Pt3	112.9 (11)	C415—C416—C412	120.00 (5)
C341—P31—Pt3	110.7 (12)	C417—N43—C407	102 (3)
C351—P32—C325	108.0 (17)	N43—C417—N44	114 (3)
C351—P32—C361	101.2 (15)	N43—C417—C418	126 (3)
C325—P32—C361	100.3 (19)	N44—C417—C418	120 (3)
C351—P32—Pt3	115.9 (12)	C408—N44—C417	105 (3)
C325—P32—Pt3	117.1 (14)	C419—C418—C422	120.0
C361—P32—Pt3	112.1 (8)	C419—C418—C417	117 (2)
C423—P41—C441	109.4 (18)	C422—C418—C417	122 (3)
C423—P41—C431	105.7 (19)	C418—C419—C420	120.0
C441—P41—C431	104.1 (16)	C419—C420—N45	120.00 (7)
C423—P41—Pt4	115.3 (15)	C421—N45—C420	120.0
C441—P41—Pt4	111.8 (10)	C421—N45—Pt6	115.4 (14)
C431—P41—Pt4	109.6 (9)	C420—N45—Pt6	123.8 (14)
C461—P42—C425	104.8 (18)	C422—C421—N45	120.0
C461—P42—C451	109 (2)	C421—C422—C418	120.00 (8)

C425—P42—C451	104 (2)	C424—C423—P41	114 (3)
C461—P42—Pt4	111.5 (14)	C425—C424—C423	120 (5)
C425—P42—Pt4	114.8 (18)	C424—C425—P42	112 (3)
C451—P42—Pt4	112.1 (12)	C432—C431—C436	120.0
C523—P51—C541	103 (3)	C432—C431—P41	124 (3)
C523—P51—C531	113 (3)	C436—C431—P41	116 (3)
C541—P51—C531	102 (2)	C433—C432—C431	120.0
C523—P51—Pt5	112 (2)	C434—C433—C432	120.0
C541—P51—Pt5	114.9 (14)	C433—C434—C435	120.0
C531—P51—Pt5	110.9 (16)	C436—C435—C434	120.0
C525—P52—C561	108 (2)	C435—C436—C431	120.0
C525—P52—C551	112 (3)	C442—C441—C446	120.0
C561—P52—C551	100 (2)	C442—C441—P41	120.4 (19)
C525—P52—Pt5	108.3 (19)	C446—C441—P41	119.6 (19)
C561—P52—Pt5	111.9 (13)	C443—C442—C441	120.00 (7)
C551—P52—Pt5	116.1 (15)	C442—C443—C444	120.0
C623—P61—C631	102.4 (17)	C445—C444—C443	120.0
C623—P61—C641	106.1 (16)	C444—C445—C446	120.0
C631—P61—C641	99.9 (15)	C445—C446—C441	120.0
C623—P61—Pt6	115.2 (14)	C452—C451—C456	120.0
C631—P61—Pt6	115.0 (9)	C452—C451—P42	123 (2)
C641—P61—Pt6	116.3 (10)	C456—C451—P42	117 (2)
C651—P62—C661	106.9 (16)	C451—C452—C453	120.0
C651—P62—C625	106.9 (18)	C452—C453—C454	120.0
C661—P62—C625	108.2 (17)	C455—C454—C453	120.0
C651—P62—Pt6	110.8 (10)	C454—C455—C456	120.0
C661—P62—Pt6	110.9 (14)	C455—C456—C451	120.0
C625—P62—Pt6	113.0 (13)	C462—C461—C466	120.00 (8)
C101—N11—C105	120.0	C462—C461—P42	123 (3)
C101—N11—Pt1	126.9 (16)	C466—C461—P42	117 (3)
C105—N11—Pt1	113.1 (16)	C463—C462—C461	120.0
N11—C101—C102	120.0	C462—C463—C464	120.00 (7)
C103—C102—C101	120.0	C465—C464—C463	120.00 (7)
C102—C103—C104	120.0	C464—C465—C466	120.0
C102—C103—C106	113 (3)	C465—C466—C461	120.00 (5)
C104—C103—C106	126 (3)	P51—C523—C524	116 (3)
C103—C104—C105	120.0	C525—C524—C523	102 (5)

C104—C105—N11	120.0	C524—C525—P52	120 (4)
C107—C106—C111	120.0	C532—C531—C536	120.0
C107—C106—C103	123 (2)	C532—C531—P51	128 (3)
C111—C106—C103	117 (2)	C536—C531—P51	112 (3)
N13—C107—C106	134 (3)	C533—C532—C531	120.00 (9)
N13—C107—C108	106 (3)	C532—C533—C534	120.00 (6)
C106—C107—C108	120.0	C533—C534—C535	120.0
N14—C108—C107	115 (3)	C534—C535—C536	120.00 (9)
N14—C108—C109	125 (3)	C535—C536—C531	120.00 (9)
C107—C108—C109	120.0	C542—C541—C546	120.00 (8)
C110—C109—C108	120.0	C542—C541—P51	124 (4)
C110—C109—C112	120 (3)	C546—C541—P51	116 (4)
C108—C109—C112	119 (3)	C541—C542—C543	120.00 (6)
C109—C110—C111	120.0	C544—C543—C542	120.0
C110—C111—C106	120.0	C545—C544—C543	120.00 (9)
C113—C112—C116	120.0	C544—C545—C546	120.00 (6)
C113—C112—C109	113 (3)	C545—C546—C541	120.0
C116—C112—C109	127 (3)	C552—C551—C556	120.00 (10)
C114—C113—C112	120.0	C552—C551—P52	109 (4)
N12—C114—C113	120.0	C556—C551—P52	131 (4)
C114—N12—C115	120.0	C551—C552—C553	120.00 (17)
C114—N12—Pt2	119.7 (18)	C552—C553—C554	120.00 (5)
C115—N12—Pt2	120.3 (18)	C555—C554—C553	120.00 (8)
N12—C115—C116	120.0	C554—C555—C556	120.00 (18)
C115—C116—C112	120.0	C555—C556—C551	120.00 (6)
C107—N13—C117	108 (4)	C562—C561—C566	120.0
C118—C117—N13	121 (5)	C562—C561—P52	123 (3)
C118—C117—N14	131 (4)	C566—C561—P52	117 (3)
N13—C117—N14	107 (4)	C563—C562—C561	120.0
C108—N14—C117	103 (3)	C564—C563—C562	120.0
C117—C118—C119	127 (4)	C563—C564—C565	120.0
C117—C118—C122	113 (4)	C566—C565—C564	120.0
C119—C118—C122	120.0	C565—C566—C561	120.0
C118—C119—C120	120.0	C624—C623—P61	109 (3)
N15—C120—C119	120.0	C623—C624—C625	113 (3)
C121—N15—C120	120.0	C624—C625—P62	113 (3)
C121—N15—Pt5	121 (2)	C632—C631—C636	120.0

C120—N15—Pt5	119 (2)	C632—C631—P61	119 (3)
C122—C121—N15	120.0	C636—C631—P61	121 (3)
C121—C122—C118	120.0	C633—C632—C631	120.00 (6)
C124—C123—P11	113 (3)	C632—C633—C634	120.0
C125—C124—C123	103 (3)	C635—C634—C633	120.0
C124—C125—P12	105 (3)	C634—C635—C636	120.00 (7)
C132—C131—C136	120.0	C635—C636—C631	120.0
C132—C131—P11	116 (3)	C642—C641—C646	120.00 (8)
C136—C131—P11	123 (3)	C642—C641—P61	124.8 (18)
C133—C132—C131	120.00 (8)	C646—C641—P61	115.2 (18)
C134—C133—C132	120.0	C643—C642—C641	120.0
C133—C134—C135	120.0	C644—C643—C642	120.0
C136—C135—C134	120.00 (8)	C643—C644—C645	120.00 (7)
C135—C136—C131	120.0	C644—C645—C646	120.0
C142—C141—C146	120.00 (6)	C645—C646—C641	120.0
C143—C142—C141	120.0	C652—C651—C656	120.0
C142—C143—C144	120.0	C652—C651—P62	121 (2)
C145—C144—C143	120.00 (5)	C656—C651—P62	119 (2)
C146—C145—C144	120.0	C653—C652—C651	120.00 (7)
C146—C145—P11	122 (2)	C652—C653—C654	120.0
C144—C145—P11	118 (3)	C655—C654—C653	120.0
C145—C146—C141	120.00 (6)	C656—C655—C654	120.00 (7)
C152—C151—C156	120.0	C655—C656—C651	120.0
C152—C151—P12	120 (2)	C662—C661—C666	120.00 (7)
C156—C151—P12	119 (2)	C662—C661—P62	116 (2)
C151—C152—C153	120.00 (9)	C666—C661—P62	124 (2)
C154—C153—C152	120.00 (6)	C661—C662—C663	120.0
C153—C154—C155	120.0	C662—C663—C664	120.0
C156—C155—C154	120.00 (6)	C663—C664—C665	120.00 (5)
C155—C156—C151	120.0	C666—C665—C664	120.0
C162—C161—C166	120.0	C665—C666—C661	120.0
C162—C161—P12	120 (3)	O14—S5—O13	115.1 (11)
C166—C161—P12	120 (3)	O14—S5—O15	113.7 (11)
C161—C162—C163	120.0	O13—S5—O15	113.2 (11)
C164—C163—C162	120.0	O14—S5—C5T	105.4 (13)
C163—C164—C165	120.0	O13—S5—C5T	101.4 (13)
C164—C165—C166	120.0	O15—S5—C5T	106.5 (12)

C165—C166—C161	120.0	F15—C5T—F13	113.8 (13)
C201—N21—C205	120.00 (6)	F15—C5T—F14	112.7 (13)
C201—N21—Pt2	120.1 (17)	F13—C5T—F14	112.2 (13)
C205—N21—Pt2	119.9 (17)	F15—C5T—S5	106.0 (15)
N21—C201—C202	120.0	F13—C5T—S5	104.7 (14)
C201—C202—C203	120.0	F14—C5T—S5	106.7 (15)
C204—C203—C202	120.00 (5)	O2—S1—O3	117.8 (13)
C204—C203—C206	117 (2)	O2—S1—O1	114.1 (12)
C202—C203—C206	123 (2)	O3—S1—O1	114.6 (12)
C203—C204—C205	120.0	O2—S1—C1T	104.5 (17)
C204—C205—N21	120.00 (5)	O3—S1—C1T	108.0 (16)
C207—C206—C211	120.0	O1—S1—C1T	94.1 (16)
C207—C206—C203	120 (2)	F2—C1T—F1	115.5 (14)
C211—C206—C203	120 (2)	F2—C1T—F3	115.4 (14)
N23—C207—C206	130 (2)	F1—C1T—F3	114.8 (14)
N23—C207—C208	109 (2)	F2—C1T—S1	105.7 (19)
C206—C207—C208	120.0	F1—C1T—S1	101.8 (19)
N24—C208—C209	135 (2)	F3—C1T—S1	100.9 (18)
N24—C208—C207	105 (2)	O6—S2—O5	116.8 (13)
C209—C208—C207	120.0	O6—S2—O4	113.8 (13)
C208—C209—C210	120.0	O5—S2—O4	113.8 (13)
C208—C209—C212	121 (2)	O6—S2—C2T	110.9 (18)
C210—C209—C212	119 (2)	O5—S2—C2T	104.9 (17)
C211—C210—C209	120.0	O4—S2—C2T	93.6 (16)
C210—C211—C206	120.0	F4—C2T—F5	116.9 (14)
C213—C212—C216	120.0	F4—C2T—F6	116.7 (14)
C213—C212—C209	121 (2)	F5—C2T—F6	114.5 (13)
C216—C212—C209	119 (2)	F4—C2T—S2	96.6 (18)
C212—C213—C214	120.0	F5—C2T—S2	103.9 (18)
N22—C214—C213	120.0	F6—C2T—S2	104.5 (18)
C215—N22—C214	120.0	O9—S3—O8	116.0 (13)
C215—N22—Pt3	120.7 (11)	O9—S3—O7	113.1 (13)
C214—N22—Pt3	119.3 (11)	O8—S3—O7	113.1 (13)
C216—C215—N22	120.0	O9—S3—C3T	113.2 (18)
C215—C216—C212	120.0	O8—S3—C3T	103.2 (17)
C207—N23—C217	106 (3)	O7—S3—C3T	96.1 (16)
N24—C217—N23	112 (3)	F8—C3T—F7	115.9 (14)

N24—C217—C218	122 (3)	F8—C3T—F9	115.4 (14)
N23—C217—C218	126 (3)	F7—C3T—F9	116.8 (14)
C217—N24—C208	107 (3)	F8—C3T—S3	104.5 (18)
C219—C218—C222	120.0	F7—C3T—S3	95.9 (17)
C219—C218—C217	119 (2)	F9—C3T—S3	104.4 (18)
C222—C218—C217	121 (2)	O10—S4—O11	115.5 (13)
C218—C219—C220	120.0	O10—S4—O12	115.2 (13)
N25—C220—C219	120.0	O11—S4—O12	113.0 (13)
C221—N25—C220	120.0	O10—S4—C4T	99.9 (16)
C221—N25—Pt6	121.6 (15)	O11—S4—C4T	103.8 (18)
C220—N25—Pt6	117.3 (15)	O12—S4—C4T	108 (2)
N25—C221—C222	120.0	F12—C4T—F11	115.6 (14)
C221—C222—C218	120.00 (5)	F12—C4T—F10	115.8 (14)
C224—C223—P21	109 (4)	F11—C4T—F10	115.8 (14)
C223—C224—C225	118 (6)	F12—C4T—S4	101 (2)
C224—C225—P22	111 (3)	F11—C4T—S4	107 (2)
C232—C231—C236	120.0	F10—C4T—S4	97.9 (19)
C232—C231—P21	115 (4)	O17—S6—O18	115.1 (13)
C236—C231—P21	125 (4)	O17—S6—O16	112.3 (13)
C233—C232—C231	120.0	O18—S6—O16	111.2 (12)
C234—C233—C232	120.0	O17—S6—C6T	109.8 (15)
C233—C234—C235	120.00 (5)	O18—S6—C6T	111.3 (17)
C236—C235—C234	120.0	O16—S6—C6T	95.5 (16)
C235—C236—C231	120.0	F18—C6T—F17	115.0 (14)
C242—C241—C246	120.0	F18—C6T—F16	114.5 (14)
C242—C241—P21	115 (3)	F17—C6T—F16	112.7 (14)
C246—C241—P21	125 (3)	F18—C6T—S6	105.6 (17)
C243—C242—C241	120.00 (7)	F17—C6T—S6	109.1 (17)
C244—C243—C242	120.00 (7)	F16—C6T—S6	98.0 (18)
C245—C244—C243	120.0	O20—S7—O19	114.6 (14)
C244—C245—C246	120.00 (6)	O20—S7—O21	114.7 (13)
C245—C246—C241	120.0	O19—S7—O21	114.1 (13)
C252—C251—C256	120.0	O20—S7—C7T	104.3 (16)
C252—C251—P22	126 (3)	O19—S7—C7T	97.9 (18)
C256—C251—P22	114 (3)	O21—S7—C7T	109.2 (19)
C253—C252—C251	120.0	F21—C7T—F19	115.3 (14)
C252—C253—C254	120.0	F21—C7T—F20	115.9 (14)

C255—C254—C253	120.0	F19—C7T—F20	115.6 (14)
C254—C255—C256	120.0	F21—C7T—S7	103 (2)
C255—C256—C251	120.0	F19—C7T—S7	98.9 (19)
C262—C261—C266	120.00 (8)	F20—C7T—S7	105 (2)
C262—C261—P22	120 (3)	O24—S8—O23	112.0 (13)
C266—C261—P22	119 (3)	O24—S8—O22	112.1 (13)
C261—C262—C263	120.00 (16)	O23—S8—O22	110.5 (14)
C264—C263—C262	120.0	O24—S8—C8T	119.7 (17)
C263—C264—C265	120.00 (8)	O23—S8—C8T	103.8 (17)
C266—C265—C264	120.00 (10)	O22—S8—C8T	97.6 (17)
C265—C266—C261	120.0	F24—C8T—F22	115.3 (15)
C301—N31—C305	120.0	F24—C8T—F23	114.6 (14)
C301—N31—Pt3	117.7 (13)	F22—C8T—F23	113.2 (14)
C305—N31—Pt3	122.1 (13)	F24—C8T—S8	106.7 (18)
N31—C301—C302	120.0	F22—C8T—S8	99.3 (18)
C303—C302—C301	120.0	F23—C8T—S8	105.7 (19)
C302—C303—C304	120.0	O25—S9—O26	115.1 (14)
C302—C303—C306	122 (2)	O25—S9—O27	114.4 (13)
C304—C303—C306	117 (2)	O26—S9—O27	113.2 (13)
C305—C304—C303	120.0	O25—S9—C9T	101.0 (17)
C304—C305—N31	120.0	O26—S9—C9T	103.5 (17)
C307—C306—C311	120.0	O27—S9—C9T	107.9 (19)
C307—C306—C303	121.9 (19)	F25—C9T—F26	115.5 (14)
C311—C306—C303	117.8 (19)	F25—C9T—F27	115.1 (14)
C308—C307—C306	120.0	F26—C9T—F27	114.7 (14)
C308—C307—N33	114 (2)	F25—C9T—S9	102.1 (19)
C306—C307—N33	126 (2)	F26—C9T—S9	104.7 (19)
C307—C308—C309	120.00 (6)	F27—C9T—S9	102.3 (18)
C307—C308—N34	104 (2)	O29—S10—O30	114.7 (14)
C309—C308—N34	136 (2)	O29—S10—O28	114.6 (14)
C310—C309—C308	120.0	O30—S10—O28	114.3 (14)
C310—C309—C312	122 (2)	O29—S10—C10T	104.8 (19)
C308—C309—C312	118 (2)	O30—S10—C10T	109 (2)
C311—C310—C309	120.0	O28—S10—C10T	97.8 (19)
C310—C311—C306	120.00 (7)	F28—C10T—F29	116.3 (15)
C313—C312—C316	120.0	F28—C10T—F30	115.3 (15)
C313—C312—C309	122 (2)	F29—C10T—F30	115.6 (14)

C316—C312—C309	118 (2)	F28—C10T—S10	99 (2)
C312—C313—C314	120.0	F29—C10T—S10	105 (2)
C313—C314—N32	120.0	F30—C10T—S10	102 (2)
C315—N32—C314	120.0	O31—S11—O33	116.8 (13)
C315—N32—Pt4	119.6 (16)	O31—S11—O32	115.2 (13)
C314—N32—Pt4	120.4 (16)	O33—S11—O32	113.6 (13)
C316—C315—N32	120.0	O31—S11—C11T	99.0 (17)
C315—C316—C312	120.0	O33—S11—C11T	107.5 (18)
C317—N33—C307	103 (3)	O32—S11—C11T	102.1 (16)
N33—C317—N34	114 (3)	F33—C11T—F31	116.1 (14)
N33—C317—C318	127 (3)	F33—C11T—F32	115.7 (14)
N34—C317—C318	119 (4)	F31—C11T—F32	115.7 (14)
C317—N34—C308	105 (3)	F33—C11T—S11	98.7 (18)
C319—C318—C322	120.00 (6)	F31—C11T—S11	101.6 (18)
C319—C318—C317	123 (2)	F32—C11T—S11	105.6 (18)
C322—C318—C317	117 (3)	O35—S12—O34	115.3 (13)
C318—C319—C320	120.0	O35—S12—O36	115.1 (12)
N35—C320—C319	120.0	O34—S12—O36	114.9 (13)
C320—N35—C321	120.00 (6)	O35—S12—C12T	103.8 (16)
C320—N35—Pt5	116.3 (16)	O34—S12—C12T	97.7 (16)
C321—N35—Pt5	123.1 (15)	O36—S12—C12T	107.5 (17)
N35—C321—C322	120.0	F36—C12T—F35	116.4 (14)
C321—C322—C318	120.0	F36—C12T—F34	116.0 (14)
C324—C323—P31	115 (3)	F35—C12T—F34	115.1 (14)
C325—C324—C323	111 (3)	F36—C12T—S12	103.2 (18)
C324—C325—P32	111 (2)	F35—C12T—S12	105.6 (18)
C332—C331—C336	120.0	F34—C12T—S12	97.0 (17)

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