Axially Chiral Ligands for Helical Coordination Complexes

By

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Abstract

The work described in this thesis is focused on the use of novel axially chiral ligands as building blocks for interesting coordination structures, with particular emphasis on constructing helical coordination complexes. Ligands were designed in light of the preferred coordination geometries of specific metals in order to attempt to control the final structures.

The synthesis of a new series of binaphthyl-based amide and imine ligands was developed, and their coordination to palladium, platinum, nickel, rhenium, ruthenium, and cobalt investigated.

In addition, the synthesis of biphenanthroline and biaryl ligand systems was explored and the chemistry of their precursors examined.

Finally, a novel range of biquinazolinones were synthesised and their behaviour as ligands was probed. The previously unreported coordination chemistry of this new class of axially chiral ligands is demonstrated by their complexation with rhenium, palladium and ruthenium. The first examples of crystal structures of biquinazolinone metal complexes are presented in this thesis.

Acknowledgements

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Thanks to Mum, Dad and Owain for always being at the end of the phone and believing in me. Also thanks so much to Chris who has been there for me all the way through and has supported and believed in me.

Lastly I'd like to thank Dr. Mike Coogan, who's advice, support and kind words are the main reason that I got this far.

Contents

Abbreviations

Abs	Absorption
Ala	Alanine
BINAM	2,2'-Diaminobinaphthalene
BINAP	2,2'-Diphosphinobinaphthalene
BINOL	2,2'-Dihydroxybinaphthalene
Biphen	Bi(1,10-phenanthroline)
Boc	t-Butoxycarbonyl
Bn	Benzyl
bpy	2,2'-Bipyridine
br	Broad
Bu	Butyl
Clphen	5-Chloro-1,10-phenanthroline
cm^{-1}	Reciprocal centimetres
d	Doublet
DCE	Dichloroethane
DCM	Dichloromethane
DDM	4,4-Diaminodiphenylmethane
d.e.	Diastereoselective excess
Dichlorophen	5, 5'-Dichloro-1,10-phenanthroline
DMF	Dimethylformamide
DPPA	Diphenylphosphoryl azide
ε	Extinction coefficient
e.e	Enantioselective excess
EI	Electron Impact
Epoxyphen	5-Epoxy-1,10-phenanthroline
ES	Electrospray
MS	Mass spectrometry
Et	Ethyl
Hydroxy-phen	5-Hydroxy-1,10-phenanthroline
IR	Infrared
J_{ab}	Coupling constant in hertz
m	Multiplet

Me	Methyl
Mes	Mesityl/ 2,4,6-trimethylphenyl
MLCT	Metal-to-Ligand Charge Transfer
NLO	Non-linear optics/optical
NMR	Nuclear magnetic resonance
Ph	Phenyl
Phen	1,10-Phenathroline
ppm	Parts per million
Pr	Propyl
Pr^i	Isopropyl
s	Singlet
t	Triplet
TBA	Tetra-butyl ammonium
TBDMS	t-Butyldimethylsilyl
THF	Tetrahydrofuran
Tol	Tolyl
UV-vis	Ultra-violet-visable

Chapter 1- Introduction

1.1 Chirality-Origins and Applications

Optically active compounds have been of much interest to scientists since the first observation of this phenomenon by Biot in 1815.[1] For a molecule to be able to show optical activity it must exist in two isomeric forms related as non-super imposable mirror images. In other words it must have no centre of inversion, no plane of symmetry, and no alternating rotation-reflection axis of symmetry i.e. no improper symmetry elements. These isomers, or enantiomers, have identical magnitudes of properties but with opposite signs of optical rotation and circular dichroism. When interacting with other chiral molecules, as found in biological systems, the reaction transition states are diastereomeric so have different energies therefore the enantiomers react differently. Consequently, the synthesis of enantiomerically pure chiral molecules is of great importance in drug synthesis, but also difficult due to separation problems.

1.2 Axial Chirality

There are several geometric origins of optical activity in a molecule; one being a tetrahedral carbon atom with four different groups attached, known as a chiral centre or an asymmetric carbon atom. Another is a chiral axis, which occurs in molecules that have restricted rotation around an axis resulting in no plane of symmetry. An example is shown in figure 1.1 where the non-identical groups at one end of the allene are held perpendicular to the non-identical groups at the other end.

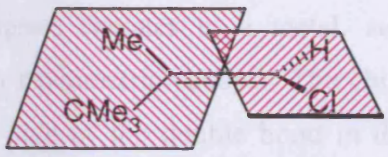

Figure 1.1 An allene with a chiral axis.

A whole set of these compounds exist with restricted rotation around a carbon-carbon bond that results in axial chirality or atropisomerism. A very early example is that of optically active biphenyl compounds such as 6,6'-dinitrobiphenyl-2,2'-dicarboxylic

acid. The racemic form was synthesized in 1921 by Kenner and Stubbings[2] and resolved with brucine by Kenner and Christie in 1922.[3] The groups in the ortho positions restrict rotation around the carbon-carbon single bond.

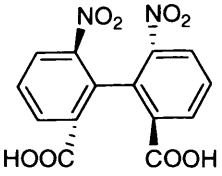

Figure 1.2 6,6'-Dinitrobiphenyl-2,2'-dicarboxylic acid

Another example of atropisomerism occurs in tertiary aromatic amides, as shown in figure 1.3. Restricted rotation occurs around the C-C single bond attached to the phenyl ring and amide. A very well known example showing axial chirality is BINAP

Figure 1.3 Atropisomeric benzamide

(figure 1.4), which is used commercially in asymmetric hydrogenation reactions. The

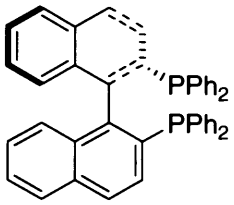

Figure 1.4 BINAP

optically active BINAP ligand chelates to a metal, such as ruthenium, and the complex can be used as an asymmetric catalyst. The chiral catalyst will only add a hydrogen molecule to one side of the double bond in the substrate resulting in an induced chiral centre. [(S)-BINAP]Ru$(OAc)_2$ is particularly good at hydrogenating allylic alcohols and α,β unsaturated carboxylic acids, so is used in the synthesis of the analgesic drug naproxen[4] (see figure 1.5).

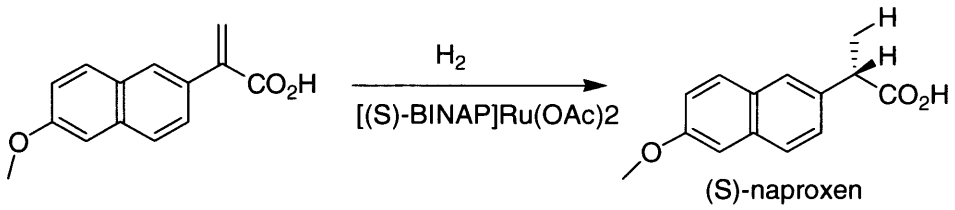

Figure 1.5 Synthesis of Naproxen

Due to their importance in asymmetric reactions, many analogous substituted 1,1-binaphthyls have been developed,[5-7] as well as molecules with restricted rotation around N-N bonds.[8, 9]

1.3 Applications in Non-Linear Optics

Chiral compounds can exhibit second order non-linear optical properties, such as second harmonic generation.[10] Non-linear materials interact with light and modulate its properties, for example, they can double the frequency of laser light (second harmonic generation). To exhibit second order non-linear properties it is necessary to have no centre of symmetry and to have a polarisable structure often containing donor and acceptor groups. Such materials are important in the development of photonics: the use of photons, instead of electrons, for information, and image processes.[11] This is of considerable interest for the high-speed processing of data, which is essential to computing and telecommunication. Advantages of photonic devices include speed, efficiency and the ability to store more information than conventional magnetic materials.[12] For these reasons and for their use in asymmetric catalysis and molecular recognition, axially chiral molecules have been incorporated into a variety of macromolecular and supramolecular structures.[10, 13-17]

1.4 Helical Chirality

Early studies by Fresnel[18] implied that optically active molecules must be helical, but this was not followed up for a long time. Helices are intrinsically chiral and so may have applications in non-linear optics.[10] The helical shape interacts with light producing large optical rotations and second-order non-linearities. There have been several approaches to the formation of helices but all involve taking smaller molecule building blocks and binding them together in order to produce a helical superstructure. One approach is to take axially chiral molecules and covalently bind them together to form organic helical polymers; the chirality in the components can

control the chirality of the helix. Several helical oligomers and polymers have been synthesised which include axially chiral binaphthyl units[19-23] including polymer **1** which is thought to have a propeller-like structure.[21] Polymerization occurs through the 3,3' positions, a strategy used in various examples in the literature.[10, 21, 24]

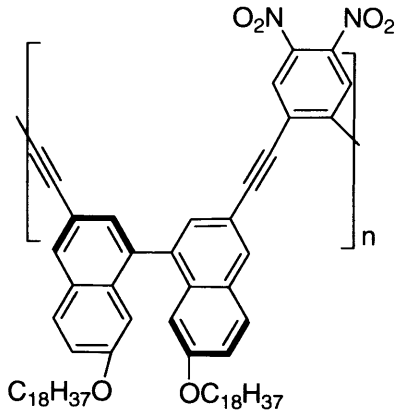

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Figure 1.6 Organic helical polymer 1 with acetylene and aryl spacers at the 3,3' positions.

Of particular interest is polyarylene **2** which can catalyse the asymmetric reaction between aldehydes and diethylamine with diethylzinc.[24]

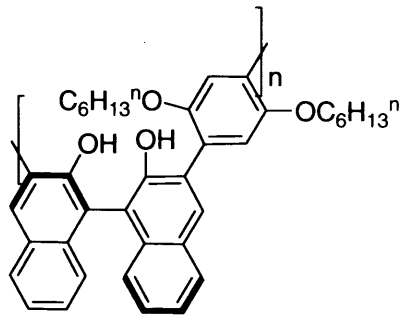

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Figure 1.7 Organic helical polymer 2 with aryl spacers at the 3,3' positions.

Another example is helical polymer **3,** which contains the chiral binaphthyl-unit preventing centrosymmetric crystal growth, π-conjugated bridges and e-donor and acceptor groups in order to optimize NLO properties.[10] The polymers were deposited in Langmuir-Blodgett films and showed high NLO efficiencies.

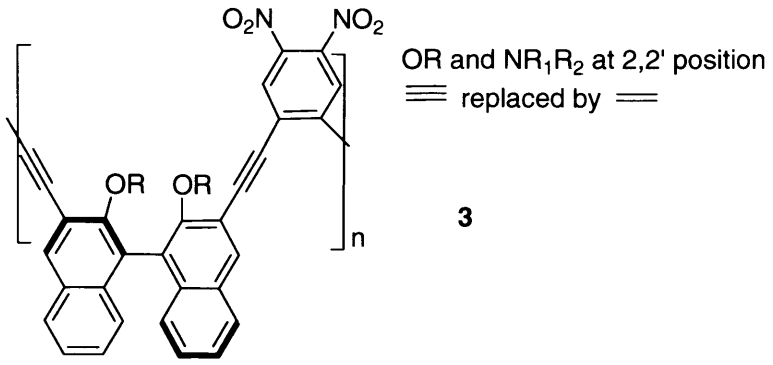

Figure 1.8 Organic helical polymer 3 with acetylene and aryl spacers.

An optically active monomer **4** was polymerized as shown in figure 1.9 to give polymer **5** with a single-handed helical conformation which is joined through the 2,2' position.[25] This polymerization was also achieved with the analogous biphenyl-based monomer.[26, 27]

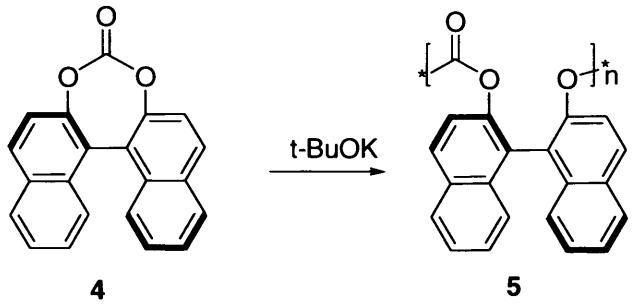

Figure 1.9 Organic helical polymer 5 with polymerisation at the 2,2' positions.

Polymerization along the chiral axis was achieved via a Suzuki coupling reaction with phenyl spacers in between each binaphthyl unit.[28]

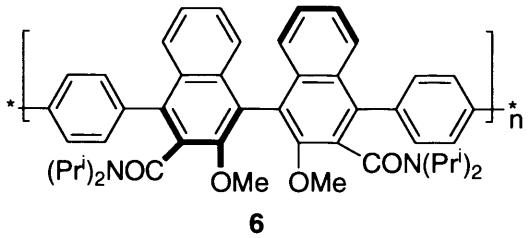

Figure 1.10 Organic helical polymer 6 with aryl spacers at the 4,4' positions.

1,1'-Binaphthyl oligomers and polymers were reviewed by Pu *et al* and their group has synthesized polymers linked through the 3,3' position, as seen earlier, as well as

at the 6,6' position of the binaphthyl and mixtures of the two.[24, 29] The hydroxyl groups of Binol are ideal binding sites for aluminium (III), zinc (II) or, if Binap is incorporated, ruthenium (III); and have been utilised in various asymmetric catalytic reactions.

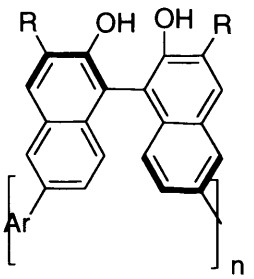

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Figure 1.11 Organic helical polymer 7 with aryl spacers at the 6,6' positions.

Another approach is to rely on weaker intermolecular forces to direct helix formation through self-assembly of the smaller molecules. Self-assembly results from the random motion of molecules and the affinity of their binding sites for one another. For example, DNA strands spontaneously assemble into a double helix through hydrogen bonding between donor and acceptor base pairs. Hydrogen bonding has also been used to direct the self-assembly of synthetic macromolecules such as peptide nanotubes[30] and catenanes.[17, 31] The formation of the latter, interlocked macrocycles, is also known to be driven by the self-assembly of aromatic π-donor and π-acceptors.[17] Various examples of axially chiral catenanes were reported by J.F. Stoddart such as catenane **10.**

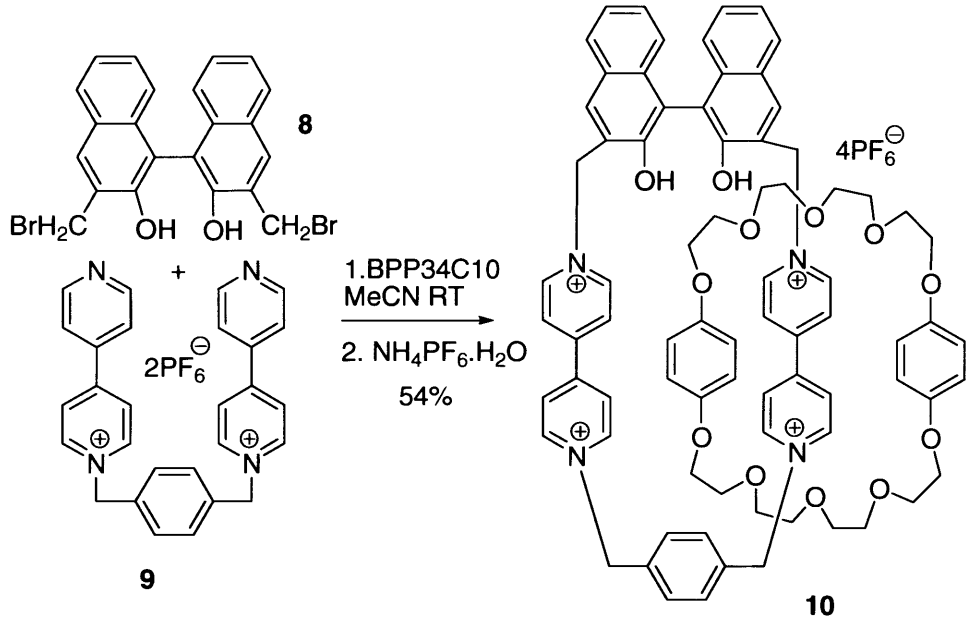


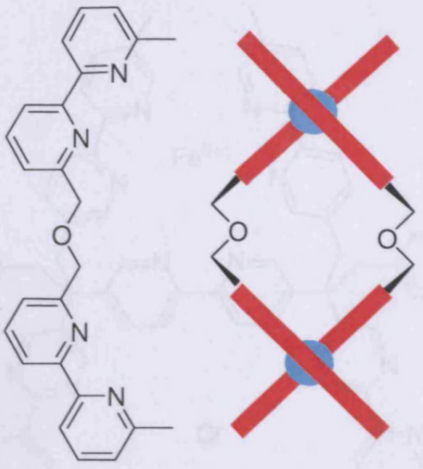
Figure 1.12 Self-assembly of catenane 10

1.5 Helicates and other coordination structures

Helicates involve the use of transition metal ions to help direct the self-assembly process. The metal-ligand dative covalent bonds are thermodynamically strong but also have varying degrees of lability meaning that kinetic stabilities can be used to form various stable structures. Also, ligand field effects mean that transition metal ions prefer certain geometry in their coordination sphere. For example, a metal ion that prefers tetrahedral geometries is likely to bind to a bidentate ligand to form a double helix of stoichiometry $[M_2L_2]^{n+}$ [32] This means one can have precise control over the molecular geometry, which is essential in self-assembly processes. The binding of one metal ion sets up the system for binding to build up a helical structure, as long as this structure is the most stable product.

1.51 Racemic helicates

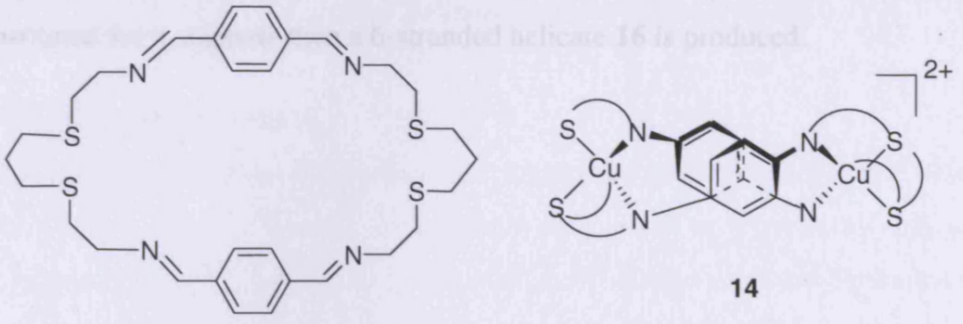
One approach to making helicates is to use achiral ligands that bind to the metal forming a helical structure. An example of this could be two long chain ligands bound together by the metal to form a double helix, as in the work of Lehn and co-workers and Constable *et al* (reviewed by Piguet *et al*[33]). Figure 1.13 shows a dinuclear copper (I) complex **12** of the substituted 2,2' bipyridyl/ether derivative **11.**[34]



11 **12**

Figure 1.13 A dinuclear copper (I) complex 12 of substituted 2,2' bipyridyl/ether derivative 11.

Some macrocyclic ligands have been shown to bind to metals to form double helical structures. The example in figure 1.14 shows a macrocycle **13** in its uncoordinated form and figure of eight coordinated structure **14**. The arrangement on the right reflects the preferred tetrahedral co-ordination of the copper (I) ions and π-stacking of the phenylene rings.[35]



13 **14**

Figure 1.14 A Macrocycle, uncoordinated and coordinated with Copper (I).

A particularly interesting example is the circular helicate developed by Lehn and co-workers, where the structure depends on the counter ion present.[36]

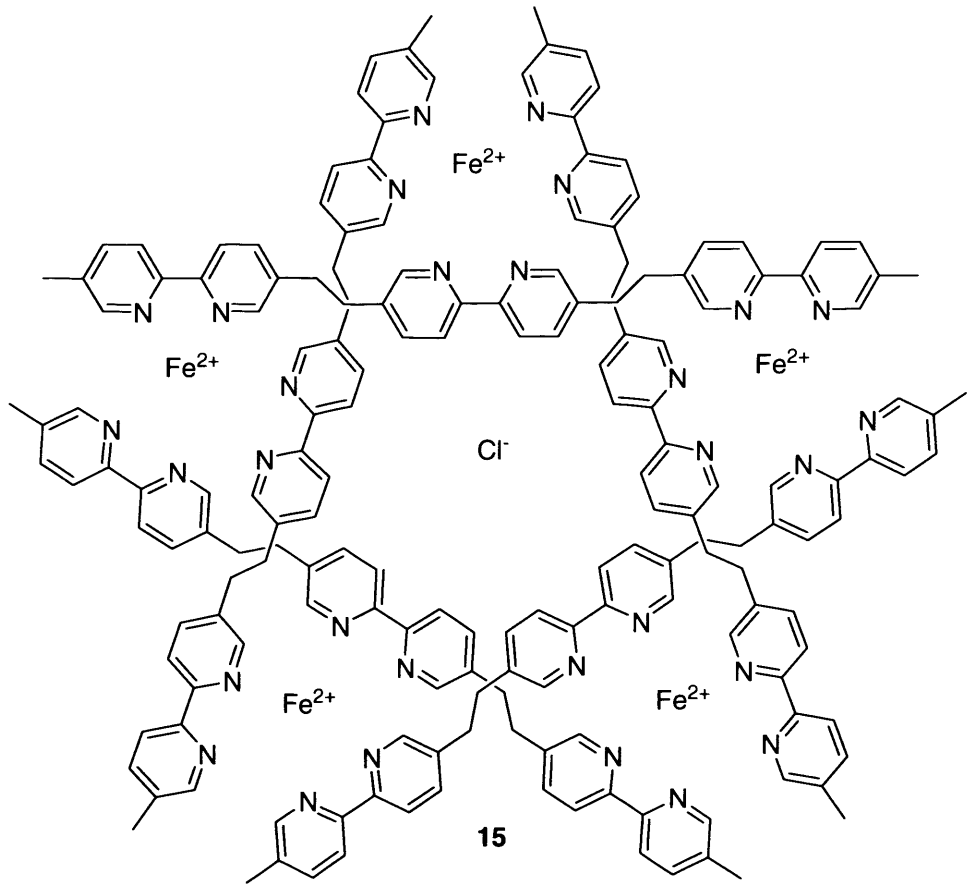


Figure 1.15 Circular Helicate 15 in the presence of $FeCl_2$

In the presence of chloride ions a 5-stranded helicate **15** forms but when the chloride is substituted for a sulphate then a 6-stranded helicate **16** is produced.

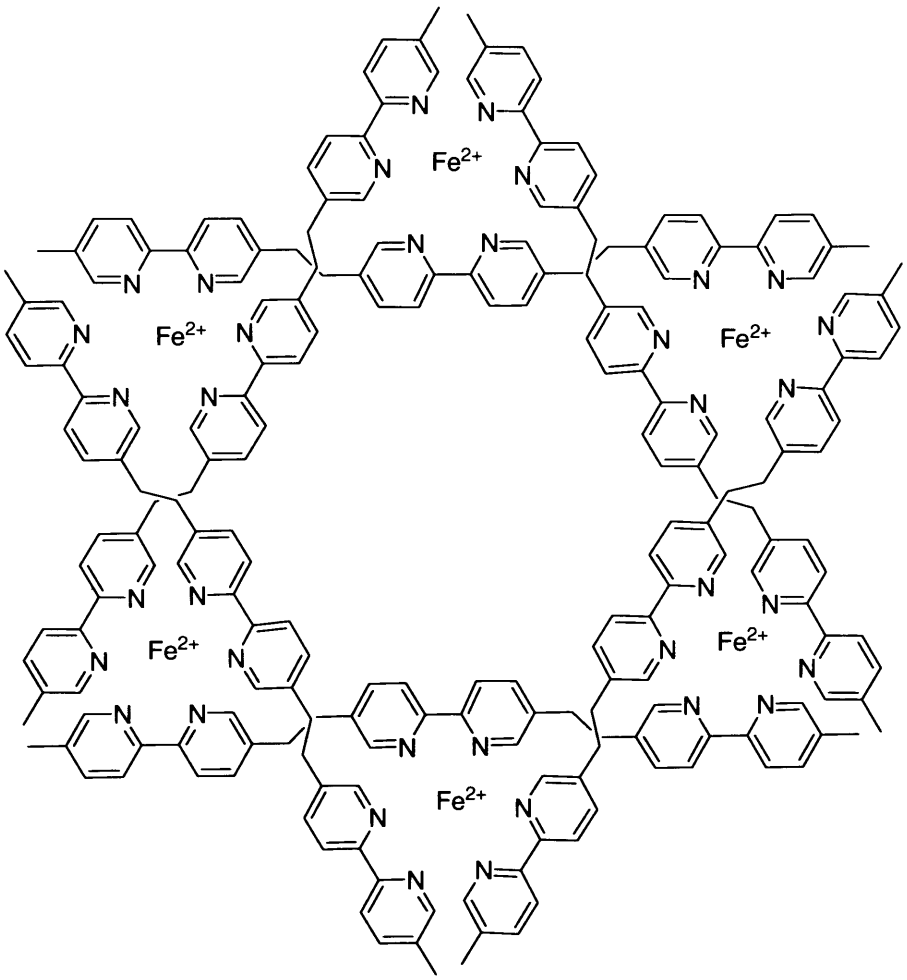


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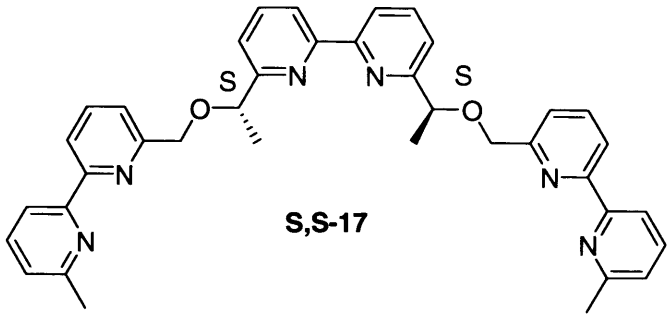
Figure 1.16 Circular helicate in the presence of $FeSO_4$

1.52 Non-Racemic Helicates

A problem with using achiral ligands is that the resultant chiral helicates are obtained as a racemic mixture.[37] Various groups have used resolved asymmetric ligands to solve this problem. [38-41] Lehn *et al* introduced chiral centres (of S-configuration) into each ligand strand resulting in a predominately right-handed double helicate copper (I) complex.[38]



S,S-17

Figure 1.17 Oligobipyridyl strand of S,S configuration

An interesting way of controlling helicate structure was to tether the strands to an enantiopure axially chiral molecule as in double-helicate **18.** The pyridyl groups were bound to silver (I) or copper (I) ions to form enantiopure helicates.

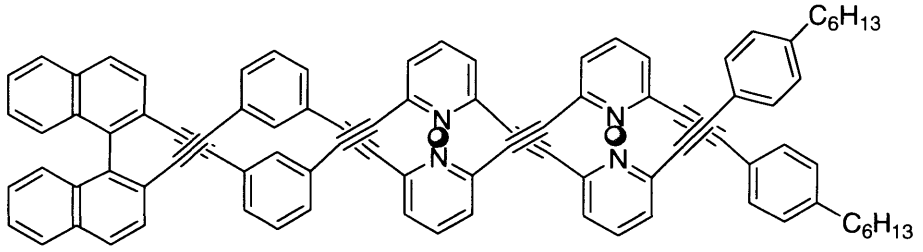


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Figure 1.18 One-handed double-stranded helicate 18

When a binaphthyl is bound to fused phenyl rings, as in figure 1.19, the rigid backbone twists to reduce steric repulsion, like in helicene, but with the twist predetermined by twist of the binaphthyl.[42] Addition of zinc (II) or iron (II) forms a mononuclear helicate **19;** the position of the binding sites enables the ligand to bind to just one metal.

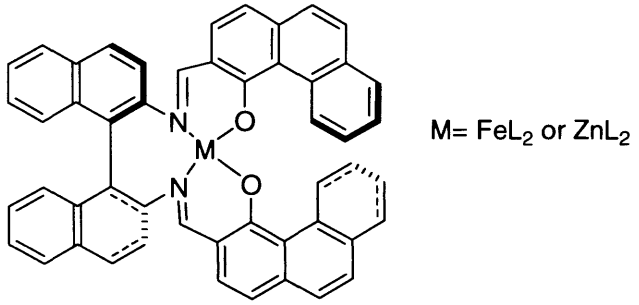

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Figure 1.19 Helicene type helicate with a rigid backbone

Another way to approach this problem would be to use resolved axially chiral ligands bound alternately to metal ions. This would mean making small ligand building blocks rather than long chain ligands. There is already an M or P (minus or plus) twist in the ligand so if arranged in the same orientation each time should form a helical polymer. The stereochemistry around the metal ion must be predictable, resulting from steric and electronic factors. Depending on the binding site on the ligand different structures can be formed, as shown by the review written by Telfer and Kuroda.[13]

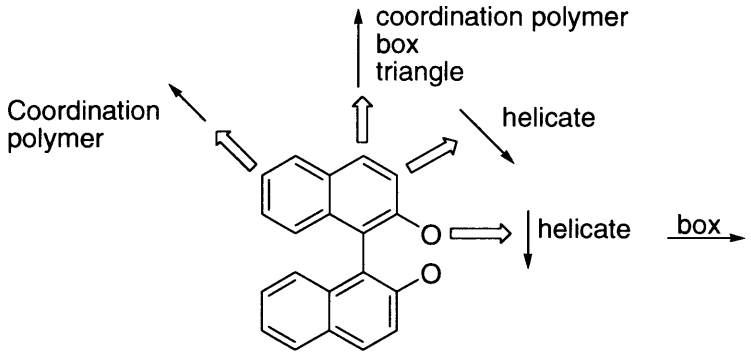

Figure 1.20 Predicted supramolecular formation. The thick arrows represent binding sties and the thin arrows vectors.

1.53 Predictable Homochiral Coordination Structures.

Lin *et al* have synthesised a range of useful structures with cavities, such as triangles. When R=H the triangle acts as a ligand for titanium(IV) and this complex can be used as an asymmetric catalyst for the addition of diethyl zinc to aromatic aldehydes with e.e.'s up to 92%.[43]

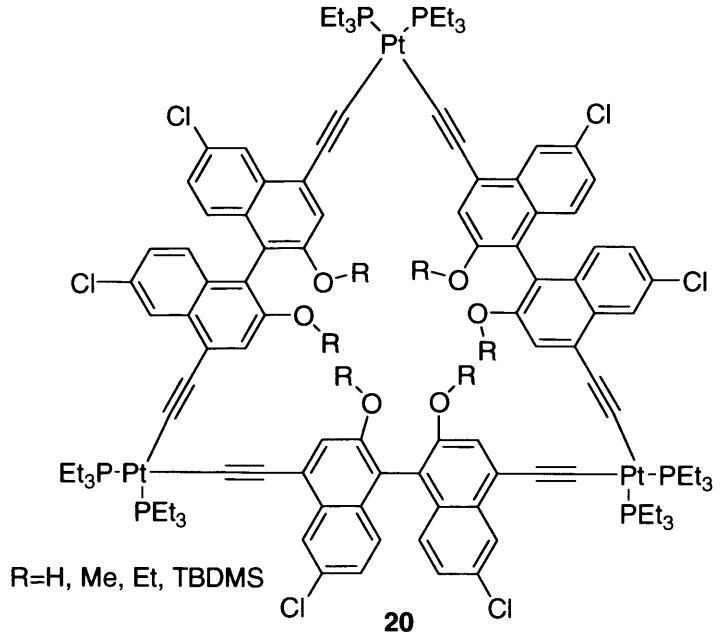

Figure 1.21 Molecular triangles with cis-platinum corners

When the alkyne binding site was moved to the 6,6' position a metallomacrocycle was formed as shown in figure 1.22. This metallocycle is a ligand which can be incorporated in a useful catalyst.[44]

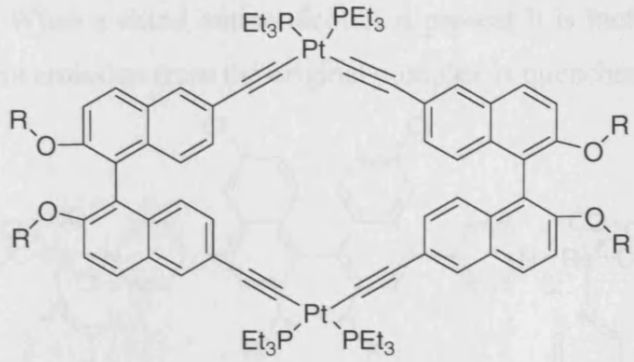

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Figure 1.22 Metallomacrocycle with cis-platinum.

Changing from cis to trans platinum(II) precursors produced six different molecular polygons in one pot, from triangle to octagon, all with enzyme-like pockets with potential uses in chiral sensing and asymmetric catalysis.[45] The acetyl groups on the molecular square were removed and interesting dendrimers were formed in subsequent work.[46]

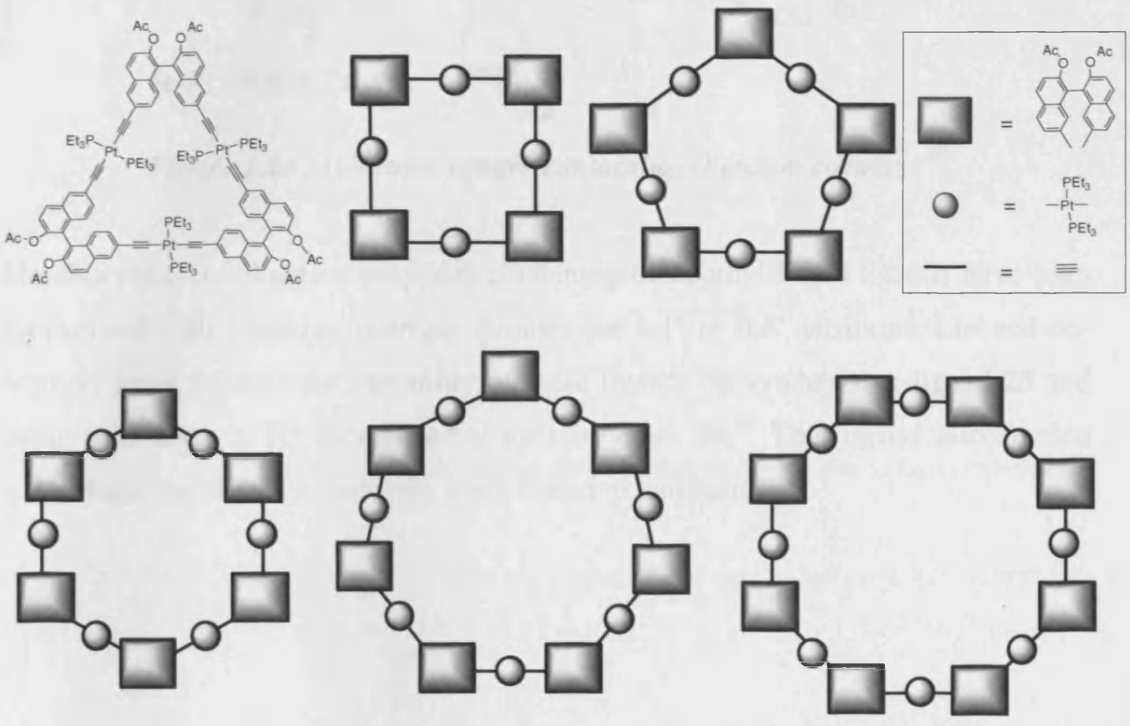

Figure 1.23 Molecular polygons with trans-platinum

Similar acetylene ligands also formed polymers when bound to palladium and platinum [47] Lin's group have also synthesised molecular squares **22** containing luminescent rhenium corners, which can act as enantioselective sensors for chiral

amino alcohols.[48] When a chiral amino alcohol is present it is included in the cavity and the luminescent emission from the original complex is quenched.

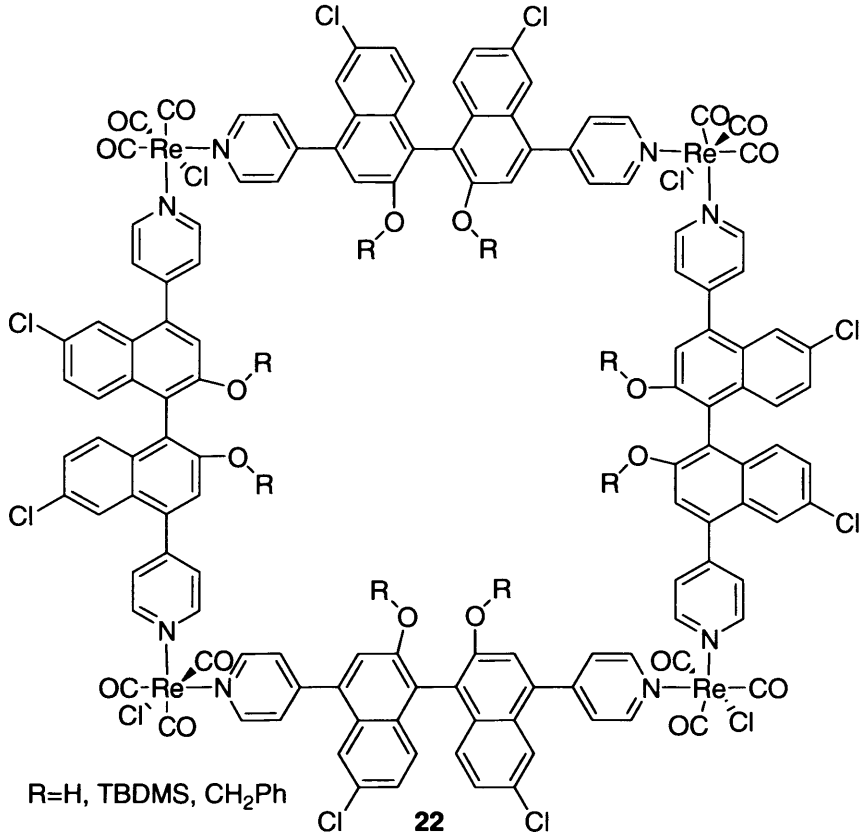

Figure 1.24 Molecular square containing rhenium corners. [48]

Metal-organic coordination polymers containing binaphthyl-based ligands have been synthesised with binding occurring through the 4,4' or 6,6' positions. Lin and co-workers again showed the versatility of these ligands by synthesising ligand **23** and using it to form a 2D rhombohedral grid structure **24.**[49] This ligand also formed homochiral coordination networks when bound to lanthanides.[50]

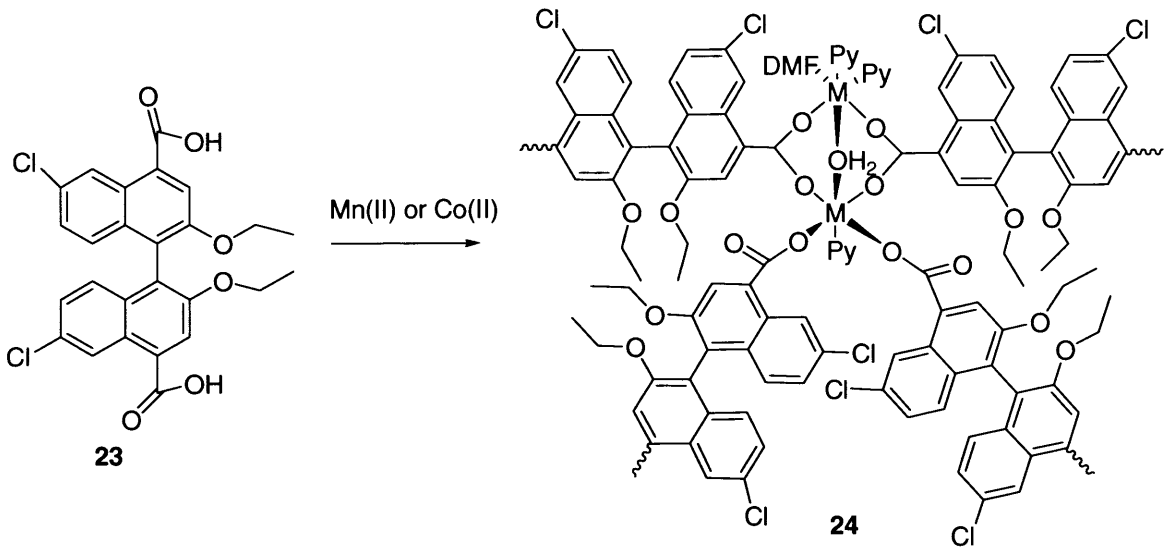

Figure 1.25 2D rhombohedral grid.

Coordination of bisphosphonate ligand **25** to the carbonates of manganese, cobalt and nickel, nickel hydroxide, copper (II) oxide or zinc (II) perchlorate also produced homochiral networks.[51] Bisphosphonate **26** was bound to lanthanides ions and formed similar networks but with a more compact structure.[52]

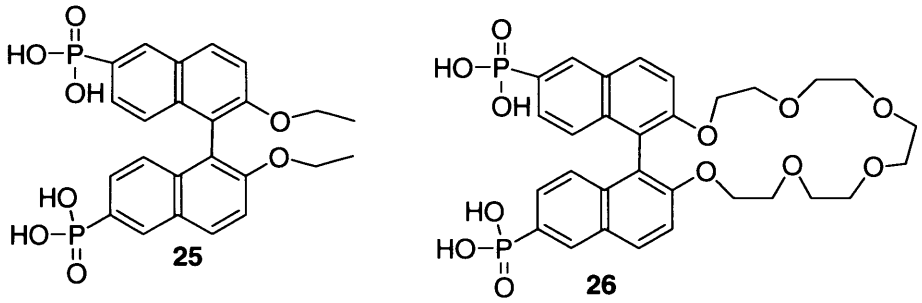

Figure 1.26 Bisphosphonate ligands that form homochiral coordination networks.

A single-stranded polymer was formed by Kimura *et al* using bridging 6,6'-terpyridyl ligand **27** with iron to form $[Fe_nL_n]^{2n+}$.

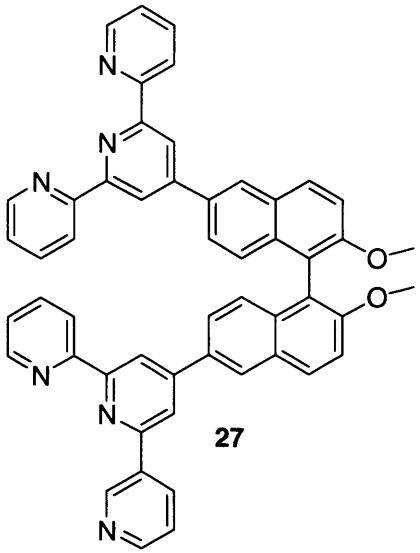

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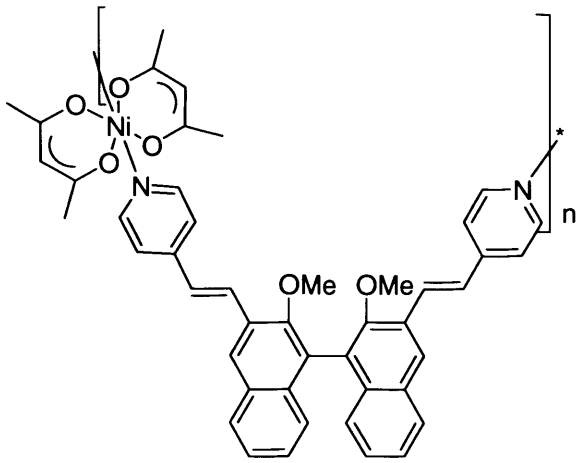
Figure 1.27 6,6'-Terpyridyl 27 which forms single stranded polymers.

1.54 Homochiral Helicates Containing Axially Chiral Molecules.

There are several examples of binaphthyl-based helicates in the literature. The combination of trans-nickel acac with 2,2'-dimethoxy-1,1'-binaphthyl-3,3'-bis(4-vinylpyridine produced a left-handed helical chain. Three of these chains self-assembled through Van der Waals forces to form a triple-helicate.[53]



28

Figure 1.28 Nickel helicate 28

A similar ligand synthesised by Lutzen *et al* produced triple helicates when bound to zinc(II) and double helicates with the metal ions copper(I) and silver(I), which prefer tetrahedral geometry.[54]

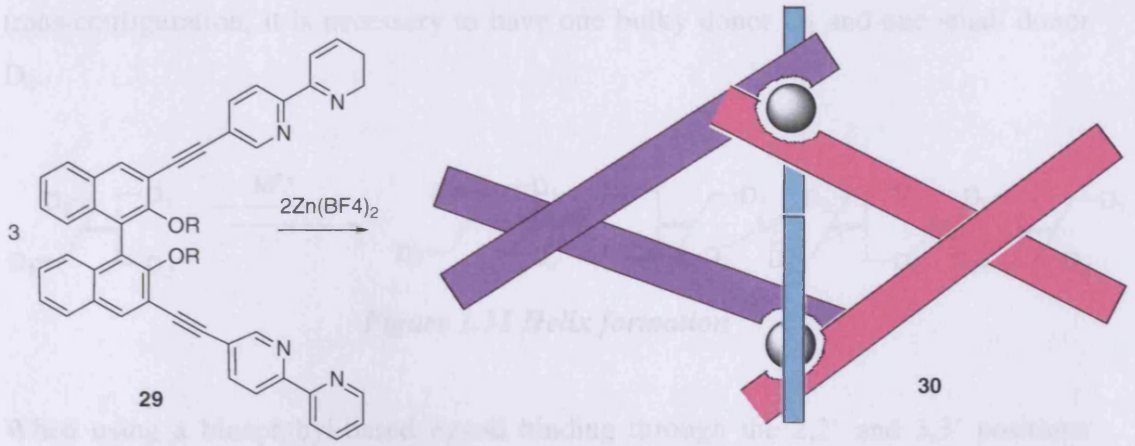


Figure 1.29 Triple helicate 30.

Takata *et al* showed helicate formation can depend on the structure of the ligand with the synthesis of two salen type binaphthyl ligands different only in the length of spacer binding the binaphthyl groups together.[55] When the ligand had a propanyl spacer, a trinuclear circular helicate was formed on addition of copper (II) acetate; whereas a pentanyl spacer induced a dinuclear side-by-side structure. In both cases the copper ions were bound to the imine and hydroxyl groups of two different ligands in a distorted square planar geometry.

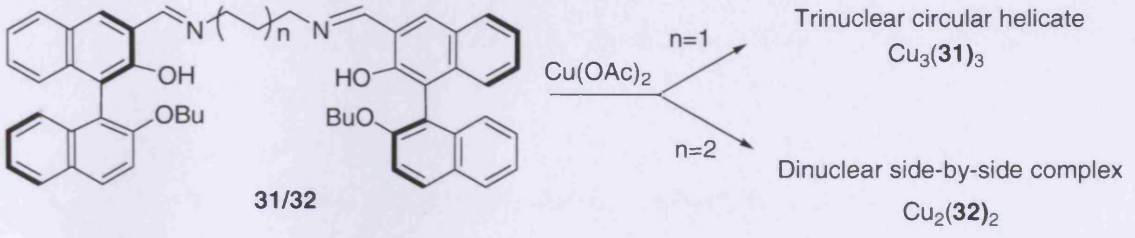


Figure 1.30 Two ligands which show length of spacer can vary structure formed.

1.6 Aim

The aim of this project was to make optically pure axially chiral ligands and bind them to metals to form helical structures. These ligands must be able to bridge the metal ions to form polymers or oligomers, so they need to be able to bind to two metals. For the macromolecular structure to be predictable the stereochemistry at the metal must be predictable. For a metal with square planar preferred geometry, a trans-orientation of ligands is necessary to form a continuous structure, as shown earlier. The trans-effect should destabilise the two best σ-donors, so, in order to keep the

trans-configuration, it is necessary to have one bulky donor D_1 and one small donor D_2.

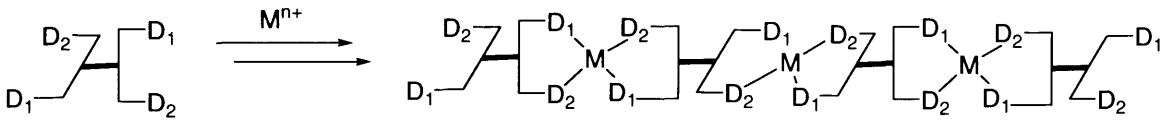


Figure 1.31 Helix formation

When using a binaphthyl-based ligand binding through the 2,2' and 3,3' positions seems to favour helicate formation. Chelate binding at both of these positions should mean more predictable structure and stability.

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Chapter 2- Experimental Methods

2.1 General Methods

All starting materials, reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. All ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker DPX-250, Bruker DPX-400 or Bruker Avance 500 spectrometer, with ^{1}H spectra being recorded at 250, 400 or 500 MHz and ^{13}C spectra being recorded at 62.5, 100 or 125 MHz respectively. ^{31}P spectra were recorded on a Jeol Eclipse 300 spectrometer at 121 MHz. Unless otherwise stated, all spectra were recorded in deuterated chloroform at ambient temperature, all chemical shifts are reported in δ (ppm) and coupling constants (J) are reported in Hertz. ^{1}H NMR spectra were referenced to the residual proton impurity in the solvent ($CHCl_3$, 7.26 ppm). ^{13}C spectra were referenced against the solvent resonance ($CDCl_3$, 77.0 ppm). ^{31}P-NMR spectra were externally referenced by a program incorporated in Jeol. ^{13}C-NMR and ^{31}P-NMR spectra were recorded proton decoupled.

UV spectra were recorded on a Jasco V-570 spectrophotometer and mass spectra were obtained using a Fisons VG platform II spectrometer or at the EPSRC mass spectrometry service in Swansea. Mass spectra have been recorded as low resolution unless otherwise stated. Melting points were determined on a Kofler Hot Stage Micro Melting Point Apparatus and are uncorrected. Infrared spectra were recorded in the range 4000–600 cm^{-1} at a resolution of $4cm^{-1}$ using a Perkin–Elmer 1600 series spectrophotometer or using a Nicolet 510 FT-IR spectrometer as nujol mulls between sodium chloride plates or in solution cell bearing sodium chloride windows or as thin films or as part of potassium bromide discs. Optical rotations were measured on an Optical Activity AA-1000 polarimeter at room temperature. Elemental analysis was performed by Warwick Analytical Services (University of Warwick).

When appropriate, reactions were conducted in oven-dried apparatus under an atmosphere of dry nitrogen using standard Schlenk techniques. All organic solutions from aqueous work-ups were dried by brief exposure to dried magnesium sulfate, followed by gravity filtration. The resulting dried solutions were evaporated using a Büchi rotary evaporator under reduced pressure using a Büchi vacuum pump, at an appropriate temperature unless otherwise stated. Column chromatography was carried out using Merck Silica Gel 60 (230–400 mesh). TLC analyses were carried out using

Merck silica gel 60 F_{254} pre-coated, aluminium-backed plates, which were visualized using ultraviolet light or potassium permanganate or vanillin or iron chloride dips.

2.2 X-ray Crystallography

Part of this research project involved being responsible for x-ray crystallography for the research group and therefore running and solving the majority of the crystal structures reported in this thesis. In order to obtain a crystal structure it was necessary to grow suitable single crystals of a diameter 0.2-0.4 mm. Crystals were grown using the following methods (adapted from the methods suggested by Paul D. Boyle, NCSU):

Slow Evaporation

A saturated or nearly saturated solution of the solid was prepared, filtered into a clean sample tube, loosely covered with a lid with holes or film and left to evaporate until suitable crystals formed.

Slow Cooling

A saturated solution was prepared using hot solvent. The solution was filtered while hot into a clean sample tube and put into a flask of hot water, hot oil or kept insulated with polystyrene and left to cool until suitable crystals form. It is necessary to use a solvent that the solid is only moderately soluble in at room temperature, a combination of solvents can be used to inhibit or increase solubility.

Vapour Diffusion

A saturated solution was prepared, in a solvent that the solid is very soluble in and filtered into a clean small sample tube and covered in Nescofilm®. This was placed inside a larger sample tube containing a poorer solvent of similar volatility to the first solvent. The system was sealed and left to diffuse and form suitable crystals.

Solvent Diffusion

A saturated solution was prepared and filtered into a clean small sample tube. A layer of a poor solvent is carefully layered on top and the system was sealed and left to slowly diffuse until a suitable crystal formed.

Once grown, one clear, clean, crack-free crystal, of the correct size, was chosen and mounted on a glass fibre with silicon oil. This was attached to the goniometer head.

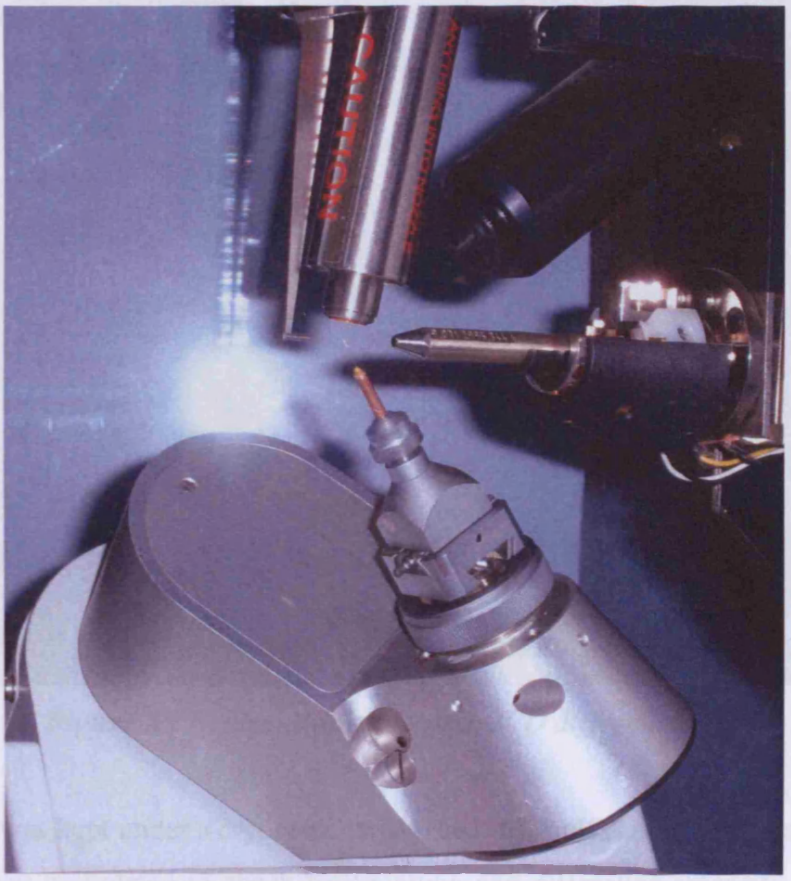

Figure 2.1 Goniometer head under a cryostream

Data for all compounds were collected on a Bruker-Nonius Kappa CCD diffractometer, equipped with a CCD detector, a liquid-nitrogen low-temperature device and a Bruker-Nonius FR590 X-ray generator with a molybdenum sealed tube (λ=0.7093 Å).

Figure 2.2 Bruker-Nonius Kappa CCD diffractometer

The crystal was kept under a cryogenic stream at 150K unless otherwise stated. Firstly a test run was completed to check for twinning and diffraction intensity and then a single short phi scan was run to determine the unit cell. From looking at the diffraction patterns, the unit cell parameters, the volume, mosaicity and chi values it was possible to judge the quality of the crystal and the data. A larger scan set was then generated in order to obtain enough data to solve the crystal structure. Collection times varied from ninety minutes to a day. Data collection and cell refinement were carried out using DENZO[1] and COLLECT[2] through Nonius SUPERGUI. Structure solution and refinement was accomplished by DIRDIF-99[3] (Patterson method), SIR-92,[4] SIR-97[5] SIR-2002[6] (direct methods) and SHEXL-97[7] through MAXUS[8] and WinGX32[9] graphical interfaces; absorption corrections were performed using SORTAV.[10] All non-hydrogen atoms were refined in anisotropic approximation (with exception to disordered atoms) with hydrogen atoms placed in calculated positions using the riding model. Structure visualization was facilitated by Xseed[11] and POV-ray.

2.3 References

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Chapter 3- Binaphthoic acid and binaphthyl-amides

3.1 Introduction

Binaphthyl derivatives have been studied for many years, the two most famous being BINOL and BINAP. These molecules have restricted rotation around the central carbon-carbon bond which causes axial chirality. As these molecules can be bi-dentate ligands the chirality can induce an asymmetric environment around the metal making them great candidates for asymmetric catalysis,[1, 2] chiral molecular recognition[3] and formation of chiral superstructures.[4, 5]

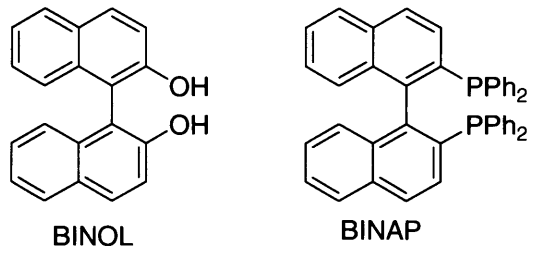


Figure 3.1 BINOL and BINAP

BINOL was first synthesised by Pummerer *et al* in 1926 using iron chloride[6] as shown in figure 3.2. This reaction probably proceeds through a free radical oxidative coupling mechanism[7] shown in figure 3.3.

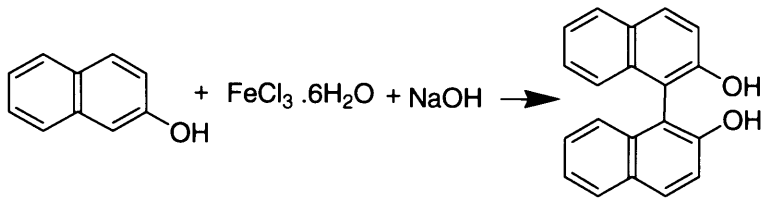


Figure 3.2 Oxidative coupling to form BINOL.

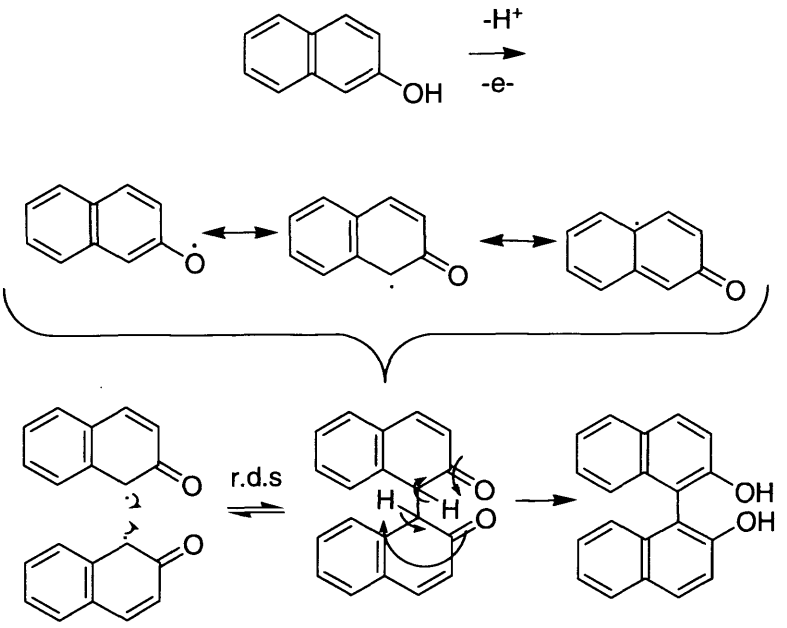


Figure 3.3 Free radical oxidative coupling mechanism

BINOL was first resolved through the cichonine salt of its phosphate ester by Jacques and co-workers.[8] BINAP was introduced by Noyori *et al* in 1980 and has been extensively used in asymmetric catalysis.[1]

Largely due to the success of BINOL and BINAP, development of analogous compounds with useful properties is now a major research area. Their synthesis has been approached in several ways, firstly, oxidative coupling of the naphthalene monomer with metallic salts. As referred to above, the racemic product then needs to be resolved through addition of a chiral resolving agent and subsequent crystallisation of diastereomeric salts or separation of derived diastereomers through column chromatography. Early examples used iron chloride in stoichiometric amounts to perform a free radical coupling,[6] however iron chloride is also a Lewis acid and acts as a Friedel-Crafts catalyst so this reaction can form additional by-products in reactions with aromatic systems. Another coupling agent used to couple β-naphthol was manganese (III) acetylacetonate (MTA) with a yield of 69%.[9] Coupling using copper-amine complexes[10, 11] is particularly popular, Tsubaki *et al* obtained 3,3'-bis(benzyloxy)-1,1'-binaphthalene-2,2'-ol with 99% yield using copper (II) chloride/α-methylbenzylamine in stoichiometric amounts.[12] This product was resolved by esterification with Boc-Ala-OH, separating by column chromatography and hydrolyzing to produce 92% R and 91% S. Other resolving agents used have been

amino acid derivatives,[13] copper chloride/ sparteine[14, 15] BH_3/proline[16] and $B(OH)_3$//α-methylbenzylamine.[11] Wang *et al* condensed the amino acid derivative (S)-proline methyl ester with 3-hydroxy-2-naphthoic acid then coupled with copper chloride, and separated the resulting diastereomers by chromatography giving a 30% yield and 97% e.e; having the electron withdrawing carboxyl group in the two position means that the coupling reaction is considerably slower than when coupling naphthol and low yields tend to be obtained.

More popular in the last twenty years has been asymmetric oxidative coupling, which has the advantage of often higher overall yields and fewer steps compared to previous methods. The role of copper ions in enzymatic phenol oxidations is well established so copper complexes with chiral amines have been widely studied as catalysts.[14, 17-23] Other catalysts have been based on oxovanadium[24, 25] or ruthenium systems.[26]

Finally, certain binaphthalene derivatives are commercially available, racemic or in optically pure form, which can be functionalised with similar methods to the monomer or phenyl rings.

There are many examples of the use of binaphthyls in asymmetric catalysis including hydrogenation of ketones,[27] allylic substitutions[28] and N-arylation of amines.[29] Binaphthyls have been incorporated into catenanes,[30] macrocycles, [31, 32] microporous materials,[31] organic helical polymers,[5, 33] binaphthyl oligomers/polymers,[34-38] chiral molecular polygons[39] and coordination[40, 41] and metallosupramolecular structures.[4, 5] These compounds have shown NLO properties,[33] molecular recognition,[30] transition metal tuning,[32] photoluminescence[40] and Metal-to- Ligand Charge Transfer (MCLT).[41]

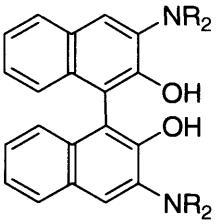
Like other binaphthyls, binaphthylamide compounds have been synthesised by several groups through oxidative coupling of the amide monomer followed by resolution,[42] asymmetric oxidative coupling,[20] or conversion of more readily available binaphthyls to amides.[20, 42-45]

These amides have been used as ligands in asymmetric catalysts for example, coordinated to zinc in phenyl transfer to aldehydes,[46] and asymmetric Simmons-Smith cyclopropanation of E-allylic alcohols.[45] Binaphthylamide titanium complexes have even been grafted to a polystyrene resin to be used in the enantioselective addition of diethyl zinc to aldehydes, for efficient recovery of the catalyst.[43] Binaphthamides

have also been incorporated into calixarenes as possible catalysts of use in molecular recognition.[47]

Helical polymers based on binaphthylamides have yet to be studied so are an interesting research avenue.

The initial approach was to synthesise optically pure axially chiral ligands based on a 1,1' binaphthyl skeleton.



1

Figure 3.4 Binaphthyl 1

Each ligand needed four coordination sites in order to bind with two metal ions. For the macromolecular structure to be predictable the stereochemistry at the metal must be predictable. For a metal with square planar preferred geometry, a trans orientation of ligands is necessary. The trans-effect should destabilise the two best σ-donors, so, in order to keep the trans configuration, it is necessary to have one bulky donor and one small donor. The first example to be attempted was amine **1,** with hydroxyls as the small donors, and bulky amines as the other donors.

An example of a desirable structure is shown in figure 3.5.

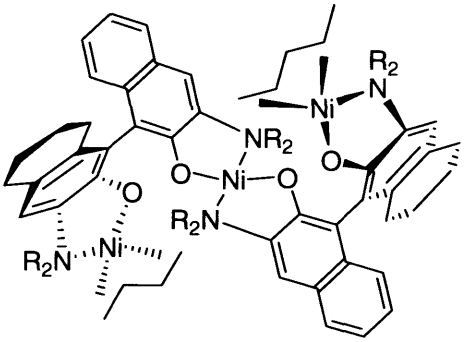


Figure 3.5 A fragment of a nickel-amine helix.

3.2 Results and Discussion

3.21 Ligand Synthesis

The first step in the synthetic approach to ligands, which were hoped to be suitable for helix formation, was the dimerisation of 3-hydroxy-2-naphthoic acid to form 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2**. [30]

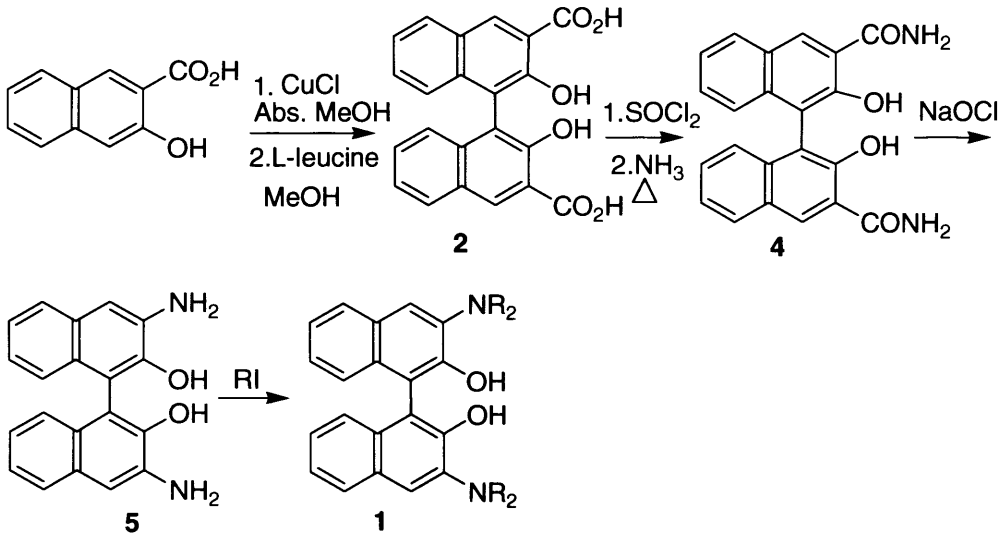


Figure 3.6 Dimeric binaphthyl-amine synthesis.

Initially iron chloride was used as the oxidizing agent in this free radical oxidative coupling. This resulted in a yield of 17% after washing repeatedly with acetic acid and water. This was very time consuming and some of the dimeric acid **2** was probably lost in the process (as well as Friedel-Crafts reaction products) which would explain the low yield. The final product showed all the characteristic NMR peaks, as in the literature,[30] but showed a ratio of dimeric acid **2** to 3-hydroxy-2-naphthoic acid of 10:3. This reaction was time consuming and resulted in an impure product, so another procedure was used; an adaptation of a reaction developed by Xin *et al.*[48] The free radical oxidative coupling was catalyzed by copper chloride and the oxidant was provided by air or oxygen bubbling through it. Crude yields were 43% and 54% respectively, comparable to the crude yield obtained when just left open to air for ten days, 44%. The reaction under oxygen was left for only forty four hours compared to ninety hours for the air reaction showing that oxygen increased the rate of oxidation. After recrystallisation from methanol, the yields were 32% and 34% respectively so the overall yields were not significantly different.

In order to form single-handed helices it was necessary to use enantiomerically pure ligands, so the next step was to optically resolve dimeric acid **2**. L-Leucine methyl ester was used as the resolving agent, as in the literature.[30] Resolution yields were as high as 40.9% based on the racemate and gave a good enantiomeric excess of 96.4% taking into account the accuracy of the polarimeter. Crystal structures of the dimeric acid with methanol and the resolution with L-leucine methyl ester have been obtained.

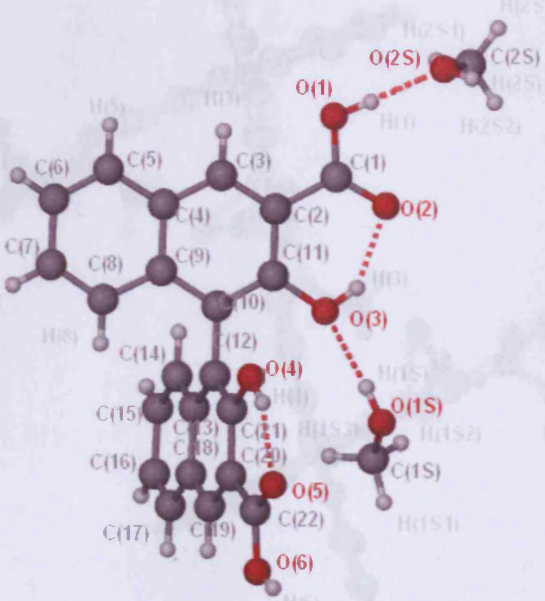


Figure 3.7 Molecular Structure of Dimeric acid 2.

Table 3.1 Crystallographic details for Dimeric Acid 2

Compound	**2**
Formula	$C_{22}H_{14}O_4.2CH_3OH$
M	438.4
a (Å)	11.432(5)
b (Å)	12.086(5)
c (Å)	19.517(5)
α (°)	90.000
β (°)	100.191(5)
γ (°)	90.000
V (Å^3)	2147.0(24)
T (K)	150
Crystal system	Monoclinic
Space group	P21/a
Z	4
μ (mm^{-1})	0.102
Reflections collected	24776
Independent reflections (R_{int})	4882[R(int)=0.0807]
Final R indices (all data)	R_1=0.0557, wR_2=0.1257

Table 3.2 Hydrogen bond lengths (Å) between dimeric acid 2 and methanol

H-Bond	H_1-O_{2S}	H_3-O_2	$H_{6'}$-O_2	H_{1S}-O_3	H_{2S}-$O_{1S'}$
Distance(Å)	1.700	1.867	1.878	2.096	1.849

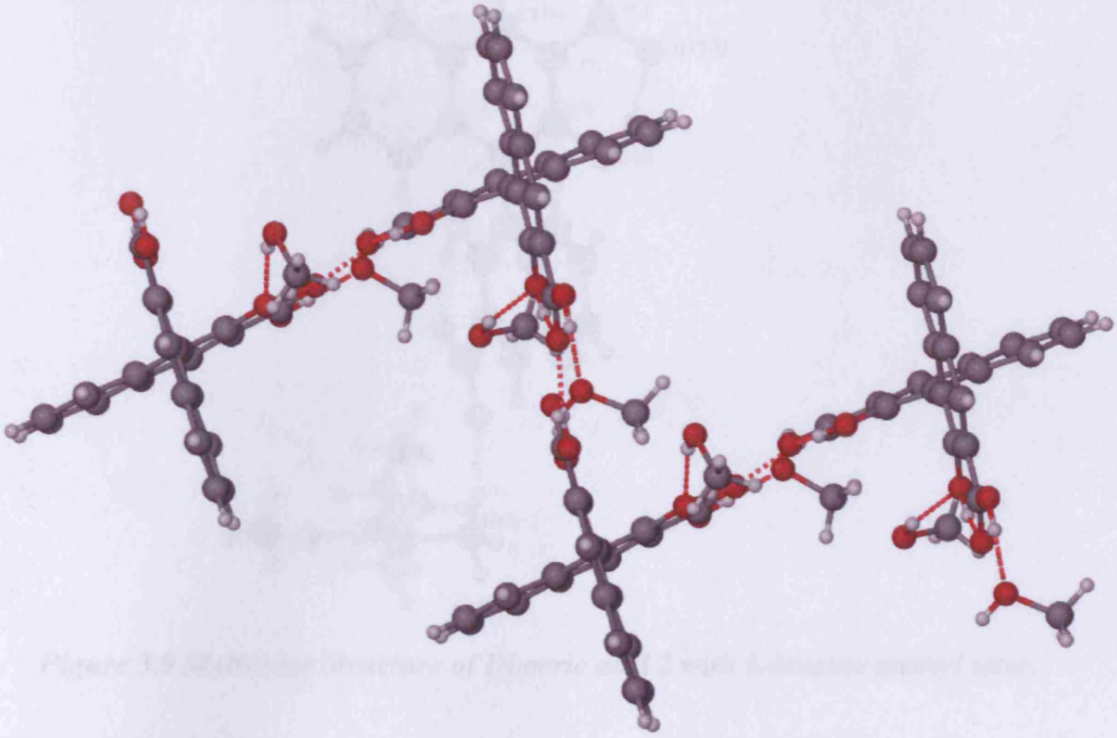


Figure 3.8 Helical structure of dimeric acid 2 with methanol

As can be seen from figures 3.7 and 3.8, dimeric acid **2** forms a hydrogen bonded network bound together by methanol molecules to form a helical structure. The methanol molecules are not located in the desired positions for metals but it still bodes well for the possibility of helicate formation using binaphthyl ligands. The space group P21/a is not a chiral space group so a helix related by reflection must be present which is possible as this crystal structure was obtained from the racemic product before resolution was performed.

Figures 3.9 and 3.10 show the crystal structure of dimeric acid **2** being resolved with L-leucine methyl ester, also demonstrating a hydrogen bonded network with a helical twist. As can be seen from the crystal structure a P helix is formed.

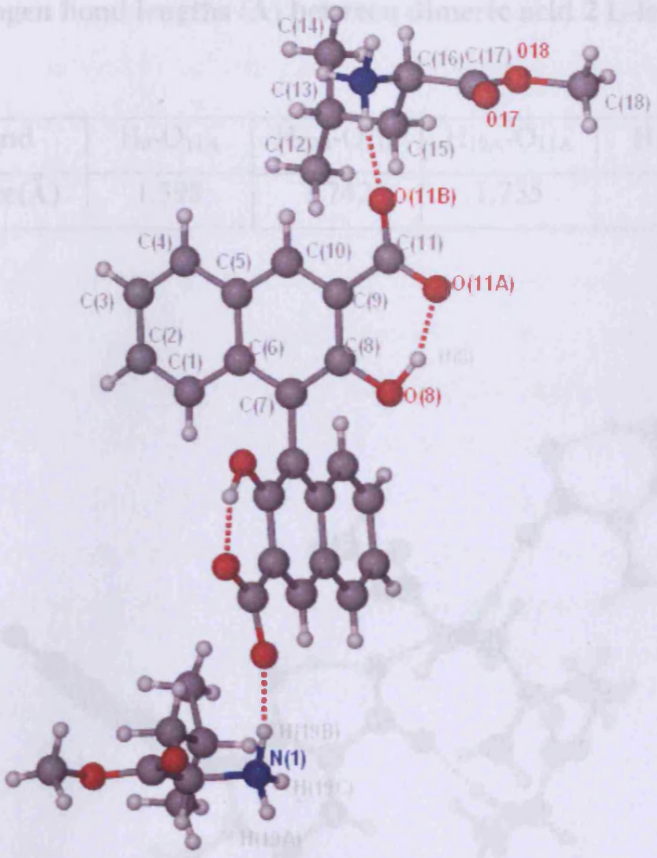


Figure 3.9 Molecular Structure of Dimeric acid 2 with L-leucine methyl ester.

Table 3.3 Crystallographic details for Dimeric acid 2 with L-leucine methyl ester.

Compound	**2a**
Formula	$C_{22}H_{14}O_4.C_{14}H_{30}O_6N_2$
M	664.73
a (Å)	8.87100(10)
b (Å)	8.87100(10)
c (Å)	43.9149(6)
α (°)	90.000
β (°)	90.000
γ (°)	90.000
V (Å^3)	2147.0(24)
T (K)	150
Crystal system	Tetragonal
Space group	P41212
Z	4
μ (mm^{-1})	0.093
Reflections collected	20059
Independent reflections (R_{int})	3690[R(int)=0.0816]
Final R indices (all data)	R_1=0.0463, wR_2=0.1026

Table 3.4 Hydrogen bond lengths (Å) between dimeric acid 2 L-leucine methyl ester

H-Bond	H_8-O_{11A}	H_{19B}-O_{11B}	H_{19A}-O_{11A}	H_{19C}-O_{17}
Distance(Å)	1.598	1.742	1.735	2.187

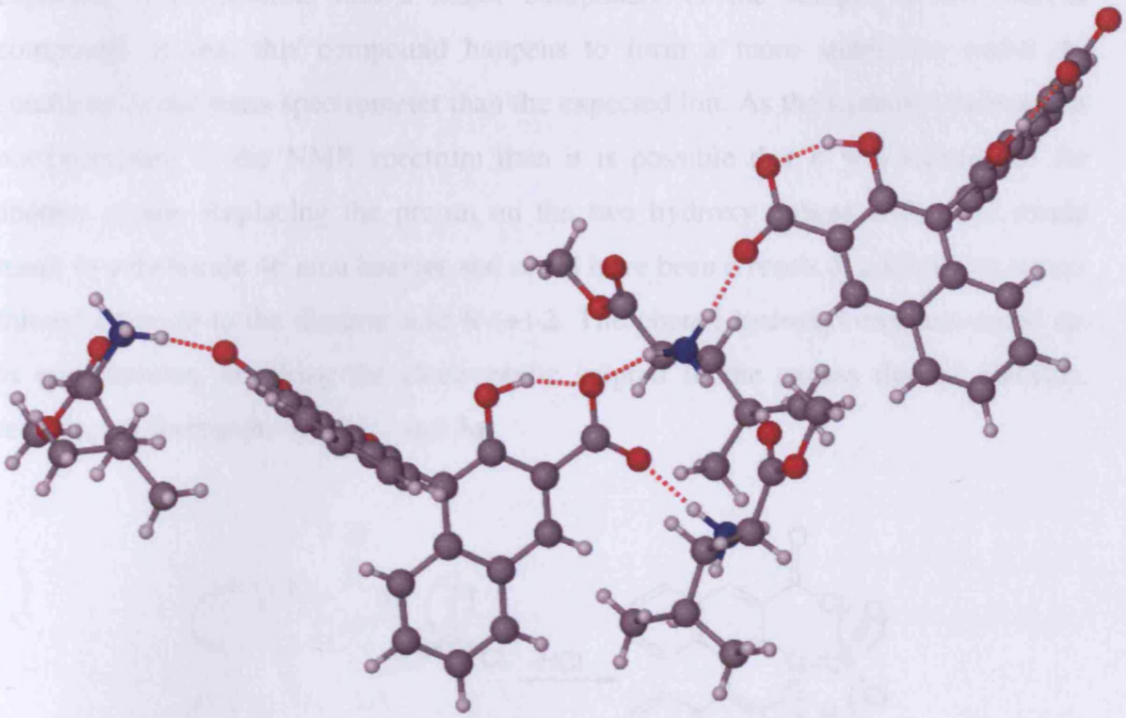
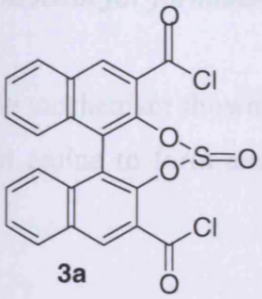


Figure 3.10 Hydrogen bonded helical structure of dimeric acid 2 with L-leucine methyl ester

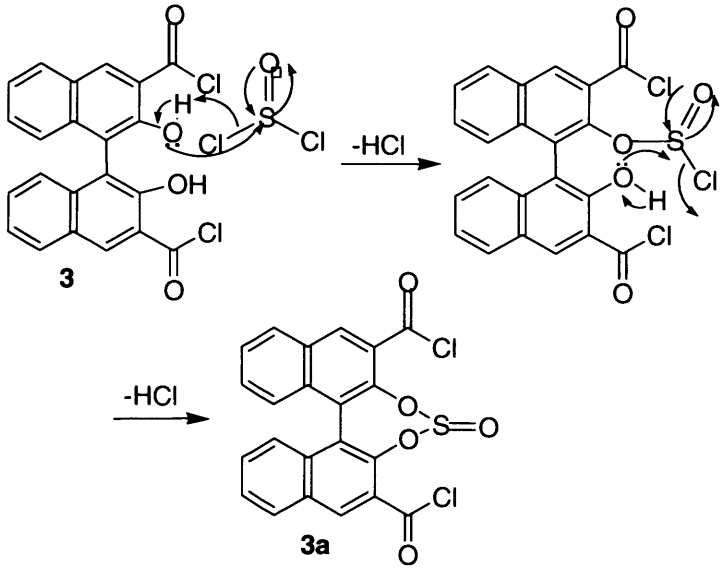
The next step was to transform the carboxylic acid group to a more reactive diacid chloride. Early attempts produced a by-product cyclic sulphite ester **3a** as well as the diacid chloride **3.** Due to the instability of dimeric acid chloride **3**, it was used *in situ*.



3a

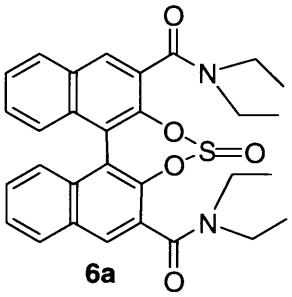
Figure 3.11 Thionyl compound 3a

Amine addition to the acid chloride formed the corresponding amide; amide formation will be discussed in full later. It was found that on addition of diethylamine, two amides were produced. The mass spectrum showed a peak at 531 of 67% as well as a peak at 485 of 27%, the latter showing the proposed Mr +H of amide **6**. Therefore the most abundant ion, and therefore the most stable ion was 46 amu heavier than expected. It is possible that a major componant of the sample is this heavier compound or that this compound happens to form a more stable ion under the condtions in the mass spectrometer than the expected ion. As the hydroxyl proton was not prominent in the NMR spectrum then it is possible that it was substituted for another group. Replacing the proton on the two hydroxy groups with S=O would result in a molecule 46 amu heavier and could have been a result of addition of excess thionyl chloride to the dimeric acid R-(+)-**2**. The phenol hydroxyl oxygens could act as nucleophiles, attacking the electrophilic sulphur in the excess thionyl chloride, resulting in formation of compound **3a**.



Scheme 3.12 Possible mechanism for formation of thionyl compound 3a.

The reaction could proceed by the mechanism shown in figure 3.12. The acid chloride **3a** would then react with diethyl amine to form amide **6a,** the compound shown in figure 3.13.



6a

Figure 3.13 Amide 6a.

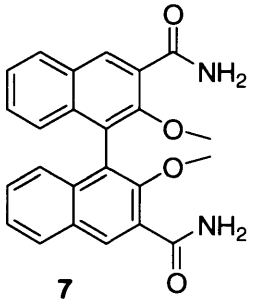
The lack of protons in the thionyl group, make it impossible to see in the proton NMR spectrum and can only be speculated from the lack of hydroxyl peak. The hydroxyl could show in the proton spectrum if water was present in the solvent which could react with the thionyl to form the hydroxyl groups back, thus giving a false positive result as a test for hydroxyl groups. Formation of the diacid chloride shifted the chemical shift of H_5 in the dimeric acid from δ7.2 to δ8.8 ppm. This is due to the positioning of H_5 compared to the other naphthalene ring; it must be different in the sulphonyl **3a** than in the dimeric acid which is to be expected. The IR spectrum of amide **6/6a** did not show an hydroxyl absorption but showed an absorption at 1632 cm^{-1}, which is consistent with a tertiary amide carbonyl stretch, confirming the formation of the amide.

In subsequent acid chloride formation less thionyl chloride was used and has resulted in a different proton NMR spectrum than the previous attempt. The ^1H NMR peaks have all shifted downfield from their positions in the dimeric acid spectra, which is to be expected as the diacid chloride **3** should have a higher electron withdrawing effect, de-shielding these protons. H_5 has the lowest chemical shift, as in the dimeric acid NMR spectrum, showing similar interaction with the naphthalene ring. Infrared spectroscopy showed an absorption at 3146 cm^{-1} which is consistent with the phenolic hydroxyl and absorptions at 1820 and 1790 cm^{-1} would be typical for a diacid chloride carbonyl stretch. This is considerably higher than 1660 cm^{-1} that was seen in the dimeric acid infrared spectrum, which was to be expected.

Once the diacid chloride **3** had been successfully formed it was converted into diamide **4** (see compound list p. 66). This was initially attempted by dissolving the diacid chloride in dichloromethane and then adding aqueous ammonia drop-wise to the solution at 0°C. Aqueous work-up proved difficult as the product was insoluble in

diethyl ether, toluene, dichloromethane and ethyl acetate. This low solubility in non-polar solvents could be due to strong intermolecular hydrogen-bonding as it was partially soluble in methanol. Due to insolubility during reaction the yield was poor at 20% after recrystallisation from methanol. The reaction was repeated with the diacid chloride dissolved in a small amount of dry acetone and then added to a large excess of aqueous ammonia. This was then precipitated by adding six molar hydrochloric acid resulting in a crude yield of 95% with very little impurity visible in the aromatic region of the proton NMR spectrum. After recrystallisation from methanol and water, a yield of 71% was obtained.

The next step in this scheme was to convert the amide to an amine which is commonly performed using a Hofmann degradation with sodium hypochlorite (bleach).[49] The reaction was attempted several times without the required amine being formed. It is thought that the phenol might have interfered with the reaction process so the Hofmann was attempted using the protected amide **7**. Methylation was performed by de-protonating the hydroxyls with potassium carbonate followed by electrophilic addition of the methyl group from methyl iodide.



7

Figure 3.14 Methylated amide 7

The Hofmann degradation was attempted twice using amide **7** again with sodium hypochlorite at 40 °C for several hours, but the product was very impure and not the amine required. This result was consistent with Jambusermala *et al*;[50] they attempted a Hofmann degradation on the monomer of amide **7**, which was also unsuccessful. As a result they used a Curtius rearrangement to obtain the amine. In the Curtius reaction, sodium azide was used, so it was preferable to find a safer alternative. A possible solution was using diphenylphosphoryl azide (DPPA)[51] to take the dimeric acid directly to the Boc-protected amine, as shown in figure 3.15.

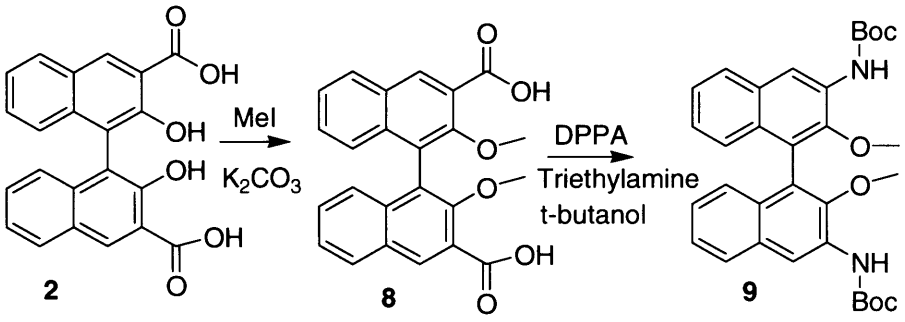


Figure 3.15 Protected Amine formation using DPPA

Firstly the phenol group on dimeric acid **2** needed to be protected, so methyl iodide was used to methylate the ether group. Stoichiometric amounts of methyl iodide and potassium carbonate were used but it was difficult to determine whether the phenol hydroxyl, or the carboxylic acid hydroxyl, was methylated.

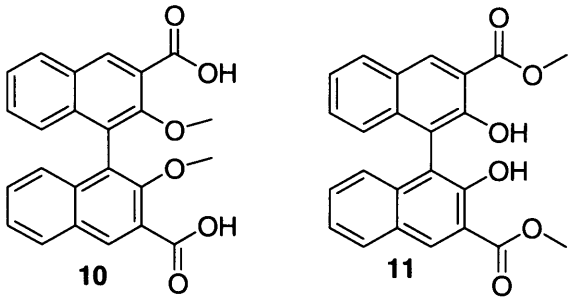
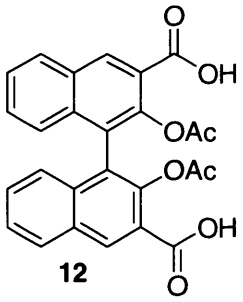


Figure 3.16 Methyl ether 10 and methyl ester 11.

The proton NMR spectrum was consistent with both structures as each peak was in-between typical values for the phenolic ether and ester. The IR spectrum was also consistent with either compound because changing either group made the compound less conjugated increasing the IR stretch. To differentiate between the two, the methylated compound was treated with thionyl chloride and then refluxed with methanol. If the wanted methyl ether **10** was the starting material then the product would be tetra-methylated, if not the NMR spectrum would be the same as before. The NMR spectrum showed a small amount of starting material but mainly the acid chloride of the original dimeric acid. It is more probable that the thionyl chloride removed the methyl group from the ester so it was decided that the methyl ester **11** was formed. The methyl ether **10** was also synthesised by using excess methyl iodide, tetra-methylating the dimeric acid and then hydrolysing with potassium hydroxide to

remove two methyl groups. Acetylating the dimeric acid by refluxing with acetic anhydride was implemented making ester **12** with a good yield. [52]



12

Figure 3.17 Acetyl ester 12

Acetyl ester **12** was then reacted with DPPA, triethylamine and t-butanol in order to make the Boc-protected amine.

The t-butanol was frozen at room temperature, but for safety reasons the mixture was not heated until all reagents were added. Once refluxing, the acetyl ester was not soluble in t-butanol so was unable to react efficiently. A small amount of product was isolated and NMR and IR spectra were consistent with an amine but there were no Boc groups, the unprotected amine was formed. It was evident that the majority of product or bi-products were left in the aqueous layer but it was not possible to extract the desired product. A protected amine would be less water soluble so it would be more easily extracted. The reaction was repeated with ethanol as the solvent, to form the carbamate. This yielded a high amount of ethyl diphenyl phosphate and no other purified products.

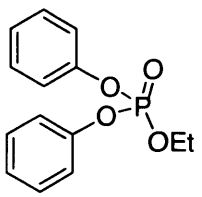


Figure 3.18 Ethyl diphenyl phosphate

It is possible that the amine or carbamate was formed but was not easily removed from the water layers from the aqueous work-up. Benzylation of the hydroxyl groups was also attempted in order to have a protecting group that cannot be removed by hydrolysis. Benzylation did not occur even after four days of refluxing with benzyl

bromide and potassium carbonate. The reaction failure might be due to the carboxylic acid group deactivating the nucleophilicity of the hydroxyl group.

The next amine formation reaction attempted was with polyphosphoric acid and hydroxylamine hydrochloride as the reagents. This is a known reaction for synthesizing β-naphthylamine from naphthoic acid.[53]

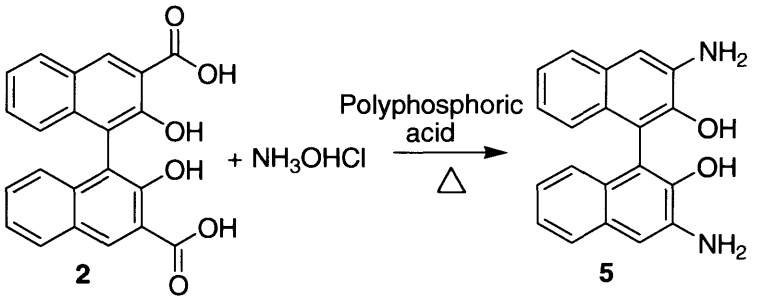


Figure 3.19 Synthesis of Amine 5

The resulting brown solid, although a naphthalene derivative showing peaks in the aromatic region of the proton NMR spectrum, was neither starting material nor the desired amine. The IR spectrum had a carbonyl stretch at 1775 cm^{-1} which should not be present in amine **5**. This stretching frequency is also considerably higher than the stretching frequency expected for the dimeric acid **2** or the stretching frequency expected if an amide had been formed. The expected molecular ion 316 did not show up in the mass spectrum either. It is thought that the amine was synthesized, but due to the small scale, it was all dissolved in the aqueous solution. Repetition of the reaction on a larger scale proved unsuccessful also.

The final attempt to synthesize this compound was following a patented procedure by dissolving BINOL in acetic anhydride then slowly adding nitric acid in acetic acid.[54] The light green reaction turned a dark green/black colour then after four hours at 0°C a dark orange/red colour. This was filtered leaving an orange solid and then an aqueous workup of the filtrate and recrystallisation resulted in a brown solid. Neither solid had the necessary NMR spectra for the dimeric amine **5.** Although a literature procedure, it is speculated that these reaction conditions would form the nitro compound rather than the amine.

After obtaining the hydrogen bonded helical crystal structure of dimeric acid **2**, it was realized that having a carbonyl in the ligand might not disturb the helical structure, so a series of amides was synthesized.

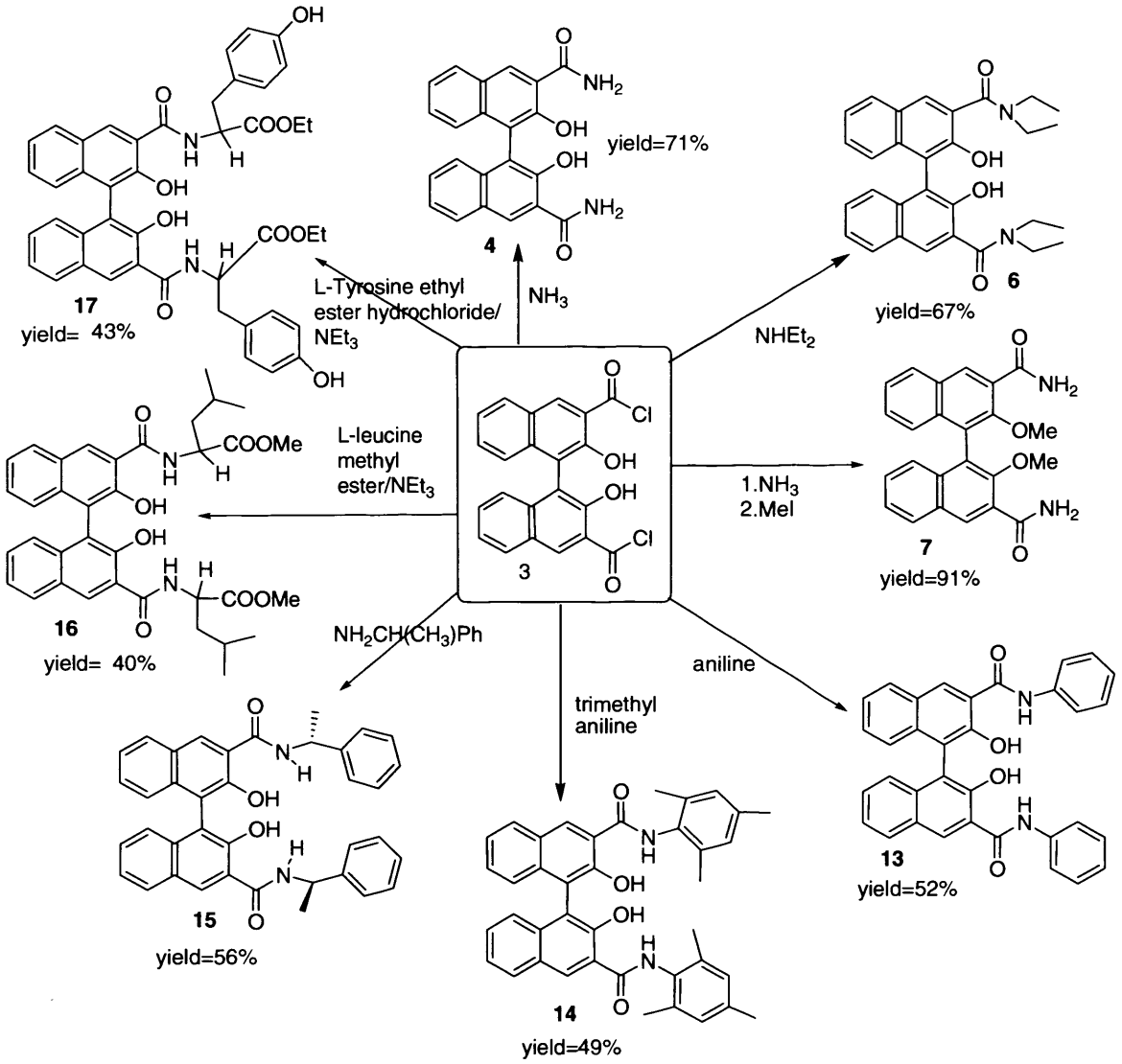
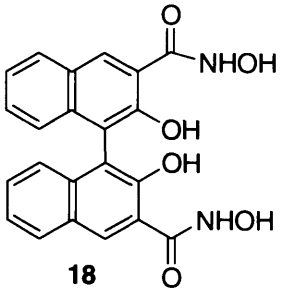


Figure 3.20 Binaphthyl Amides.

All amides were made to a similar procedure using dimeric acid chloride **3** as the starting material. Most of the yields are based on small-scale reactions, 0.1g-0.5g of acid chloride **3,** and are purified through recrystallisation, so the recovered yields are not an accurate reflection of the efficiency of the reactions, but are reasonable. It was thought that having various organic groups attached to the amide would increase the solubility of the amides in organic solvents as well as help direct helix formation. The solubility of the amides varied depending on the amine used, with amide **4** synthesised from ammonia the least soluble in organic solvents, the aniline derivative more soluble and the trimethylaniline derivative more soluble again. It was possible to recrystallise all of the amides but the only amide to produce good quality crystals was

amide **16** derived from L-leucine which could have been compared to the crystal structure of the resolution of dimeric acid **2** with L-Leucine methyl ester. X-ray crystals were grown of amide **16** but the data was not good enough to obtain an accurate crystal structure. Synthesis of the amide from L-tyrosine was unsuccessful, the solid produced was mainly salt, and the organic product was too soluble in water to be easily separated from the inorganic by-products. The synthesis of the ethyl ester derivative was unsuccessful also. Amide **15** was synthesised as an alternative to resolving the dimeric acid with L-leucine methyl ester. The diastereomers formed could be separated through recrystallisation but it was thought that recrystallisation earlier on in the synthetic route would produce better yields. Amide **16** and **17** could be hydrolyzed to remove the ethyl or methyl group to have two more binding sites when complexed with metals. These amides should be good hard, multi-dentate ligands for hard metals such as alkali metals and lanthanides. Lanthanides are large and therefore need multi-dentate ligands to complete their shell.

A variation on the amide theme; dimeric acid chloride **3** in dichloromethane was added drop wise to hydroxylamine hydrochloride in the presence of triethylamine in order to synthesise hydroxamic acid **18.**



18

Figure 3.21 Hydroxamic acid 18

After aqueous work up, the yellow solid was shown by proton NMR spectroscopy to be contaminated with an excess of triethylamine hydrochloride. There were consistent peaks in the aromatic region; an upfield shift of H_1 was consistent with oxime formation. Further aqueous washings reduced the amount of triethylamine hydrochloride but did not remove it completely. The reaction was repeated with stoichiometric amounts of triethylamine rather than the excess used previously. Aqueous work up still showed too much triethylamine hydrochloride in the product which was also impossible to remove even after several aqueous work-ups.

Another avenue was explored in parallel to the afore-mentioned work; a potential route to tetra-amines without the need to convert amides to amines. This route would not involve the problematic amide to amine conversion and would have the groups the other way round to see if there are any benefits. The route is shown in figure 3.22 and originally started with the dimerisation of 2,3-dihydroxy naphthalene using the copper chloride catalyzed reaction.

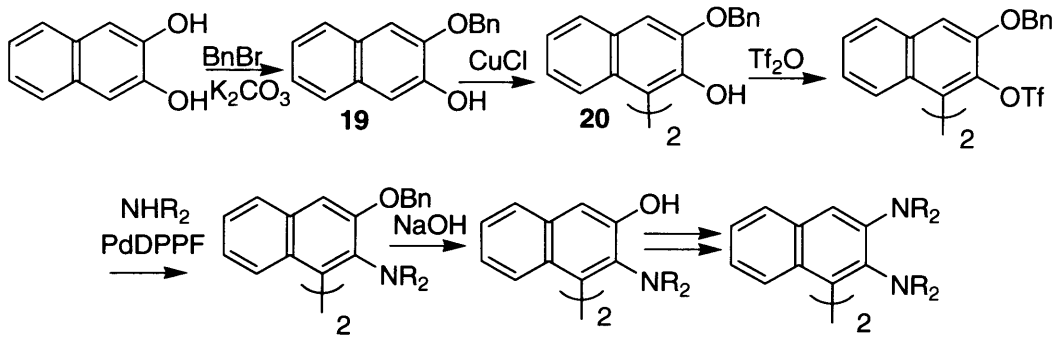


Figure 3.22 Reaction scheme for tetraamine synthesis.

As the diol was symmetrical the reaction could take place at either position alpha to the hydroxyl group. As a hydroxyl donates electron density to the aromatic system the diol was more reactive to substitution than the dimeric acid **2** so a polymer was able to form. This is consistent with the NMR spectrum, which shows a broad peak in the aromatic region.

To prevent polymerization the diol was converted to 3-benzyloxy-naphthalen-2-ol **19** using benzyl bromide and base as shown in figure 3.22. One equivalent of benzyl bromide was used so substitution would only occur at one position and only a small amount of di-substituted ether and starting material were shown in the NMR spectrum of the reaction product. Recrystallisation increased the proportion of di-substituted ether but decreased the amount of starting material. Oxidative coupling of benzyloxy ether **19** with copper chloride resulted in dimeric ether **20** in a reasonable yield of 72% with almost full conversion of monomer to dimer according to the NMR spectrum. After recrystallisation the mass spectrum showed a highest mass ion of 499, showing the correct relative molecular mass of the dimeric benzyloxy ether **20**. The dimeric benzyloxy ether **20** formed was racemic so resolution was necessary. So a method for dimerisation of the benzyloxy ether **19**, using a vanadyl complex **21,** was pursued. [24] Vanadyl **21** has been shown to be an asymmetric catalyst in coupling

reactions[24]; this reaction was meant to be partially enantiomerically selective so on further recrystallisation more of a single enantiomer would be obtained.

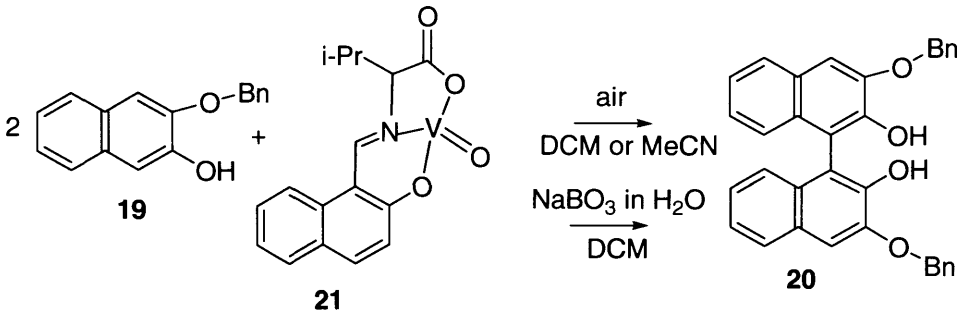


Figure 3.23 Dimerisation reactions with a vanadyl complex as the catalyst.

As shown above, this reaction took place with air as the oxidant or sodium perborate. The reactions were followed by TLC and both resulted in a great deal more monomer than dimer, even after two weeks. It is possible that the vanadyl complex was not the required complex, the only characterisation given in the literature was a mass spectrum. [24] So this route was abandoned due to length of route, problems with purification and problems with resolution.

3.22 Complexes

The dimeric acid **2** has been complexed with potassium tetrachloroplatinate(II) and this complexation was successful for a one to one polymeric complex. The NMR spectrum showed a shift up-field of all the peaks, especially H_1 which should be nearest the platinum, which is consistent with being coordinated to a metal. The IR spectrum showed a shift of the carbonyl stretch of 10 cm^{-1} compared to the dimeric acid **2** by itself which would also be consistent with coordination to a metal. Unfortunately the mass spectrum did not show any desired ions, it is possible that the complex broke apart under mass spectrum conditions. Dichloro dipyridyl platinum (II) was synthesised from a literature procedure[55] in order to complex it with dimeric acid **2** but this did not result in a dimeric acid complex, just starting materials as seen in the proton NMR spectrum. It is possible that dichloro dipyridyl platinum (II) was too stable to want to form complexes with a hard ligand like dimeric acid **2.**

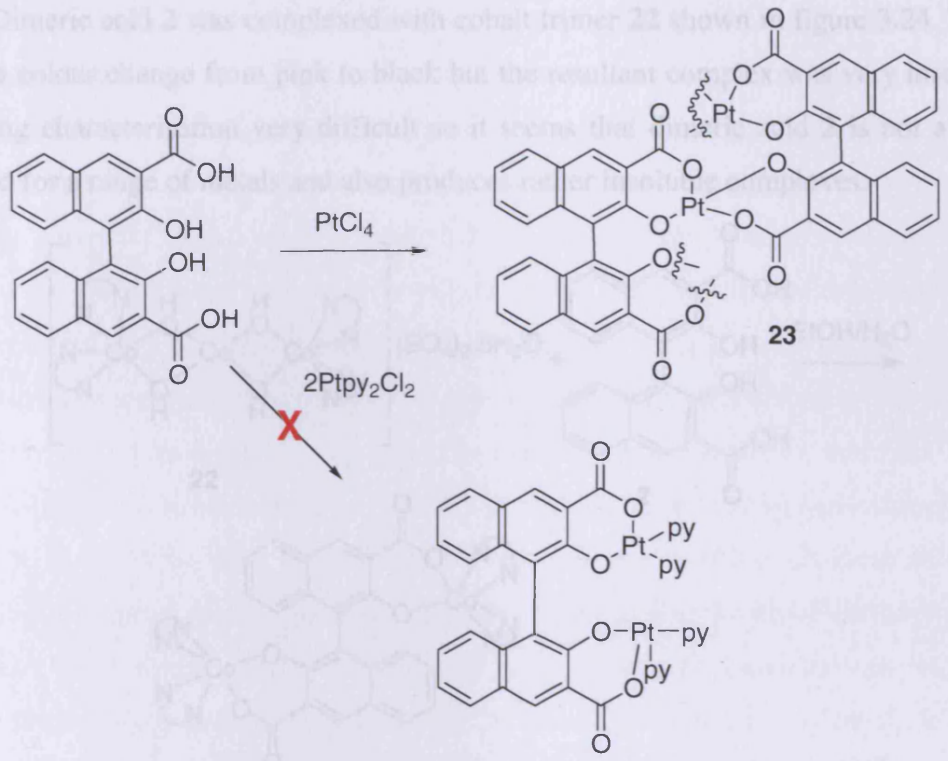


Figure 3.24 Platinum complexes of dimeric acid 2

An attempt was made to complex dimeric acid **2** with zirconium tetrachloride under nitrogen, but the result was just a mixture of starting ligand and pyridine according to the NMR spectrum. This result is surprising because zirconium is thought to be an oxophilic ligand. It is possible that the zirconium reacted with water in the solvent before it had a chance to react with the dimeric acid **2.** This is likely because zirconium tetrachloride is very reactive with water and pyridine being a polar solvent is likely to have water in it unless thoroughly dried.

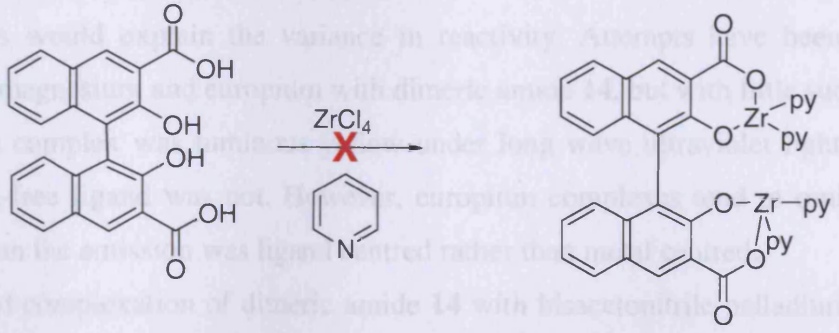


Figure 3.25 Attempted Zirconium complex synthesis.

Complexation of dimeric acid **2** with cadmium nitrate tetrahydrate was attempted several times, crystals were attained but the crystal structure showed just dimeric acid

2.[40] Dimeric acid **2** was complexed with cobalt trimer **22** shown in figure 3.24. There was a colour change from pink to black but the resultant complex was very insoluble making characterisation very difficult so it seems that dimeric acid **2** is not a good ligand for a range of metals and also produces rather insoluble complexes.

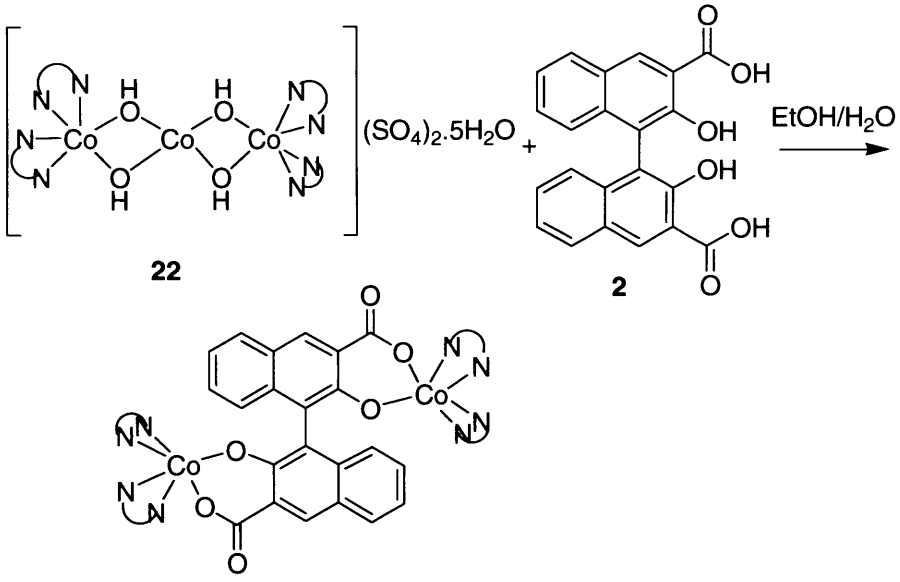


Figure 3.26 Cobalt based dimeric acid complex

Dimeric amide **14** was also tried as a ligand for cobalt using the same reaction but no reaction occurred leaving a pink solid soluble in water which was the original cobalt trimer **22**, and a yellow solid soluble in chloroform, which was dimeric amide **14.** Dimeric amide **14** is a bulkier ligand than dimeric acid **2** and therefore it is more difficult to complex with metals that already have a lot of steric bulk, like cobalt complex **22**. Also the amide **14** is even less soluble in a lot of organic solvents than the dimeric acid **2,** which make any reactions in solution less likely to occur. These arguments would explain the variance in reactivity. Attempts have been made to complex magnesium and europium with dimeric amide **14**, but with little success. The europium complex was luminous yellow under long wave ultraviolet light, whereas the metal-free ligand was not. However, europium complexes tend to omit red this could mean the emission was ligand centred rather than metal centred.

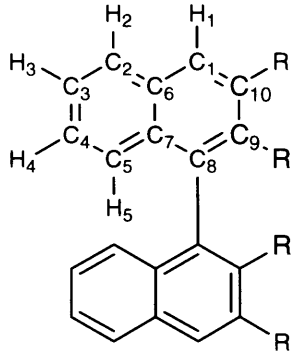
Attempted complexation of dimeric amide **14** with bisacetonitrile palladium chloride only resulted in bisacetonitrile palladium chloride crystals forming and ligand being left in solution after recrystallisation.

A solution of nickel chloride hexahydrate in methanol was added to the two of the ligands in order to form a nickel-ligand complex that would, ideally, form helices. At

this point it was still thought that the hydroxyl on the amide **6/6a** was free, and therefore it could act as a chelating ligand. There was no colour change on addition of nickel chloride to both ligands and the optical rotation reduced, proportionally as more nickel chloride solution was added to amide **6/6a**. From this, one would conclude that the optical rotation reduced due to the decrease in concentration of ligand and there was no coordination with the metal. The optical rotation varied when different amounts of nickel chloride solution were added to amide **15**. As the concentration and optical rotations were low, the results are probably not very accurate. For amide **6a,** this result would be expected; as the hydroxy, that would have formed a coordinate bond as O^- to the metal, was bound to sulphur in the cyclic sulphite so could not bind. When a base was added to the amide/nickel chloride solution the optical rotation increased probably meaning that the metal bound to the ligands. This is to be expected for amide **15** as a base would remove the protons from the hydroxy groups making it chelate with the nickel. The optical rotation of the nickel chloride/amide **6/6a** changed sign when base was added, this could mean that the optical rotation is so high it has rotated past the limit of the polarimeter and so looks like there is a positive rotation but this is unlikely.

A large range of novel amide ligands have been synthesised and their coordination chemistry investigated. The crystal structure of precursor dimeric acid **2** showed that it packed into hydrogen bonded helical chains in the solid state.The coordination behaviour if dimeric acid **2** was also studied; but due to the low yielding resolution process, poor solubility of ligands and lack of success in complex formation further study concentrated on different ligands.

3.3 Experimental



Synthesis of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2 using $FeCl_3$

3-Hydroxy-2-naphthalenecarboxylic acid (24.02g, 0.13 mol) and NaOH (4.85g, 0.12 mol) were dissolved in H_2O (300 ml) in a 1000 ml round-bottomed flask. The solution was brought to reflux and a solution of $FeCl_3.6H_2O$ (36.09g, 0.13 mol) in hot H_2O (200 ml) was added drop wise over a period of 45 minutes, with magnetic stirring. A black precipitate formed immediately. After the addition was completed, the mixture was refluxed for three hours with H_2O (150 ml) being added at intervals. Once cooled to room temperature, the pH of the solution was adjusted to pH>7 with a 2M aqueous solution of NaOH. The suspension was filtered producing an orange solution. This was concentrated and then precipitated with HCl (6 M)(pH<2). The yellow precipitate was filtered off, washed with H_2O and with a solution of ethanoic acid in H_2O (80:20, 1750 cm^3) to remove the unreacted starting material. After drying in vacuo, 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (4.01g, 17%) was left as a yellow solid, δ_H (400 MHz, DMSO): 8.8 (2H, s, H_1), 8.1 (2H, m, H_2), 7.4 (4H, m, H_3, H_4), 7.0 (2H, m, H_5).[56]

Synthesis of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2 using CuCl

A solution of 3-hydroxy-2-naphthoic acid (19.58g, 0.10 mol) in absolute MeOH (150 ml) was made up in a 3-necked 500 ml round-bottomed flask. CuCl (5.30g, 0.05 mol) was added to the solution and this was stirred at room temperature, with air bubbling through it, for 90 hours. During this time, the reaction was followed by TLC; UV active spots RF 0.7 (starting material) and 0.3 (product) (40/60 methanol/ethyl acetate). The bright green reaction mixture was evaporated leaving a mixture of brown and green solids. This was dissolved in ethyl acetate and 3M hydrochloric acid and separated. The green aqueous layer was extracted with ethyl acetate and the orange organic layer was washed with saturated brine solution and dried over $MgSO_4$.

The ethyl acetate was evaporated off and the remaining solid was washed in 80/20 acetic acid/ water (1200 ml) leaving a yellow solid and an orange filtrate (8.41g, 43% crude).

The yellow solid was recrystallised from methanol leaving 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2**[30] (6.26g, 32%) as a yellow solid ; mp>300 °C, ν_{max} (nujol)/cm^{-1} 3300-2500(CO*OH*), 1658 (CO); δ_H (400 MHz, DMSO): 8.8 (2H, s, H_1), 8.1 (2H, m, H_2), 7.4 (4H, m, H_3 ,H_4), 7.1 (2H, m, H_5). This was repeated with oxygen bubbling through the reaction mixture for 44 hours, which, after recrystallisation, resulted in 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (3.23g, 34%) as a yellow solid, NMR identical to the previous procedure.

Optical resolution of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2.

Sodium carbonate solution was added to solid L-leucine methyl ester hydrochloride (10.28g, 0.06 mol) until the solution was pH 10. The ester was extracted with ethyl acetate, and washed with saturated brine solution. The organic layer was dried over magnesium sulphate and evaporated leaving L-leucine methyl ester (6.04g, 74%) as a yellow oil with an amine odour; ν_{max} (film)/cm^{-1} 3382 (NH), 3313 (NH), 2956 (CH), 2870 (CH), 1739s (C=O), 1603 (COO^-). A solution of L-leucine methyl ester (6.04g. 0.04 mol), in the minimum of MeOH, was added to a solution of racemic 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid (6.50g, 0.02 mol) in the minimum of MeOH (500ml). The yellow/brown solution was heated in a water bath for 15 minutes and cooled to 25 °C for 1 day and to 0°C for 2 days. The salt that separated was filtered, washed with a small amount of MeOH, and dried to give yellow crystals (3.04g). The final powder was dissolved in 40 ml of H_2O containing NaOH (0.46g, 0.01mol). The resulting solution was washed with ether and acidified to pH 1 with hydrochloric acid 1M to give a yellow precipitate. This precipitation was washed with H_2O and dried to give (R)-(+)- 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (1.93g, 6.06 mmol). The recrystallisation liquor was concentrated by half and the above procedure was repeated with NaOH (0.21g, 5.22 mmol) in H_2O (15 ml) resulting in (R)-(+)- 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (0.65g, 2.03 mmol), in total giving(R)-(+)- 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (2.58g, 40%) as a bright yellow solid, $[\alpha]_D$=193° (c=0.015, THF) (lit.[30] 200°), e.e=96.4%. Other properties identical to racemic material.

Synthesis of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbonyl dichloride 3

Racemic 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (1.87 g, 5.00 mmol) was added to a two-necked round-bottomed flask under a N_2 atmosphere. Thionyl chloride (12.29 g, 0.10 mol) was added drop wise as well as a drop of pyridine as a catalyst. The reaction was left stirring overnight. The thionyl chloride was removed to give 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbonyl dichloride **3** to be used in situe; δ_H (400MHz, $CDCl_3$): 9.3 (2H, s, O*H*), 8.9 (2H, s, H_1), 8.0 (2H, s, H_2), 7.4 (2H, m, H_3+H_4), 7.1 (2H, m, H_5); ν_{max} ($CDCl_3$)/cm^{-1} 3146 (OH), 1820, 1790 (C=O).

Following the same procedure (**R**)-(+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** gave (**R**)-(+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbonyl dichloride **3** with an identical NMR spectrum.

Using excess $SOCl_2$ gave sulphonyl compound **3a;** δ_H (400 MHz, $CDCl_3$): 8.8 (4H, s, H_1+H_5), 8.5 (2H, t *J=8 Hz*, H_2), 7.9 (4H, m, H_3+H_4); ν_{max} ($CDCl_3$)/cm^{-1} No OH, 1801 (C=O).

Synthesis of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide 4

(R)-(+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbonyl dichloride **3** (0.27g, 0.65 mmol) was dissolved in acetone (20 ml) and added drop wise to aqueous ammonia (100ml, 35% NH_3) while stirring at 0°C. This orange solution was left stirring at room temperature overnight. 6M HCl was added drop wise until acidic, the precipitate was filtered off and washed with water resulting in 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide **4** (0.23g, 95%) as a yellow solid which was recrystallised from MeOH and H_2O (0.17g, 71%); mp 308 °C; [α]D= +136° (c=0.009, MeOH); (Found: C, 68.7; H, 4.4; N, 6.5 $C_{22}H_{16}N_2O_4.CH_3OH$ requires C, 68.3; H, 5.0; N, 6.9 %); ν_{max} (nujol)/cm^{-1} 3348 (NH), 3181 (NH), 1667 (C=O), 1627 (C=C ar), 1582 (C=C ar); δ_H (400 MHz, MeOD), 8.5 (2H, s, H_1), 7.9 (2H, m, H_2), 7.2 (4H, m, H_3, H_4), 7.0 (2H, m H_5); δ_C (DMSO): 173.1 (C=O), 155.3 (C_9), 136.1 (C_7), 129.7 (C_6), 129.6 (C_1), 128.9 (C_2), 126.7 (C_4), 124.4 (C_{10}), 123.8 (C_5), 117.0 (C_3), 116.4 (C_8); *m/z* (EI) 373 (28%, M+H), 356 (30, M-NH_2).

Attempted Hofmann degradation to form 3,3'-diamino-1,1'-binaphthyl-2,2'-diol 5

NaOCl solution (4ml, 2.54 mmol of Cl_2) was added to 2,2'dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide **4** (0.20g, 0.54mmol) with stirring. The mixture was heated to 40°C for 2.5 hours. This was then left to cool to room temperature, neutralised with 1M HCl and corrected with 2M NaOH. The solution was checked with starch iodide paper and there was no trace of oxidant. The product was soluble in the aqueous solution so this was condensed to 2ml and left to crystallise. No diamine present in NMR spectrum.

Repeated with OH protected with a methyl group, also did not produce diamine.

Synthesis of 2,2'dimethoxy-1,1'-binaphthyl-3,3'-dicarboxamide 7

Diamide **4** (0.25g, 0.67 mmol) was dissolved in acetone (15 ml) and then potassium carbonate (0.19g, 1.41 mmol) was added while stirring vigorously. Methyl Iodide (0.17 ml, 2.66 mmol) was added via syringe and the reaction was refluxed for 2 days. The acetone was removed at high vacuum; the solid was washed with ammonium chloride until acidic, extracted into dichloromethane and washed with brine. The DCM was evaporated leaving a yellow solid (0.26g, 97%) still with some impurities. The solid was recrystallised from ethyl acetate resulting in 0.07g and then recrystallised in diethyl ether and precipitated with petroleum ether resulting in another 0.02 g of 2,2' dimethyl-1,1'-binaphthyl-3,3'-dicarboxamide **7** (0.09g, 35%) as a yellow solid; mp 250°C; ν_{max} (nujol)/cm^{-1} 3426, 3337, 3267, 3176 (NH_2), 1659 ($O{=}CNH_2$), 1582, 1494 (ar C=C); δ_H (250 MHz, $CDCl_3$): 8.9 (2H, s, H_1), 8.0 (2H, d *J=8 Hz*, H_2) 7.8 (2H, d *J=8 Hz*, NH), 7.45 (2H, m, H_3), 7.3 (2H, m, H_4) 7.0 (2H, d, *J=8 Hz*, H_5), 6.0 (2H, d, *J=8 Hz* NH), 3.4 (6H, s, $2CH_3$); δ_C (400 MHz, $CDCl_3$) 167.4(*C*=ONH_2), 153.9 (C_9), 136.0, 134.9, 130.6, 130.2, 129.2, 126.4, 125.8, 125.6, (18arC), 62.4 ($2CH_3$); m/z (EI) 416 (16%, $[M+Me+H]^+$), 401(100, $[M+H]^+$).

Synthesis of 2,2'dihydroxy-1,1'-binaphthyl-3,3'-dimethyl ester 11.

Dimeric acid **2** (0.20g, 0.54 mmol) was dissolved in acetone (50 ml) and then potassium carbonate (0.16g, 1.08 mmol) was added while stirring vigorously. Methyl iodide (0.07 ml, 1.08 mmol) was added via syringe and the reaction was refluxed for 2 days. The acetone was removed on a vacuum line; the solid was washed with

ammonium chloride until acidic, extracted into DCM and washed with brine. The DCM was evaporated leaving a yellow solid which was recrystallised from ethyl acetate leaving 2,2'dihydroxy-1,1'-binaphthyl-3,3'-dimethyl ester.**11** (0.15g, 68%) as a white solid; ν_{max} (nujol)/cm^{-1} 3167 (OH), 1682 (*C*=*O*-OMe); δ_H (400 MHz, $CDCl_3$): 10.7 (2H, s, PhO*H*), 8.7 (2H, s, H_1), 7.9 (2H, m, H_2), 7.3 (4H, m, H_3+H_4), 7.1 (2H, s, H_5), 4.0 (6H, s, CH_3).[57]

Synthesis of 2,2'diacetoxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 12.[52]

Dimeric acid **2** (0.26g, 0.69 mmol) was dissolved in acetic anhydride (40 ml) to form a pale yellow solution. This was refluxed for 1 hour at 160 °C. The solution was cooled a little, water (35 ml) was added and it was refluxed for 30 minutes, then left to cool. A pale yellow solid precipitated, was filtered off under suction and was washed with water and cold ethanol leaving 2,2'diacetoxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **12** (0.249g, 67%) as a white solid; mp >280 °C; ν_{max} (nujol)/cm^{-1} 3400-2400 (COOH), 1764 (OC=OCH_3), 1685 (HOC=O), 1622, 1592, 1500 (C=C); δ_H (400 MHz, acetone-d_6): 8.8 (2H, s, H_1), 8.1 (2H, *d J=8 Hz*, H_2), 7.5 (2H, m, H_3), 7.3 (2H, m, H_4) 7.0 (2H, d *J=8 Hz*, H_5), 1.7 (6H, s, Me). [52]

Attempted synthesis of 2,2'diacetoxy-1,1'-binaphthyl-3,3'-diamine

2,2'-Diacetoxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **12** (0.18g, 0.34 mmol) was mixed in a 100 ml round-bottomed flask with t-butanol (25 ml) and triethylamine (0.11ml, 0.78 mmol). DPPA (0.17 ml, 0.78 mmol) was added *via* plastic syringe without a metal needle. The reaction was heated to 110 °C overnight. The mixture was extracted into ethyl acetate, washed with 1M HCl, $NaHCO_3$ and brine, evaporated and recrystallised in ethyl acetate leaving a white solid believed to be 2,2'dihydroxy-1,1'-binaphthyl-3,3'-diamine **5** (0.02g, 10%); ν_{max} (nujol)/cm-1 3578, 3408 (NH_2), 1766 (OC=O), 1624, 1534 (ar C=C); δ_H (400 MHz, DMSO): 7.5 (2H, s, H_1), 7.4 (2H, t, H_2) 7.2 (2H, m, H_3), 7.1 (2H, m, H_4), 6.7 (2H, m, H_5), 1.4 (6H, s, 2CH_3). Required ion not found in mass spectrum.

Attempted synthesis 2,2'dibenzyloxy-1,1'-binaphthyl-3,3'-dicarboxylic acid

Dimeric acid **2** (0.100g, 0.26 mmol) was dissolved in acetone (50 ml), K_2CO_3 (0.07g, 0.54 mmol) and benzyl bromide (61 µl, 0.51 mmol) were added. The reaction mixture was heated to reflux for four days. After 2 days extra benzyl bromide (20 µl) was added. The reaction was monitored by TLC but did not go to completion within four days, with mostly starting material left remaining as indicated by TLC, spot R.f. 0.3.

Attempted synthesis of 3,3'-diamino-1,1'-binaphthyl-2,2'-diol 5

Polyphosphoric acid (20 ml) was added to a 100 ml round bottomed flask and heated to 50 °C. Dimeric acid **2** (0.22 g, 0.57 mmol) and NH_4OHCl (0.10g, 1.5 mmol) were added and the mixture was heated gradually to 150 °C. The reaction mixture was kept at this temperature for 6 hours with regular stirring with a glass rod. The reaction was followed by TLC (ethyl acetate 2.8/acetic acid 0.2) and after 6 days a sample of the reaction mixture treated with either water or base showed only a blue spot on the baseline and no dimeric acid (UV active RF 0.31). The reaction mixture was left to cool to 40 °C then poured over ice resulting in a brown solution. This was filtered and the filtrate was extracted into ethyl acetate with a small amount of ethanol. Separation resulted in three layers; the top organic layer was evaporated to give a brown solid which was a mixture of a lot of compounds. The bottom layer was polyphosphoric acid and its derivatives so were discarded and the middle layer was water and some phosphorous compounds.

Attempted synthesis of 3,3'-diamino-1,1'-binaphthyl-2,2'-diol 5

1,1'-Binaphthol (3.84g, 0.01 mol) was dissolved in acetic anhydride (50 ml). Nitric acid (62%, 5 ml) was slowly added to acetic anhydride (25 ml) resulting in an orange solution. This solution was slowly added to the light green 1,1-binaphthol solution turning it dark green/black. Once added completely the reaction mixture was left stirring at 0°C for four hours in which time the reaction turned dark orange/red. The orange solid (0.20g) was filtered off and the filtrate was poured slowly into ice water (450 ml) and filtered, leaving brown substance. This was dissolved in toluene and precipitated with petroleum ether resulting in a brown solid (1.01g). Neither solid were the required dimeric amine **5**.

Synthesis of N3,N3,N3',N3'-tetraethyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide 6

The (R)-(+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarbonyl dichloride **3** (0.08g, 0.18 mmol) was dissolved in DCM (25 cm^3) and added to a solution of diethyl amine (0.5 ml, 4.833 mmol) in DCM under a nitrogen atmosphere. This reaction was left stirring at 0°C and was followed by TLC. After 4 hours the reaction was complete; UV active spots 0.92 and 0.81 (**6** and **6a**) (20/80 methanol/ethyl acetate), no spot at 0.30 (2a). The reaction mixture was washed with HCl (2M, 2x25cm^3), $NaHCO_3$ (25 cm^3) and H_2O (25 cm^3). The aqueous layer was washed with DCM (25 cm^3). The organic layer was dried over magnesium sulphate and evaporated resulting in a yellow solid (0.26g, 67%); δ_H (400 MHz, $CDCl_3$) 7.0-8.0 (10H, m, Ar*H*), 2.9-3.9 (8H, m, CH_2), 0.8-1.8 (12H, m, CH_3). A portion was recrystallised from toluene and 60-80 °C petrol ether producing pale yellow crystals, that was found to be mostly sulphonyl **6a** with some N3,N3,N3',N3'-tetraethyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide **6** as a yellow solid; mp 148-152°C; $[\alpha]_D$= -136° (c=0.009, DCM); ν_{max} (nujol): 1632 (C=O); δ_H (400MHz, $CDCl_3$) 7.9 (2H, s, H_1), 7.8 (2H, d, *J=8 Hz*, H_2), 7.3 (4H, m, H_3, H_4), 7.1 (2H, d, *J=8 Hz*, H_5), 3.7-3.1 (8H, m, 4CH_2), 1.3-0.8 (12H, m, 4CH_3); δ_C ($CDCl_3$): 170.4(*C*=O), 169.0 (*C*=O), 151.2, 134.6, 128.8, 128.3, 128.1, 127.5, 124.8, 124.1, 122.5, 59.5 (4 x CH_2), 15.0, 1.0(4 x CH_3); *m/z*(EI) 531 (67%, $[C_{30}H_{31}O_3N_2S + H]^+$), 485 (27, $[C_{30}H_{33}O_4N_2+H]^+$.

Synthesis of 2,2'-dihydroxy-N3,N3'-diphenyl-1,1'-binaphthyl-3,3'-dicarboxamide 13

Aniline (1ml, 1.02g, 0.01 mol) was dissolved in DCM (5ml) and this was added to a 100ml round bottomed flask at 0°C. The acid chloride **3** (0.11g, 0.28 mmol) was dissolved in DCM (40 ml) and added drop wise to the 0°C solution under a nitrogen atmosphere. This solution was stirred at room temperature overnight. The resulting milky yellow suspension was worked up through addition of ethyl acetate and washing with 2M HCl and water twice, dried over sodium sulphate, filtered and evaporated. The crude solid was recrystallised from ethanol and petroleum ether producing 2,2'-dihydroxy-N3,N3'-diphenyl-1,1'-binaphthyl-3,3'-dicarboxamide **13** (0.06g, 52%); as a yellow solid; mp >327°C; (Found: C, 75.1; H, 4.6; N, 5.0 $C_{34}H_{24}N_2O_4.H_2O$ requires C, 75.3; H, 4.8; N, 5.2 %); ν_{max} (KBr)/cm^{-1} 3367 (NH/OH),

1651 (HNC=O); δ_H (400 MHz, DMSO): 11.7 (2H, s, NH), 11.0 (2H, s, OH), 9.0 (2H, s, H_1), 8.1 (2H, d *J=7 Hz,* H_2), 7.8 (4H,d *J=10 Hz,* H_o), 7.45 (8H, m, H_m, H_3, H_4), 7.25 (2H, t *J=7 Hz,* H_p), 7.05 (2H, d *J=8 Hz,* H_5); δ_C (DMSO): 168.9 (*C*=O), 154.2 (C_9), 138.1 (C-NH), 136.0 (C_7), 130.0 (C_1), 129.8 (C_6), 129.2 (C_m, C_2), 127.0 (C_4), 125.1 (C_{10}), 124.4 (C_3), 124.1 (C_8), 122.1 (C_o), 118.5 (C_p), 117.1 (C_5); *m/z* (EI) 525 (100%, $[M+H]^+$).

Synthesis of 2,2'-dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide 14

Trimethylaniline (1ml, 0.96g, 7.08mmol) and DCM (5ml) were added to a 100ml round bottomed flask at 0°C. Acid chloride **3** (0.42g, 1.03 mmol) was dissolved in DCM (40 ml) and added drop wise to the 0°C solution under a nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight. The DCM solution was washed with 2M HCl twice and water twice and dried over sodium sulphate, filtered and evaporated. The crude solid was recrystallised from ethanol and hexane producing 2, 2'-dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide **14** (0.30g, 49%); as a yellow solid; mp 210°C; (Found: C, 78.7; H, 5.6; N, 4.2 $C_{40}H_{36}N_2O_4$ requires C, 78.9; H, 6.0; N, 4.6 %); ν_{max} (nujol)/cm^{-1}: 3307(NH), 3186(OH), 1649(O=CNH), 1621(arC=C), 1504(arC=C); δ_H (400 MHz, $CDCl_3$): 11.6 (2H, s, NH), 8.4 (2H, s, H_1), 8.0 (2H, s, OH), 7.9 (2H, m, H_2), 7.4 (4H, m, H_3+H_4), 7.2 (2H, m, H_5); δ_C (400MHz, $CDCl_3$): 167.7 (s, C=O), 153.4 (s, C_9), 136.3-115.9 (30arC), 17.4 ($6CH_3$); *m/z* (EI) 609 (100%, $[M+H]^+$).

Synthesis of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-R-(+)-alpha-methyl benzyl amide 15.

The racemic diacid chloride **3** (2.24g, 5.44 mmol) was dissolved in DCM (25 cm^3) and R-(+)-alpha-methyl benzylamine (2.54g, 20.95 mmol) was also dissolved in DCM (25cm^3) and added to the other solution. This mixture was left stirring at 0°C for 2 hours. The reaction mixture was washed with HCl (2M, 2x25cm^3), $NaHCO_3$ (25 cm^3) and water (25 cm^3). The orange organic layer was dried over magnesium sulphate and evaporated to give 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-R-(+)-alpha-methyl benzylamide **15** (1.87g, 65 %) as a shiny brown solid; δ_H (400 MHz, $CDCl_3$): 11.6 (1H, s, NH), 11.5 (1H, s, NH), 8.1 (2H, s, H_1), 7.8 (2H, m, H_2) 7.2-7.5 (12H, m,

H_3, H_4, H_o, H_m), 7.1 (2H, m, H_5), 6.9 (2H, d *J=6 Hz*, H_p), 5.4 (2H, q *J=7 Hz*, 2CH), 1.6 (12H, d *J=7 Hz*, $2CH_3$). The brown solid was recrystallised from ethanol and then toluene with 60-80°C petrol ether resulting in 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-R-(+)-alpha-methyl benzylamide **15** (1.62g, 56%) as a brown powder; mp 191-192°C; [α]D= -15° (c=0.003, DCM); ν_{max} (nujol): 3301(NH), 3176(OH), 1643(O=CNH); δ_H (400MHz, $CDCl_3$): 11.5 (1.3H, s, NH), 11.6 (0.7H, s, NH) other peaks under solvent peaks; m/z (EI) 582 (100%, $[M+H]^+$), 326 (97, M-CON($HCHCH_3Ph)_2$).

Synthesis of 2,2'-dihydroxy-N3,N3'-di-L-leucine methyl ester-1,1'-binaphthyl-3,3'-dicarboxamide 16

L-leucine methyl ester (0.37 g, 2.06 mmol) was dissolved in DCM (50 ml) and triethylamine (0.6 ml, 4.28 mmol) was added. The acid chloride **3** (0.33 g, 0.80 mmol) was dissolved in DCM (10ml) and added drop-wise under nitrogen at 0°C. The reaction was left stirring for 3 days at room temperature. The reaction was followed by TLC (ethyl acetate 2.8/acetic acid 0.2) on the third day only diamide (RF 0.79) and triethylamine hydrochloride (RF 0.14) were present, no mono-amide (RF 0.53) or dimeric acid (RF 0.33) were present. The reaction mixture was washed with 2M HCl, twice with sodium carbonate solution and once with brine. The solution was dried over magnesium sulphate, filtered and evaporated. The resulting solid was recrystallised from ethyl acetate and petroleum ether resulting in 2,2'-dihydroxy-N3,N3'-di-L-leucine methyl ester-1,1'-binaphthyl-3,3'-dicarboxamide **16** (0.19g, 40%) as a yellow solid; mp 231 °C; (Found: C, 68.3; H, 6.4; N, 4.3 $C_{36}H_{40}N_2O_8$ requires C, 68.8; H, 6.4; N, 4.5 %); ν_{max} ($CDCl_3$)/cm^{-1} 3444 (NH, OH), 1738 (MeOC=O), 1651 (HNC=O), 1603(C=C), 1523 (C=C); δ_H (400 MHz, $CDCl_3$): 11.4 (2H, s, NH) 8.2 (2H, s, H_1) 7.9 (2H, d *J=8 Hz* H_2), 7.3 (4H, m, H_3, H_4), 7.1 (4H, m, OH, H_5), 4.9 (2H, m, H_6), 3.8 (6H, m, COOMe), 1.8 (6H, m, CH_2, H_7), 0.9 (12H, m, $2CH_3$). D_2O shake 11.4 and 7.1 reduced in integration and 4.9 showed fewer couplings; δ_C ($CDCl_3$): 173.8 (HO*C*=O), 169.7 (HN*C*=O), 154.4 (C_9), 136.9 (C_7), 129.5 (C_1), 129.4(C_6), 128.4 (C_2), 127.4 (C_4), 125.1 (C_{10}), 124.5 (C_3), 117.8 (C_8), 117.0 (C_5), 53.1(OCH_3), 51.3 (HNCH), 42.1(CH_2), 25.3 (CH), 23.3(CH_3), 22.4 (CH_3); m/z (EI) 629 (100%, $[M+H]^+$).

Attempted synthesis of 2,2'-dihydroxy-N3,N3'-di-L-tyrosinyl-1,1'-binaphthyl-3,3'-dicarboxamide

L-tyrosine (0.10 g, 0.56 mmol) was dissolved in DCM (40 ml) and triethylamine (0.6 ml, 4.28 mmol) was added. Acid chloride **3** (0.11 g, 0.27 mmol) was dissolved in DCM (10ml) and added drop-wise under nitrogen at 0°C. The reaction was left stirring for 3 days at room temperature. The reaction was followed by TLC (ethyl acetate 2.8/acetic acid 0.2). The reaction mixture was extracted into ethyl acetate and a small amount of ethanol, washed with 1M HCl, Na_2CO_3 and brine, dried over magnesium sulphate and evaporated leaving an orange solid (0.11g, 56%); mp dec. 290°C; ν_{max} (nujol)/cm^{-1} 3418 (NH, OH), 1715 (HOC=O), 1644 (HNC=O), 1556(C=C); δ_H (400 MHz, D_2O): ratios wrong; m/z (EI) 629 (100%, $[M+H]^+$).

Synthesis of 2,2'-dihydroxy-N3,N3'-di-L-tyrosine ethyl ester-1,1'-binaphthyl-3,3'-dicarboxamide 17.

L-tyrosine ethyl ester hydrochloride (0.15g, 0.59 mmol) and triethylamine (110 µl, 1.72 mmol) was dissolved in DCM. Acid chloride **3** (0.11g, 0.27 mmol) was dissolved in DCM (10ml) and added drop-wise under nitrogen at 0°C. The solution was left to stir overnight. The reaction mixture was washed with 2M HCl twice, Na_2CO_3 twice and brine once, dried over sodium sulphate, evaporated leaving a yellow solid (0.18g, 89%) very complicated NMRs incompatible with expected product.

Attempted synthesis of 2,2'dihydroxy-1,1'-binaphthyl-3,3'-dihydroxylamide 18

Hydroxylamine hydrochloride (0.16g, 2.23 mmol) was dissolved in triethylamine (0.4 ml) and DDM (30 ml). The acid chloride (0.11g, 0.28 mmol) was dissolved in DCM and added drop-wise to the mixture, under nitrogen at 0°C. The reaction was left at room temperature stirring overnight. The reaction mixture was extracted into DCM, washed twice with 1M HCl and once with brine, dried with magnesium sulphate, filtered and evaporated resulting in a yellow solid (1.55g, >100%) which was mainly triethylamine hydrochloride. This was re-extracted into ethyl acetate and washed with water and 1M HCl but still there was an excess of triethylamine hydrochloride present; δ_H (400 MHz, MeOD): 8.3 (2H, s, H_1), 7.8 (2H, d *J=8 Hz*, H_2), 7.2 (4H, m, H_3, H_4), 6.9 (2H, d *J=8 Hz*, H_5).

Attempted synthesis of (1,1) binaphthylenyl-2,3,2',3'-tetraol

CuCl (0.04g, 0.38 mmol) was added to a solution of 2,3-dihydroxynaphthalene (0.10g, 0.62 mmol) in absolute methanol in a 100ml 2-necked round-bottomed flask. This mixture was stirred at room temperature with air bubbled through the purple suspension. The reaction mixture turned black almost instantly. Methanol was added every day and the reaction continued for 7 days. There was no product spot visible by TLC. The methanol was evaporated leaving a brown solid. This was extracted into ethyl acetate, washed with 2M HCl and brine and dried over magnesium sulphate. The ethyl acetate was evaporated to leave a brown solid (0.09g, 90%). NMR (DMSO) broad peaks in aromatic region attributed to diol polymerisation.

Synthesis of 3-benzyloxy-2-hydroxynaphthalene 19

2,3-dihydroxynaphthalene (4.98g, 0.03mol) was dissolved in acetone (500ml) and potassium carbonate (10.51g, 0.08 mol) was added to the pink solution while stirring. Benzyl bromide (3.8 ml, 0.03 mol) was added and the solution was left stirring overnight. The reaction was followed by TLC; UV active spots RF 0.75 (diol) and 0.51 (benzyl ether) (40/60 hexane/ethyl acetate). The reaction was refluxed for 3 hours until only a faint starting material spot was visible. The solution was extracted into ethyl acetate 3 times and washed with brine. The ethyl acetate was evaporated leaving brown 3-benzyloxy-2-hydroxynaphthalene (5.61g, 72%); δ_H (400 MHz, $CDCl_3$): 7.6 (2H, m, H_2, H_5), 7.5-7.3 (6H, m, PhH, H_3), 7.3 (2H, m, H_1, H_4), 7.1 (1H, s, H_6), 5.9 (1H, s, O*H*), 5.15 (2H, s, CH_2).[58]

Synthesis of 3,3'-Bis-benzyloxy-1,1'-binaphthalenyl-2,2'-diol 20

A solution of 3-benyloxy-naphthalen-2-ol **19** (0.24g, 0.98 mmol) in absolute MeOH (50 ml) was made up in a 2-necked 100 ml round-bottomed flask. CuCl (0.08g, 0.84 mmol) was added to the solution and stirred at room temperature, with air bubbling through it, for 18 days. During this time, the reaction was followed by TLC; UV active spots RF 0.7 (starting material) no product spot showed (20/80 methanol/ethyl acetate. The methanol was evaporated leaving a brown solid, which was dissolved in ethyl acetate, washed with 1M HCl and brine. The aqueous layer was extracted into ethyl acetate. The organic layer was dried over magnesium sulphate, filtered and

evaporated leaving a red/brown crystalline solid (0.24g, 98%). This was recrystallised from methanol and precipitated with water resulting in 3,3'-Bis-benzyloxy-1,1'-binaphthalenyl-2,2'-diol (0.13g, 55%) as a pink/brown powder; mp 99°C; ν_{max} (nujol)/cm^{-1} 3196(OH), 1605(arC=C), 1503(arC=C); δ_H (400 MHz, $CDCl_3$): 7.8 (2H, d, J=*8 Hz*, H_2), 7.5 (4H, m, H_o), 7.4 (8H, m, H_m, H_3, H_4), 7.3 (2H, m, H_p), 7.1 (4H, m, H_1, H_5) 5.95 (2H, s, 2OH), 5.25 (4H, s, $2CH_2$); (EI) 499 (100%, $[M+H]^+$), 341 (25, $[M-(2(C_5H_5)+3H)]^+$).[20]

Synthesis of Vanadyl complex 21[24]

L-Valine (0.59g, 5.03 mmol) and NaOAc-$3H_2O$ (1.20g, 8.79 mmol) were added to degassed water (10 ml) in a two-necked 50 ml round bottomed flask. This mixture was stirred under an inert atmosphere at 60°C for 10 minutes until dissolution. The solution was treated drop wise with a solution of 2-hydroxy-1-naphthaldehyde (0.87g, 5.05 mmol) in degassed ethanol (12.5ml). The reaction mixture was heated at 80°C for 15 minutes until homogeneous, and the mixture was cooled for 2 hours. To the resultant Schiff base was added a solution of vanadyl sulphate trihydrate (1.10g, 6.63 mmol) in degassed water (5 ml). A green complex started to precipitate immediately. The reaction mixture was stirred for 2 hours, filtered and then concentrated to half of the original solvent volume. This was filtered again and the resultant green solid **21** was dried under vacuum: (1.69g, 100%); ν_{max} (nujol)/cm^{-1} 3418 b (H_2O), 1624 b s (C=O/C=N), 1004 s (V=O). No IR in[24]

Synthesis of 3,3'-Bis-benzyloxy-1,1'-binaphthalenyl-2,2'-diol 20 with vanadyl catalyst 21.

The vanadyl complex **21** (0.04g, 0.14mmol) was dissolved in DCM (10ml) in a 100ml round-bottomed flask. The green solution was stirred for 15 minutes and then the 3-benzyloxy-2-hydroxynaphthalene **19** (0.25g, 1.02 mmol) was added. The subsequent dark blue solution was stirred at room temperature for 5 days .The DCM repeatedly evaporated so was replaced by DCE. The reaction was followed by TLC; UV active spots RF 0.72 (starting material) and 0.61 very small (product) (40/60 methanol/ethyl acetate). The final blue solution was washed with 2M NaOH which turned the solution yellow. The organic product was extracted into ethyl acetate, washed with

NaOH and brine. The organic layer was dried and evaporated leaving a brown solid (0.24g, 94%). Repeated for 2 weeks (0.25g, 99%), only monomer present.

This was repeated again with excess water and $NaBO_3$. TLC seemed to show a larger product spot than before after only 3 days but when the NMR spectrum was compared to the spectra of the authentic product and starting material it showed that only strating material was present. The reaction was repeated again in acetonitrile with oxygen for 6 days. TLC showed that some dimer had formed but NMR spectra showed only starting material

Complexation of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2 with potassium tetrachloroplatinate (II).

A solution of dimeric acid **2** (0.04g, 0.10 mmol) in MeOH (3.00ml) was added to a suspension of potassium tetrachloroplatinate (II) (0.04g, 0.10 mmol) in MeOH (1ml). On heating there seemed to be no reaction as there was no pH change or colour change, so the reaction mixture was transferred to a 100ml round-bottomed flask and more MeOH (6 ml) was added. The suspension was heated under reflux for 2 hours, after which time the suspension was pH 2. The reaction was repeated with acetonitrile as the solvent. Not all the pink starting material had reacted so triethylamine (0.3ml, 2.15 mmol) was added and the pink powder disappeared overnight. The MeCN was evaporated and the light brown solid was washed with water leaving platinum complex **23** (0.02g, 23%) as a light brown solid; mp 158 °C; ν_{max} (nujol)/cm^{-1} 1649 (C=O), 1590 (C=C), 1506 (C=C); δ_H (400 MHz, DMSO) 8.6 (2H, s, H_1), 8.0 (2H, m, H_2), 7.3 (4H, m, H_3+H_4), 7.0 (2H, m, H_5); expected ions not observed in ESI/EI mass spectrum.

Synthesis of dichloro dipyridyl platinum (II).[55]

Potassium tetrachloroplatinate (0.50g, 1.21 mmol) was dissolved in water (10 ml) in a 100ml round bottomed flask. Pyridine (0.20ml, 2.45 mmol) in water (5.00ml) was added drop-wise to the red solution while stirring vigorously. The reaction mixture was left stirring for 3 hours and then left at room temperature over night. The pale yellow precipitate was filtered off, washed with water and dried in the oven and the filtrate was left in the fridge to produce more solid (0.37g, 72%) δ_H (400 MHz, acetone-d_6) 8.7(4H, d *J=5 Hz*, H_o), 7.9 (2H, m, Hp), 7.4 (4H, m, H_m). [55]

Attempted complexation of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid with dichloro dipyridyl platinum (II).

Dimeric acid **2** (0.04g, 0.12 mmol) was dissolved in acetone (20ml) and stirred while $NaHCO_3$ (0.04g, 0.50 mmol) and $PtPy_2Cl_2$ (0.10g, 0.24 mmol) were added. The mixture was heated to 50 °C for 4 hours then left to cool. A grey precipitate formed (0.06g, 49%) which was only starting materials as judged by NMR spectrum and mass spectrum

Attempted complexation of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2 with zirconium chloride and pyridine

2,2'-Dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (0.10g, 0.29 mmol) was dissolved in DCM (50 ml); pyridine (130 µl, 1.61 mmol) and zirconium tetrachloride (0.04g, 0.19 mmol) were added at 0°C. The reaction mixture was stirred for 1 hour. A yellow precipitate was filtered off (0.03g, 23%) NMR showed a mixture of dimeric acid **2** and pyridine only.

Complexation of 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid 2 and cobalt trimer 22

2,2'-Dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid **2** (0.10g, 0.28 mmol) was mostly dissolved in ethanol (15ml) and the cobalt trimer **22** (0.24g, 0.30mmol) was partially dissolved in water (25 ml). This was added to the dimeric acid solution, while stirring, to produce a pink solution. The solution was refluxed for 1.5 hours, in which time, the reaction mixture turned black. This was cooled slightly, filtered to remove the small amount of pink solid left and then left to cool fully. The solution was condensed and left to cool, to give a black product which was too insoluble for spectroscopic characterisation.

Addition of Nickel chloride hexahydrate to 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-R-(+)-alpha-methyl benzylamide

2,2'-dihydroxy-1,1'-binaphthyl-3,3'-R-(+)-alpha-methyl benzylamide **15** (0.006g, 0.010 mmol) was dissolved in DCM (2 cm^3) and the optical rotation was measured.

$NiCl_2$ (0.026g, 0.110 mmol) was dissolved in MeOH (20 cm^3) and 0.5 cm^3 portions of the $NiCl_2$ solution were added to the amide solution. The optical rotation was measured after each addition. Sodium carbonate was added to the $NiCl_2$ solution, shaken and the liquid was filtered off. Methanol (4 cm^3) was added to the solid:

	Volume (cm^3)	[a]D	concentration	Solvent
$NiCl_2$ solution	0.5	-5.6°	0.0024	DCM/MeOH
	1	-5.8	0.002	DCM/MeOH
	1.5	-5.6°	0.0017	DCM/MeOH
	2	-9.6°	0.0015	DCM/MeOH
$NaCO_3$ added	4	-15.2°	0.0015	MeOH

The same procedure was followed with, 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-bisdiethyl amide **6** (0.018, 0.0371 mmol) and $NiCl_2$ (0.089g, 0.376 mmol).

	Volume (cm^3)	[a]D	concentration	Solvent
$NiCl_2$ solution	0.5	-124.5°	0.0072	DCM/MeOH
	1	-114.1°	0.006	DCM/MeOH
	1.5	-109.7	0.0051	DCM/MeOH
	2	-105.1°	0.0045	DCM/MeOH
$NaCO_3$ added	4	+16.8°	0.0045	MeOH

Attempted complexation of 2,2'-dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide 14 with methyl magnesium bromide.

2,2'-Dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide (0.10g, 0.16 mmol) was dissolved in dry THF (50 ml) under nitrogen in a 100 ml side arm round bottomed flask. MeMgBr (0.25 ml, 0.08 mmol) was added to the reaction mixture via syringe at 0°C. The solution was stirred for 1.5 hours. The THF was then removed under vacuum and the product was recrystallised from THF. Reaction unsuccessful as judged bythe NMR spectrum

Attempted complexation of 2,2'-dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide 14 with bisacetonitrile palladium (II) chloride

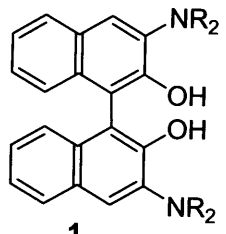
2,2'-Dihydroxy-N3,N3'-dimesityl-1,1'-binaphthyl-3,3'-dicarboxamide **14** (0.03g, 0.05 mmol) and $Pd(MeCN)_2Cl_2$ (0.03g, 0.11 mmol) were partially dissolved in acetonitrile.

The orange mixture was heated to reflux forming an orange solution. This solution was left stirring overnight and then left to cool, forming a crystalline precipitate. On recrystallisation $Pd(MeCN)_2Cl_2$ crystals formed and ligand was left in solution.

Attempted complexation of 2,2'-dihydroxy-N3,N3'-diphenyl-1,1'-binaphthyl-3,3'-dicarboxamide 13 and cobalt trimer 22.

2,2'-dihydroxy-N3,N3'-diphenyl-1,1'-binaphthyl-3,3'-dicarboxamide **13** (0.03g, 0.06 mmol) was mostly dissolved in ethanol (5ml) and the cobalt trimer **22** (0.05g, 0.06 mmol) was partially dissolved in water (15 ml). This was added to the amide solution, while stirring, to produce a peach coloured solution. The solution was refluxed for 1.5 hours and no colour change was seen. Evaporation of the solvent resulted in a mixture of yellow and pink solids (0.04g) the pink soluble in D_2O and the yellow soluble in $CDCl_3$ which were shown to be the starting materials by NMR spectroscopy.

3.4 Compound List



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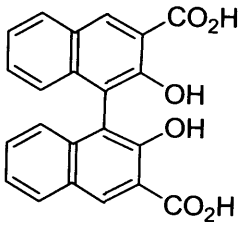

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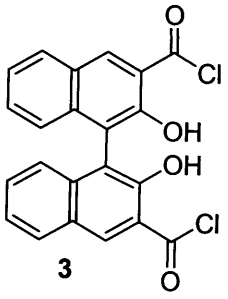

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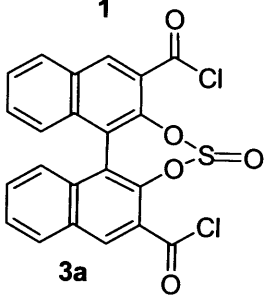

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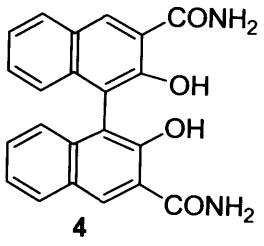

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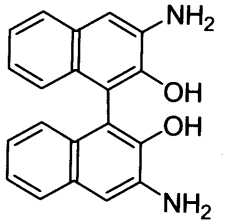

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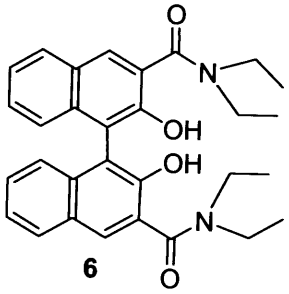

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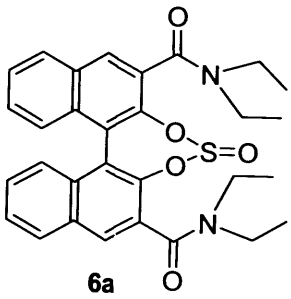

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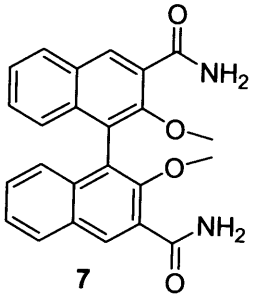

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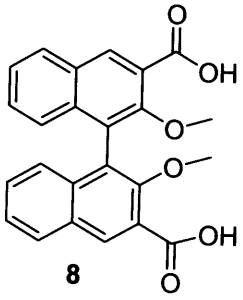

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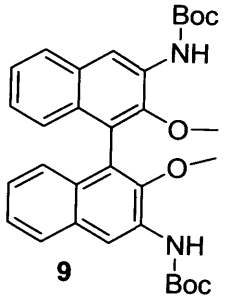

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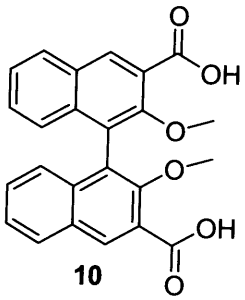

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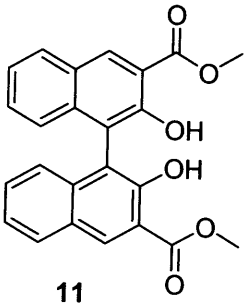

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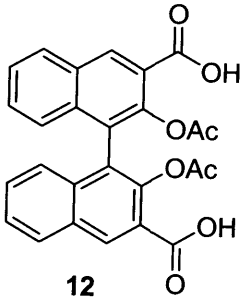

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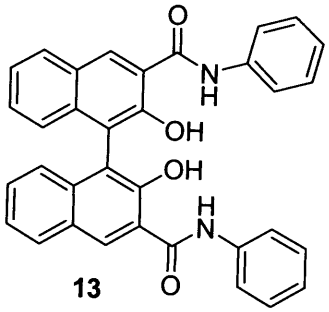

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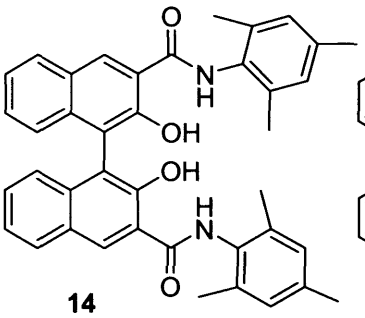

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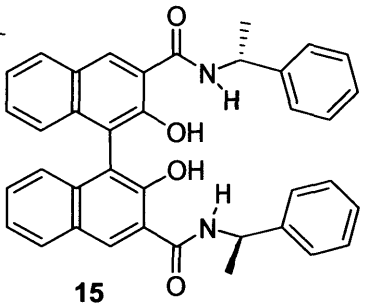

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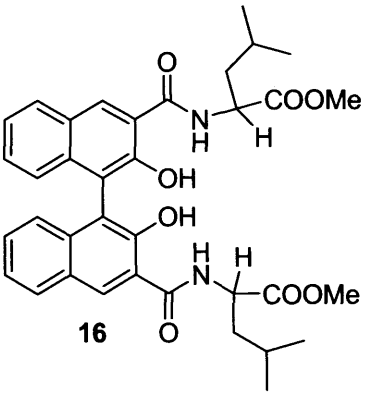

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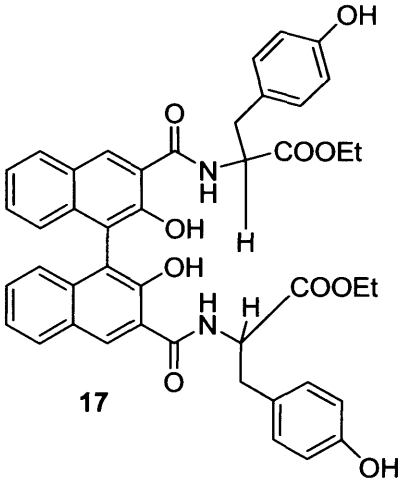

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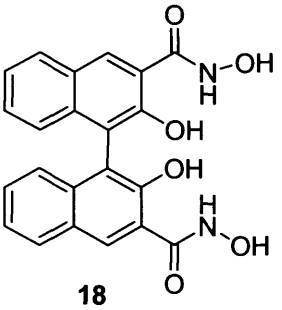

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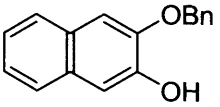

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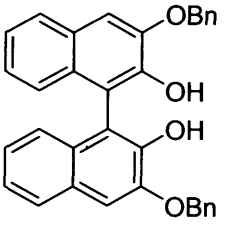

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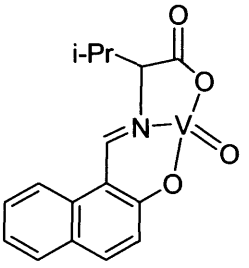

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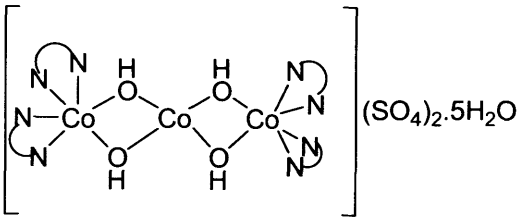

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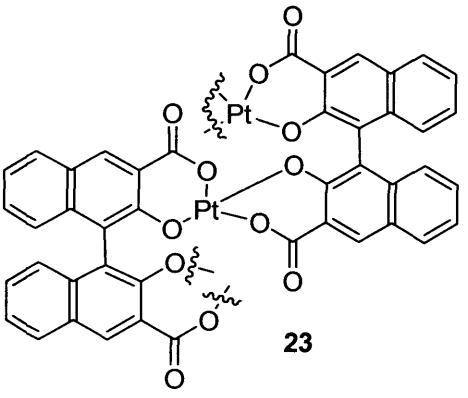

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Chapter 4- Biphenanthrolines and other Biaryls

4.1 Introduction

The first examples of biphenanthrolines (henceforth referred to as biphen) in the literature were reported by F.H. Case who synthesised 2,2' and 5,5'-bi(1,10-phenanthroline).[1] 2, 2'-biphen was synthesized by coupling 2-chloro-phen with copper powder (the Ullman coupling). 5,5'-biphen could not be synthesised using this method so was accessed from 3,3'-dinitrobiphenyl-4,4'-diamine, via a Skraup reaction (with arsenic acid and glycerol), a reduction and another Skraup reaction.

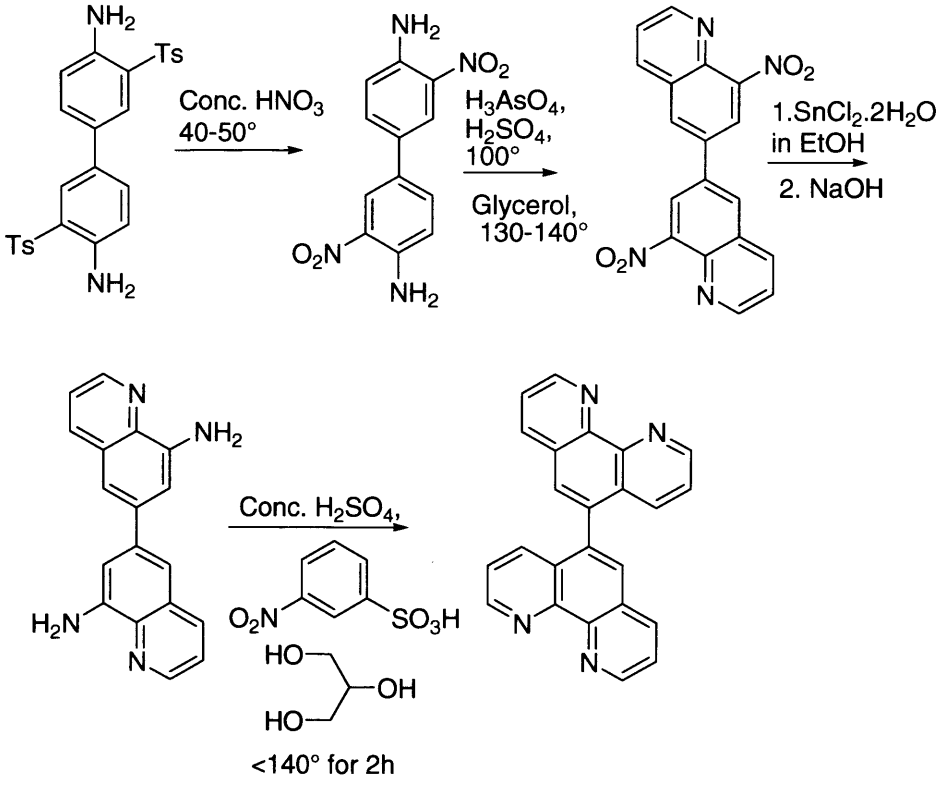


Figure 4.1 Synthesis of 5,5'-biphen

The yield was only 33% and used very toxic materials, possibly as a result of this biphenanthrolines have been little studied.

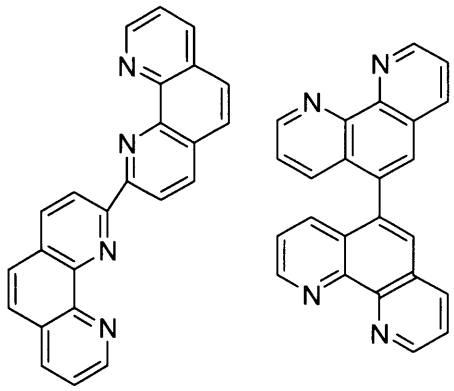


Figure 4.2 2, 2' and 5, 5'-Bis (1, 10-phenanthroline)

P. M. Griffiths *et al* synthesised iridium (III), ruthenium (II) and osmium (II) complexes with 5, 5'-Bis (1, 10-phenanthroline) through a different approach to Case.[2]

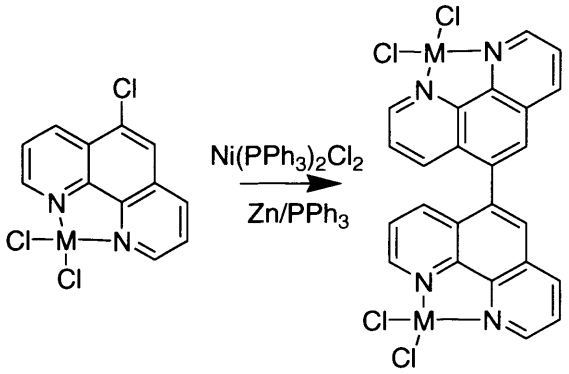


Figure 4.3 Nickel catalyzed coupling reaction

They synthesised chloro-phen complexes of these metals and performed a nickel catalyzed coupling reaction, the experimental detail of which was not published. These complexes did not have the conjugation required by Griffiths *et al*, due to the non-planar orientation of the ligand, so were not further studied. This means that there is the possibility that 5,5-biphenanthrolines have the potential to be axially chiral like the afore-mentioned binaphthalenes. By analogy to binaphthalene, rotation around the central C-C bond would be hindered if there were substituents at the 5,5' position.[3] As yet, substituted 5,5-biphens have not been reported, and there has been no mention of resolution of atropisomers.

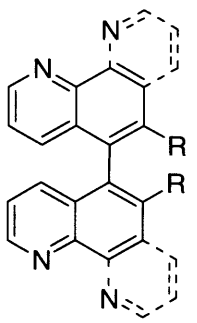


Figure 4.4 Substituents encourage hindered rotation.

Since the following work was completed Shinji Toyota et al[4] have successfully synthesised 2,2'-, 3,3'-, 4,4'- and 5,5'-biphens through direct Ni-catalysed coupling of the necessary halide, previously deemed impossible for 5,5'-biphens[1] and have investigated their spectroscopic properties and the effect of H^+ and Zn^+ on these properties. They have also formed a helical copper complex using 2,2'-biphen.

All of the biphens are potential ligands but 5,5'-biphen has the most steric hindrance so is more likely to be axially chiral and could form complexes that use the axial chirality of the ligand to form helical structures.

Other potential axially chiral ligands could be based on biphenyl systems. There are many examples of biphenyls in the literature with uses in asymmetric catalysis,[5-7] ferroelectric liquid crystals[8] and spacers in donor-acceptor compounds.[9] If a biphenyl with two donor groups on each ring could be synthesised with additional substituents which lead to restricted rotation around the C-C bond then it would be a suitable ligand to form helical complexes.

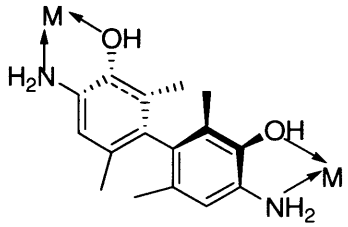


Figure 4.5 Biphenyl ligand with 4 donor sites.

4.2 Results and Discussion

The initial approach was to start with 1,10-phenanthroline, a cheap starting material, and functionalise by using a literature epoxidation reaction [10] On heating in sulphuric acid it is known that this epoxide will open, the aromatic system will be restored and a hydroxyl group will have been formed, as shown in the literature.[11] Rather than using acid to form just a hydroxyl group, a nucleophile could be added leading to a substituent alpha to the hydroxyl group. Oxidation would then reform the aromatic system.

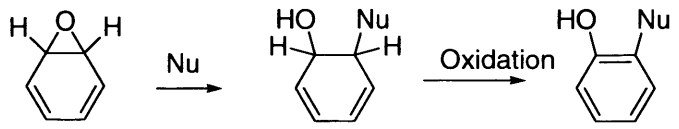


Figure 4.6 Functionalisation of phen.

This would make it possible to have a bulky substituent which would hinder rotation once the biphen is formed increasing the probability that the ligand would be axially chiral. Theoretically the hydroxyl could be converted to a chloride using the known chlorination reagents phosphoryl chloride and phosphorous pentachloride. Coupling of aryl chlorides is known to be possible using mixtures of nickel bistriphenyl phosphine dichloride, zinc and triphenyl phosphine.[2]

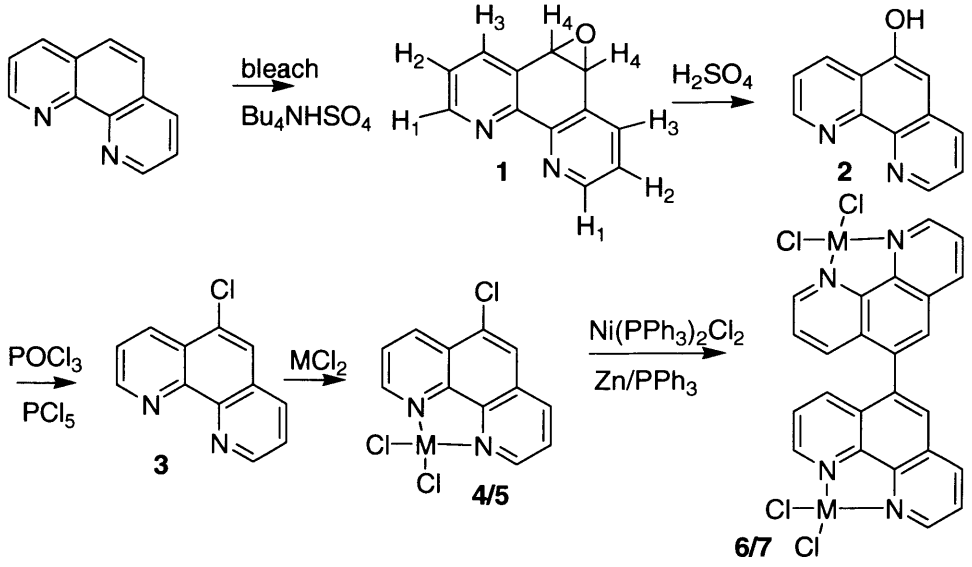
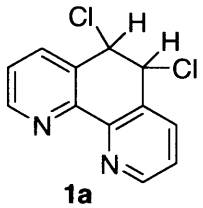


Figure 4.7 Initial Biphenanthroline synthesis

Epoxide **1** was easily obtained using the literature procedure,[10] which utilised bleach as the oxidant in the aqueous layer, with phenanthroline dissolved in chloroform with a phase transfer agent to facilitate mixing. This was followed by NMR spectroscopy, as the reaction time varied, possibly due to varying concentration of sodium hypochlorite in the bleach. However, when scaled up to more than 0.5g, mixing occurred a lot slower and therefore the reaction rate considerably decreased and an impurity became evident. This impurity was slightly more soluble in chloroform and had the same number of protons as the epoxide. The spectrum showed that the impurity was a symmetrical phenanthroline with protons H_3 and H_4 considerably shifted compared to the epoxide. H_4 has a higher chemical shift than in the epoxide and is consistent with the expected spectrum of dichloro-phen **1a**. This would explain the solubility in chloroform and was also found by Antkowiak and Antkowiak.[12]



1a

Figure 4.8 5, 5'-Dichloro-1,10-phenanthroline

To increase mixing, air was bubbled through the reaction mixture. This decreased the reaction time but also increased the proportion of **1a,** so nitrogen was bubbled through instead. This produced only a small amount of **1a** and the reaction time reduced to 1 hour. The product from this reaction was solid without recrystallisation, unlike in the other attempts, showing that **1a** formation was encouraged under an oxygen atmosphere. Suitable crystals for X-ray determination were obtained by recrystallisation from chloroform and hexane.

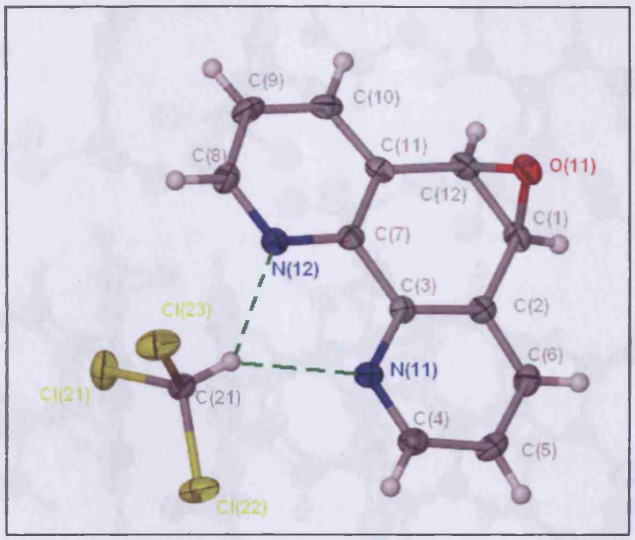


Figure 4.9 X-ray Crystal Structure of Epoxy-phenanthroline

Table 4.1 Crystallographic details for Epoxy-phen 1

Compound	1
Formula	$C_{13}H_9C_{l3}N_2O.CHCl_3$
M	434.95
a (Å)	11.432(5)
b (Å)	12.086(5)
c (Å)	19.517(5)
α(°)	90.000(5)
β(°)	90.000(5)
γ(°)	90.000(5)
V (Å^3)	2696.6(18)
T (K)	150
Crystal system	Orthorhombic
Space group	Pcab
Z	8
μ (mm^{-1})	0.671
Reflections collected	18021
Independent reflections (R_{int})	3098[R(int)=0.1365]
Final R indices (all data)	R_1=0.0898, wR_2=0.1643

Table 4.2 Hydrogen bond lengths (Å) between epoxy-phen and chloroform

H-Bond	N_{11}-H_{21}	N_{12}-H_{21}
Distance	2.285	2.370

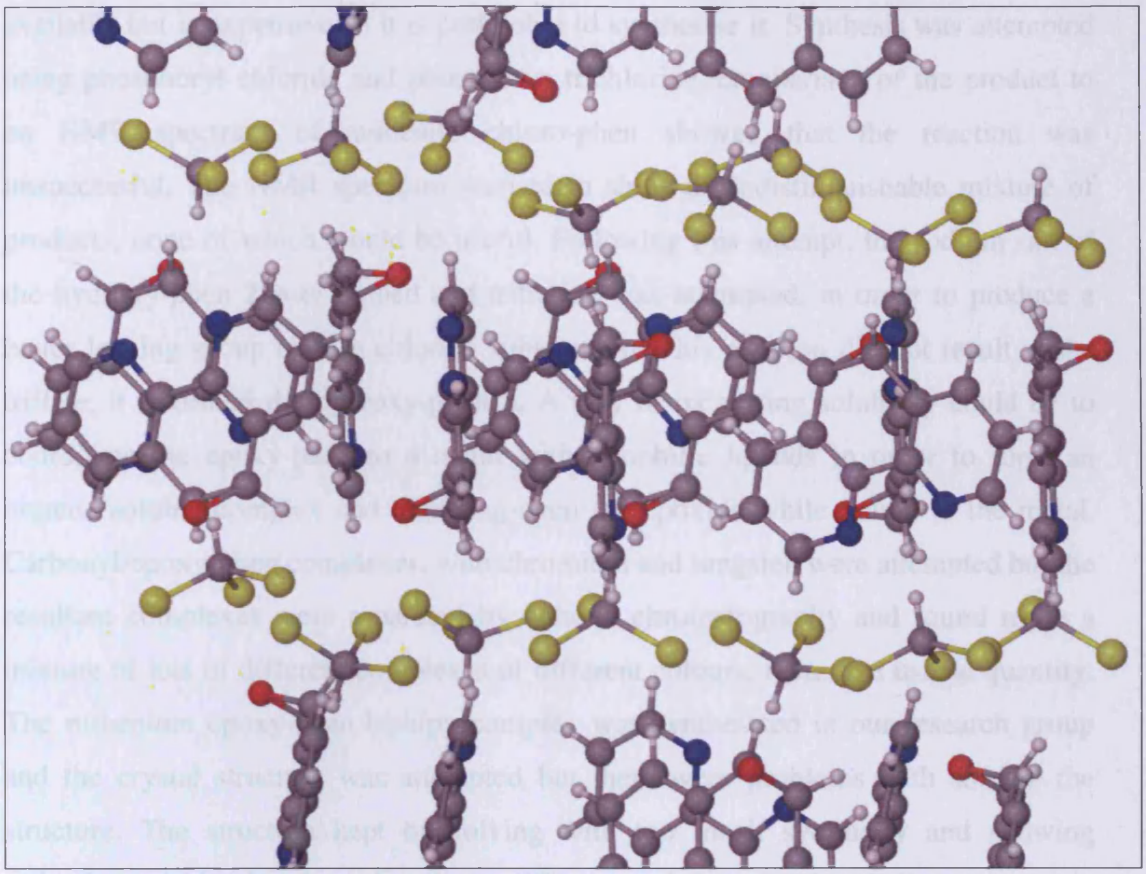


Figure 4.10 Packing of Epoxy-phen and chloroform

The epoxy-phen molecules and chloroform molecules form layers. The bond lengths between the hydrogen of the chloroform molecule and the nitrogens of epoxy-phen **1** are comparable with metal-nitrogen bonds on similar compounds, showing the possibility of metal chelating with this ligand. The only example of an epoxy-phen complex, with rhenium, was reported by Shen and Sullivan[13] and then in more detail by Marti et al in 2005,[14] after this work was completed. Marti et al reported the crystal structure of epoxy-phen and of the rhenium complex fac-Tricarbonyl(chloro)-(5,6-epoxy-1,10-phenanthroline)rhenium(I).They showed the rhenium- nitrogen bond length to be 2.179 Å which is not much shorter than the hydrogen nitrogen bonds reported here. This type of hydrogen bonding has been seen in many structures and a statistical study was undertaken by Mascal, reporting nitrogen hydrogen distances of between 2.05 and 2.45 Å.[15]

The hydroxy-phen **2**,[11] was formed from the opening of the epoxide ring with sulphuric acid then rearrangement to reform the aromatic system. It was very insoluble, making forming the chloro-phen difficult. Chloro-phen **3** is commercially

available but is expensive so it is preferable to synthesise it. Synthesis was attempted using phosphoryl chloride and phosphorus trichloride, comparison of the product to an NMR spectrum of authentic chloro-phen showed that the reaction was unsuccessful. The NMR spectrum seemed to show an indistinguishable mixture of products, none of which would be useful. Following this attempt, the sodium salt of the hydroxy-phen **2** was formed and triflation was attempted, in order to produce a better leaving group to ease chloride substitution. This reaction did not result in the triflate; it reformed the hydroxy-phen **2.** A way of increasing solubility could be to coordinate the epoxy-phen to a metal with lipophilic ligands in order to form an organic soluble complex and then ring-open the epoxide while bound to the metal. Carbonyl/epoxy-phen complexes, with chromium and tungsten were attempted but the resultant complexes were separated by column chromatography and found to be a mixture of lots of different complexes of different colours, none in a usable quantity. The ruthenium epoxy-phen bisbipy complex was synthesised in our research group and the crystal structure was attempted but there were problems with solving the structure. The structure kept on solving with too much symmetry and showing ruthenium trisbipy but the unit cell was different to that reported and all spectroscopic data proved it was the epoxy-phen complex.

Commercial chloro-phen was used to synthesise the nickel and palladium chloro-phen complexes. The nickel complex **4** seemed to be paramagnetic, giving very broad NMR spectra. Ni^{2+} has a d^8 configuration so the 8 electrons would occupy the orbitals as shown in figure 4.11 and a tetrahedral or octahedral geometry of the complex would have unpaired electrons which can result in paramagnetism. A tetragonal distortion occurs in a square planar complex splitting the t_{2g} and e_g levels further, leaving one orbital at a higher energy than before so the unpaired electrons pair up leaving the highest energy level empty. Therefore complex **4** is probably the octahedral complex $NiCl_2(H_2O)_2$Cl-phen.

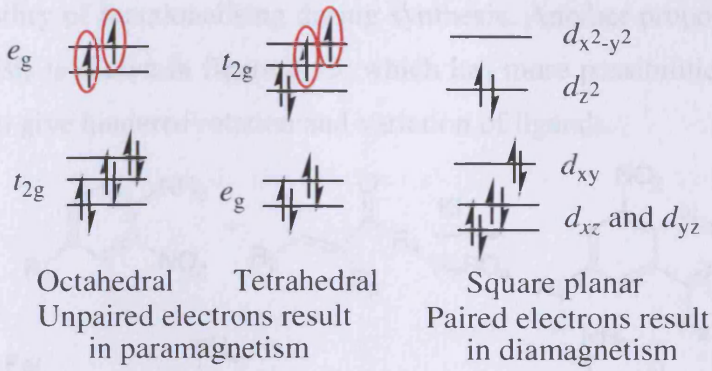


Figure 4.11 Molecular orbital diagrams for a d^8 configuration, such as in Ni^{2+} complexes.

Elemental analysis showed the presence of two waters as well as the chlorines, proving an octahedral geometry. The palladium complex **5** was diamagnetic and therefore square planar, no extra waters were present.

Coupling at the 5 position was catalysed by nickel dichloride bistriphenylphosphine with zinc dust and triphenyl phosphine in dimethylformamide. UV and IR spectra showed a slight shift in values from monomer to dimer but the mass spectrum did not show any of the required ions so it is likely that dimerisation did not occur. The palladium complex did not couple successfully and starting material was recovered.

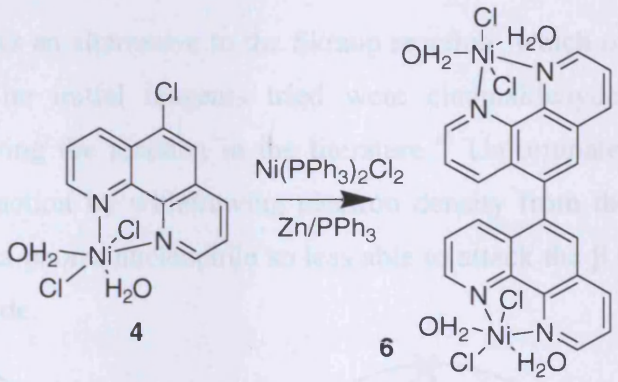


Figure 4.12 Nickel chloride complex of biphenanthroline

The above route is limited as there are no functional groups attached to the rings for easy functionalisation. To add the groups necessary for hindered rotation would involve electrophilic substitution of the rings which could involve production of positional isomers. Also, without being able to synthesise the chloro-phen, this route becomes even less attractive as this would mean starting from expensive chloro-phen

with no possibility of functionalising during synthesis. Another proposed scheme for bi-phen synthesis is shown in figure 4.13, which has more possibilities for including bulky groups to give hindered rotation and variation of ligands.

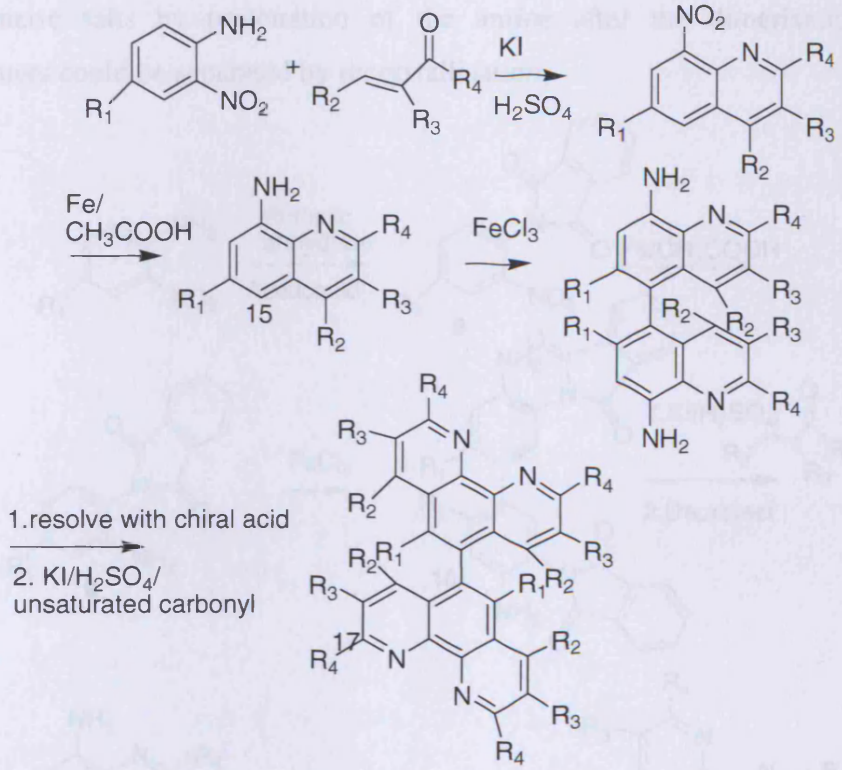


Figure 4.13 Alternative Route to Substituted Phenanthrolines

The first step shows an alternative to the Skraup reaction[1] which often involves toxic arsenic oxides. The initial reagents tried were cinamaldehyde and 4-methyl-2-nitroaniline following the reaction in the literature.[16] Unfortunately the nitro group deactivated the reaction by withdrawing electron density from the aromatic system leaving the amine a poorer nucleophile so less able to attack the β carbon of the α, β-unsaturated aldehyde.

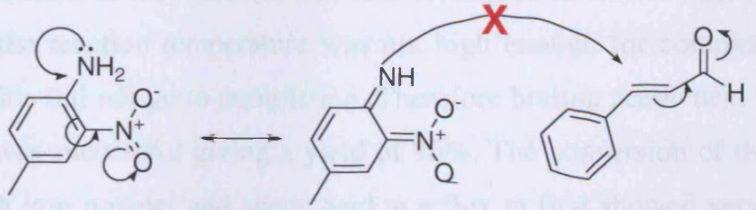


Figure 4.14 Nitro group deactivating nucleophilic attack of an α,β-unsaturated aldehyde.

After several attempts of this initial step another route was devised (see figure 4.15). This involved protecting the amino group with phthalic anhydride and converting the

nitro to an amine group. Both of these routes have the advantage of being able to vary substituents to obtain hindered rotation and improve the solubility of the ligand. In addition, there is the possibility of resolving the ligand by using a chiral acid to make diastereomeric salts by protonation of the amine after the dimerisation. These diastereomers could be separated by recrystallisation.

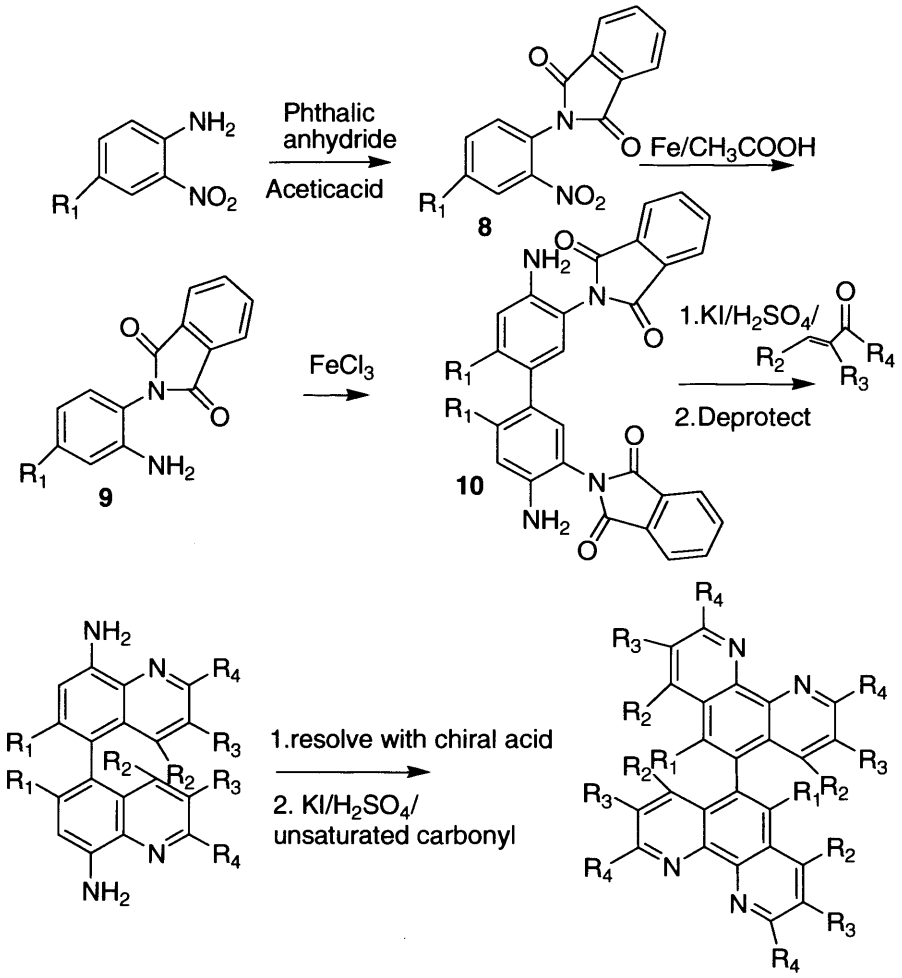


Figure 4.15 Alternative Route to Substituted Phenanthrolines

The initial reaction in this scheme was first attempted at reflux with toluene as the solvent, but the reaction temperature was not high enough for complete dissolution and the reaction did not go to completion. Therefore boiling acetic acid was used and the reaction was successful giving a yield of 96%. The conversion of the nitro group to amine with iron powder and acetic acid at reflux at first showed very broad peaks in the NMR spectrum. This could be attributed to the production of iron (III) acetate, which is paramagnetic. The broad peaks were no longer observed after recrystallisation. The resultant aniline **9** was refluxed in hydrochloric acid and water

with the known oxidative coupling reagent iron (III) chloride.[17] At reflux, all the solids dissolved and an attempt to follow by TLC showed no product at various intervals. An attempt was made to work up the reaction mixture but the remaining solids were insoluble in the solvents tried.

The biphenanthrolines synthesis was progressing very slowly and unsuccessfully, so a new synthetic route to different axially chiral ligands based on the conversion of nitro to conjugated diamine to biphenyls with hindered rotation and amine groups which is precedented in the literature[9], was pursued, as shown in figure 4.16.

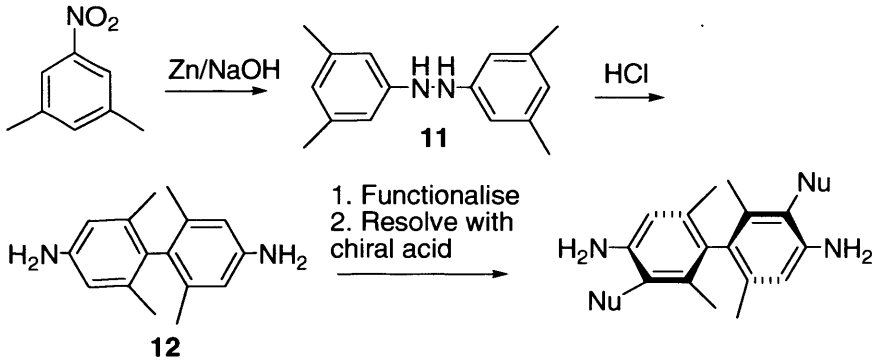
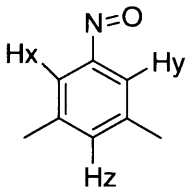


Figure 4.16 Synthesis of Dimeric amine

In the biphenyl systems the methyl groups restrict rotation around the C-C bond in dimeric amine **12**. To act as a multi-dentate ligand there needs to be a donor group alpha to the amine group. The amine can also be turned into an imine, by addition of a carbonyl, or a hydroxyl group via the diazonium salt.

The reaction to synthesise dimeric amine **11** was attempted seven times producing several different products. On the first attempt, the reaction was followed by TLC and once the starting material was used up the reaction mixture was filtered while hot as in the literature[9] and washed with acetic acid/ethanol but there were still some large orange crystals left on the filter that seemed to be a major product of the reaction. An NMR spectrum of these crystals showed a 1:1 ratio with starting material and possibly a nitroso compound **11a**, partially reduced. Further recrystallisation did not change the ratio so it is thought that the large crystals are a 1:1 co-crystal of starting material and nitroso compound.



11a

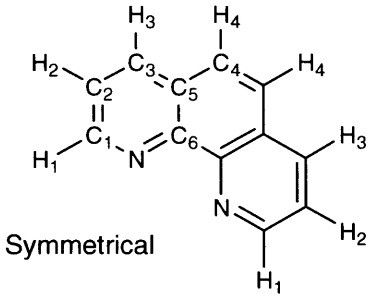
Figure 4.17 Nitroso compound

The filtrate was left overnight and an orange precipitate formed. The NMR spectrum showed co-crystal as well as the desired dimeric amine **11** in less than 5% yield. After recrystallising from petroleum ether large orange crystals of the co-crystals formed, which were more crystalline than the desired product.

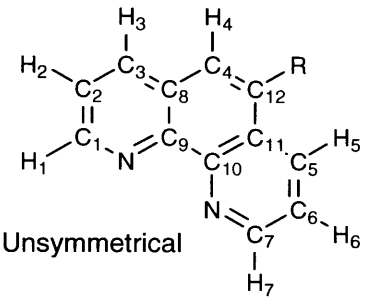
The reaction was repeated under the same conditions, but again the main product was the co-crystal. The acetic acid/sodium metabisulfite solution once filtered was left overnight, and precipitation produced a yellow solid which was the desired product **11**, but in a very small amount. On the third attempt the reaction was followed by TLC, as authentic product was available. On this occasion the zinc was activated by washing with 2M hydrochloric acid then washing with water, ethanol, and ether and dried. After two days the main product was still nitroso **11a**. The reaction was filtered hot as before but an aqueous work up was done after leaving the filtrate overnight in order to extract the amine from the nitro and nitroso compounds. 2M hydrochloric acid was added, it was washed with ethyl acetate to remove nitroso **11a**, then the solution was basified with 2M sodium hydroxide and left to precipitate. The precipitate was very insoluble, producing a poor NMR spectrum; it was not the desired product as the NMR was different to the literature and already obtained spectra. The basic solution was extracted into ethyl acetate, washed with brine and the resulting pale brown solid was not the desired dimeric amine **11** as the NMR spectrum was inconsistent with the literature and already obtained NMR spectra. Attempts to extract dimeric amine **11** from recrystallisation mother liquors and washings all resulted in an insoluble white solid, which seemed to be an inorganic salt as it was water soluble and did not show on the TLC plate or by NMR, it could have been sodium chloride

This reaction was then repeated in water, and then dilute hydrochloric acid, instead of sodium hydroxide. The water produced no reaction at all and the hydrochloric acid formed the fully reduced dimethylaniline which is commercially available.
Although several precursors, including some complexes, were successfully synthesised it was not possible to synthesise biphenanthroline via all routes attempted. The biaryl synthesis was also unsuccessful therefore studies moved on to the development of imine complex synthesis.

4.3 Experimental



Symmetrical



Unsymmetrical

Synthesis of 5,6-Epoxy-5,6-dihydro-[1,10]phenanthroline 1[10]

A stirred mixture of liquid bleach (200 ml) and water (120 ml) in a 1L round bottomed flask was adjusted to pH~8 with conc. hydrochloric acid. Phenanthroline monohydrate (1.20g, 6.05mmol) and tetrabutylammonium hydrogen sulphate (1.07g, 3.16mmol) were dissolved in chloroform (100 ml) and then added to the aqueous solution. The mixture was stirred with nitrogen bubbled through, was followed by NMR and was stopped after 1 hour, the reaction time varied due to varying concentration of commercial bleach. The layers were separated, the aqueous layer was extracted with chloroform, the organic layer was washed with water three times and brine once. This was dried over sodium sulphate, filtered and evaporated leaving a dark orange liquid. The liquid was crystallised from a small amount of chloroform with hexane, at 0 °C resulting in 5,6-Epoxy-5,6-dihydro-[1,10]phenanthroline **1** (0.9g, 69%) as a pale pink solid; δ_H (400 MHz, $CDCl_3$): 8.9 (2H, m, H_1), 8.0 (2H, m, H_3), 7.3 (2H, m, H_2), 4.5 (2H, s, H_4). [10]

Acid catalysed preparation of 5-hydroxy-1,10-phenanthroline 2[11]

Epoxy-phenanthroline **1** (0.35 g, 1.62 mmol) was slowly added to stirring conc. H_2SO_4 (1 ml) in a 100 ml schlenk, turning the solution bright yellow. The yellow solution was heated to 100 °C under N_2 for 2 hours. The solution was cooled to room temperature, cold water (10 ml) was added and the solution was neutralised while at 0 °C with 50 % NaOH solution. This was filtered and washed with water and chloroform leaving 5-hydroxy-1,10-phenanthroline **2** (0.14g, 41%) as a light brown solid; δ_H (400 MHz, DMSO): 11.0 (1H, br s, OH), 9.1 (1H, m, H_1), 8.9 (1H, m, H_7), 8.65 (1H, m, H_3), 8.2 (1H, m, H_5), 7.8 (1H, m, H_2), 7.65 (1H, m, H_6), 7.1 (1H, s, H_4). [11]

Synthesis of 5-chloro-1,10-phenanthroline 3

5-hydroxyphenanthroline **2** (0.12g, 0.55 mmol) was added to a two-necked round bottomed flask. Under a nitrogen atmosphere, PCl_5 (0.25g, 1.20 mmol) and $POCl_3$ (1 ml) were added. A separate bubbler was attached at the top of the condenser. The mixture was refluxed for 1.5 hours; the solid had dissolved within 15 minutes. The reaction was stopped once there was no more HCl evolution. Water was added slowly to quench and the product was extracted into DCM and washed with water. The DCM was evaporated leaving a solid (0.09g, 69%); NMR spectrum not consistent with 5-chloro-1,10-phenanthroline **3.**

Attempted triflation of 5-hydroxy-1,10-phenanthroline 2

The sodium salt of 5-hydroxy-phen **2** (0.09 g, 0.40 mmol) was suspended in dichloromethane (20 ml), and trifluoromethane sulfonic anhydride (0.1 ml) was added under nitrogen. This was left stirring for 1.5 hours and then heated. The mixture was left to cool, evaporated and washed with base; leaving a brown solid. This was insoluble in chloroform and was found to be 5-hydroxy-phenanthroline **2** (0.08g, 91%); δ_H (400 MHz, DMSO): 11.0 (1H, br s, OH), 9.1 (1H, m, H_1), 8.9 (1H, m, H_7), 8.7 (1H, m, H_3), 8.2 (1H, m, H_5), 7.8 (1H, m, H_2), 7.7 (1H, m, H_6), 7.1 (1H, s, H_4).

Synthesis of nickel (II) chloride chloro-phen dihydrate 4

5-Chloro-Phenanthroline **3** (0.11g, 0.50 mmol) and $NiCl_2.6H_2O$ (0.11g, 0.41 mmol) were dissolved in ethanol (20 ml) in a 100 ml round-bottomed flask. The green solution was stirred at reflux for 4 hours, by which time the solution had become a lighter green. The solution was evaporated, washed with THF and filtered, resulting in $NiCl_2$(Cl-phen)$(H_2O)_2$ **4** (0.15g, 94%) as a green crystalline solid; mp dec. 194°C; (Found: C, 38.3; H, 3.1; N, 7.6 $NiC_{12}H_{11}N_2O_2Cl_3$ requires C, 37.9; H, 2.9; N, 7.4 %); λ_{max} (MeOH)/nm 204, 233 and 274 (ε/dm^3 mol^{-1} cm^{-1} 11777, 9472 and 20231); ν_{max}(KBr)/cm^{-1} 3340 (H_2O), 1637 (CN), 1610 and 1581 (CC); *m/z*(ES) 523 (100%, [M-Cl]$^+$), 307 ([M-(Cl+(Cl-phen))]$^+$), 244 ([M-2Cl]$^{2+}$), 214 ([Cl-phen]$^+$).

Synthesis of palladium (II) chloride chloro-phen 5[18]

5-Chloro-Phenanthroline **3** (0.06g, 0.27 mmol) and $Pd(MeCN)_2Cl_2$ (0.06g, 0.22 mmol) were dissolved in acetonitrile (20ml) to form a light brown solution. This was

heated to reflux for 4 hours. A yellow precipitate formed which was filtered off leaving a colourless filtrate and Pd(ClPhen)Cl_2 **5** (0.07g, 84%) as a yellow solid; mp >330°C (Found: C, 36.5; H, 1.5; N, 7.2 $PdC_{12}H_7N_2Cl_3$ requires C, 36.7; H, 1.8; N, 7.1 %); λ_{max} (MeOH)/nm 210 and 280 (ε/dm^3 mol^{-1} cm^{-1} 12545 and 7066); ν_{max}(KBr)/cm^{-1} 1621 (C≡N), 1600 and 1580 (C=C); δ_H (400 MHz, DMSO): 9.5 (1H, m, H_1), 9.4 (1H, m, H_7), 9.2 (1H, m, H_3), 9.0 (1H, m, H_5), 8.7 (1H, s, H_4), 8.3 (1H, m, H_2), 8.2 (1H, m, H_6); δ_C ($CDCl_3$): 192.2 (C-Cl), 190.1 (2C=N), 151.4, 150.6, 140.0, 137.5, 130.8, 129.7, 127.1, 127.0 (ArC); *m/z*(FAB): 357 (100%, $[M\text{-}Cl]^+$).[18]

Dimerisation of Nickel chloro-phen complex 4

$NiCl_2$(Cl-phen)$(H_2O)_2$ **4**(0.08g, 0.22 mmol) was dissolved in dry degassed DMF (5ml) in a sidearm 100ml round bottomed flask under nitrogen. Zinc (0.17g, 2.63 mmol), Ni$(PPh_3)_2Cl_2$ (0.02g, 0.03 mmol) and triphenyl phosphine (0.30g, 1.15 mmol) were added to another sidearm 100ml round bottomed flask and then dry degassed DMF (5ml) was added. The green (Cl-phen)$NiCl_2$ solution was added *via* canula into the zinc mixture and left to stir overnight under nitrogen. After 30 minutes the reaction mixture turned from bright green to mustard green. The reaction mixture became dark brown overnight. Water was added while still under nitrogen and then filtered to remove excess zinc. Then a white solid (0.24g) precipitated off which was triphenyl phosphine oxide. The filtrate was evaporated and triturated with water, producing a yellow solution and a brown solid. The yellow solution was evaporated and salt metathesis with NH_4PF_6 resulted in precipitation of the PF_6 salt (0.06g) as a brown solid; mp dec. 265°C; λ_{max} (MeOH)/nm 214, 225 and 271 (ε/dm^3 mol^{-1} cm^{-1} 92040, 103507 and 31758); ν_{max}(KBr)/cm^{-1} 3333 (H_2O), 1637 (CN), 1620 and 1587 (CC); *m/z*(ES) did not show the required ions.

Attempted dimerisation of palladium (II) chloride chloro-phen 5

(Cl-phen)$PdCl_2$ **5**(0.05g, 0.13 mmol) was dissolved in dry degassed DMF (5ml) in a sidearm 100ml round bottomed flask under nitrogen with heating. Zinc (0.24g, 0.367 mmol), Ni$(PPh_3)_2Cl_2$ (0.01g, 0.02 mmol) and triphenyl phosphine (0.03g, 0.10 mmol) were added to another sidearm 100ml round bottomed flask and then dry degassed DMF(5ml) was added. The orange (Cl-phen)$PdCl_2$ **5** solution was transferred by canula into the round bottom flask mixture and left to stir overnight at 70 °C under

nitrogen. The reaction mixture turned purple was left to cool and quenched with water. This was filtered; the filtrate was evaporated and redissolved in hot DMF. The black solid produced was filtered off leaving an orange solution. Ethyl acetate was added to precipitate water-soluble compounds, and then ethyl acetate was removed. The resultant orange brown was shown to be palladium (II) chloride chloro-phen **5** (0.04g, 84%) ν_{max}(KBr)/cm^{-1} 1621 (C≡N), 1601 and 1580 (C=C); δ_H (400 MHz, DMSO): 9.5 (1H, m, H_1), 9.4 (1H, m, H_7), 9.2 (1H, m, H_3), 9.0 (1H, m, H_5), 8.7 (1H, s, H_4), 8.3 (1H, m, H_2), 8.2 (1H, m, H_6).

Attempted synthesis of nitro-quinoline

4-Methyl-2 nitroaniline (0.503g, 3.340 mmol) and potassium iodide (0.10g, 0.60 mmol) were dissolved in 70 % H_2SO_4 (5ml). This was stirred and heated to 110°C. Cinamaldehyde (0.70 ml, 5.57 mmol) was added, the reaction mixture was dark brown. After 1.5 hours more water was added. The reaction was followed by TLC (ethyl acetate), after 3 hours the cinamaldehyde (RF 0.69 red sw UV) was no longer visible so more was added. After 5 hours there was quinoline present (RF 0.72 orange $KMnO_4$) but also the aniline (RF 0.64 yellow $KMnO_4$) and cinamaldehyde (RF 0.69 pale yellow $KMnO_4$). After aqueous work up only starting materials present.

Synthesis of 2-(4-methyl-2-nitrophenyl)isoindoline-1,3-dione 8[19]

4-methyl-2-nitroaniline (7.15g, 0.05 mol) was dissolved in acetic acid (250 ml) producing a bright yellow solution. Phthalic anhydride (5.74g, 0.04 mol) was added and this mixture was refluxed on a heating mantle overnight. The resulting solution was a paler yellow and the phthalic anhydride had dissolved. The solution was precipitated with 2M NaOH and the yellow precipitate was dissolved in ethyl acetate. This was washed with water and brine, dried over magnesium sulphate, evaporated resulting in 2-(4-methyl-2-nitrophenyl)isoindoline-1,3-dione **8** (10.48g, 96%) as a yellow solid; δ_H (400MHz, $CDCl_3$): 8.0 (1H, s, H_3), 7.9 (2H, m, H_4), 7.8 (2H, m, H_5), 7.5 (2H, m, H_2), 7.3 (1H, d *J=8 Hz* H_1), 2.5 (3H, s, CH_3) [19].

Synthesis of 3-methyl-6-phthalimide aniline 9 [20]

Acetone (50 ml) was heated to reflux, nitrobenzene **8** (0.39g, 1.38 mmol) and 50% glacial acetic acid (10 ml) were added, after which the solid dissolved. Iron (0.85g, 15 mmol) was slowly added over an hour and the reaction mixture went from yellow to dark brown. The reaction mixture was refluxed overnight. The reaction mixture was filtered, and the solid was washed with acetone. The filtrate was neutralised with saturated sodium bicarbonate, extracted into ethyl acetate, washed with brine, dried over magnesium sulphate and evaporated resulting in **3**-methyl-6-phthalimide aniline **9** (0.19g, 55%) as a yellow solid; ν_{max}(nujol)/cm^{-1} 3445, 3346 (NH_2), 1723(C=O)1633, 1586 (C=C); δ_H (400MHz, $CDCl_3$): 7.9 (2H, br s, H_4), 7.8 (2H, br s, H_5), 7.0 (1H, d *J=8 Hz*, H_1), 6.7 (2H, br s, H_3, H_2), 3.6 (2H, br s, NH_2), 2.3 (3H, br s, CH_3); *m/z*(ES) 252 (100%, M^+), 235 ($[M-NH_2]^+$).

Attempted dimerisation of 3-methyl-6-phthalimide aniline 9

$FeCl_3.H_2O$ (0.51g, 1.88mmol), the aniline **9** (0.17g, 0.76 mmol), water (20 ml) and conc. HCl (2ml) were added to a 100ml round bottomed flask and stirred at reflux for 2 hours. After 30 mins the reaction had become red brown. The aniline **9** only dissolved on heating. After 2 hours a sample was neutralised with NaOH and extracted into ethyl acetate. The aqueous layer turned green and organic was yellow. TLC showed only starting material. The reaction was left to reflux overnight, then an aqueous work up with NaOH then extracted into ethyl acetate and evaporated did not result in the required dimer.

Attempted complexation of epoxy-phen 1 with hexacarbonyl tungsten (0).

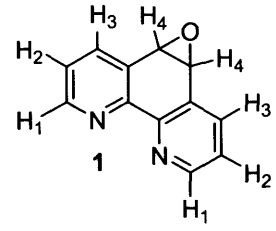
Epoxy-phen **1** (0.15g, 0.71 mmol) and $W(CO)_6$ (0.25g, 0.71 mmol) were added to degassed toluene (5ml). This light pink suspension was heated in a warm water bath until dissolved. Then TMNO (0.16g, 1.47 mmol) was added turning the pink solution instantly dark purple with evolution of carbon dioxide. The reaction was stirred until none of the $W(CO)_6$ (RF 0.70 pale yellow) was left. The reaction was followed by TLC (ethyl acetate) showing the product was a mixture of compounds yellow (RF 0.64), pink (RF 0.58), orange (RF 0.34), red (RF 0.26) and orange (base line). The product was columned with pet. ether with increasing amounts of ethyl acetate. Each fraction was evaporated resulting in a yellow, a pink, an orange and a red solid each in

only a very small quantity. The red solid was the only one to show protons in the NMR spectrum; $\nu_{max}(CDCl_3)/cm^{-1}$ 1899, 1830 (C≡O); δ_H (400 MHz, $CDCl_3$): 9.2 (2H, m, H_1), 8.1 (2H, m, H_3), 7.45 (2H, m, H_2), 4.7 (2H, s, H_4); the mass spectrum did not show required compound, nor did the mass spectra of the other compounds.

Attempted dimerisation of 5-nitro-m-xylene.

5-nitro-m-xylene (2.55g, 0.02 mol) and zinc dust (6.31g, 0.10 mol) were added to a 100ml 2-necked round-bottomed flask. Under a nitrogen atmosphere absolute ethanol (15ml) was added and the green/grey reaction mixture was heated to reflux. Once at reflux the heat was stopped and a sodium hydroxide solution (3.81g in 12.5 ml) was added drop-wise turning the reaction mixture orange. Halfway through addition the heat was turned back on and the mixture was heated at reflux for 4 hours. The reaction mixture was then filtered hot into a 0.5 M solution of sodium metabisulfite (37.5 ml) with 30% acetic acid. This was left overnight, cooled to 10°C and filtered giving an orange solid. The orange solid was recrystallised from pet. ether resulting in a 1:1 nitroso **11a**: nitro complex (1.00g, 42%) as orange crystals; ν_{max} $(CDCl_3)/cm^{-1}$ 3327 (weak NH), 2961 (C-H), 1604 (ar C=C), 1584 (ar C=C), 1493 (N=O) 1464(N=O); δ_H (400 MHz, $CDCl_3$): 7.8 (2H, s, H_x +H_y), 7.8 (2H, s, H_a, H_b), 7.1 (1H, s, H_c), 7.0 (1H, s, H_z), 6.4 (1H, s, H_1, H_2, H_3), 5.4 (1/6H, s, NH) 2.4- 2.3 (6H, 2s, $2CH_3$), 2.2 (2H, s, $4CH_3$).

4.4 Compound List



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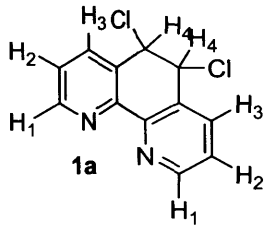

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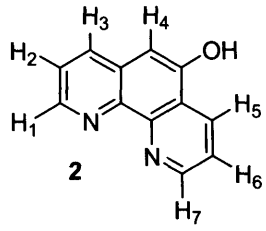

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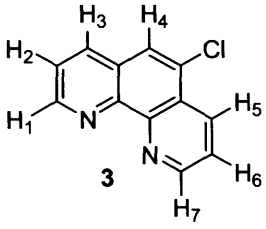

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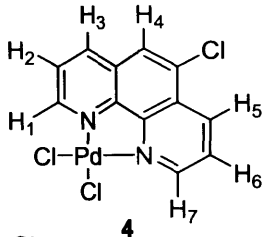

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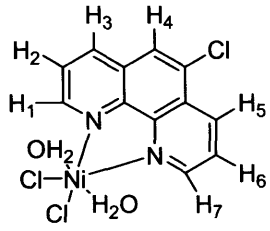

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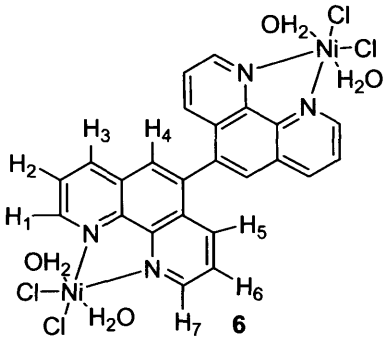

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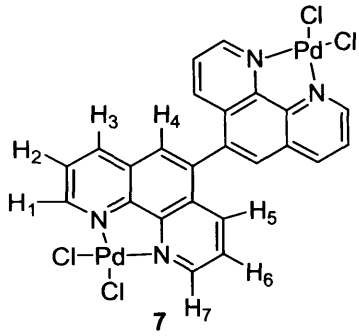

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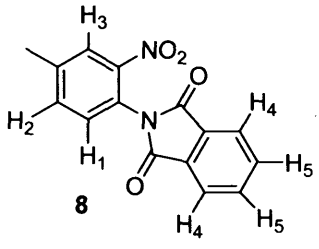

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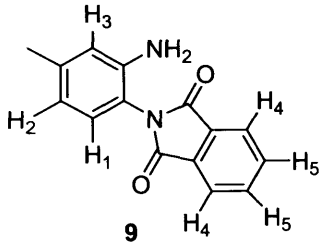

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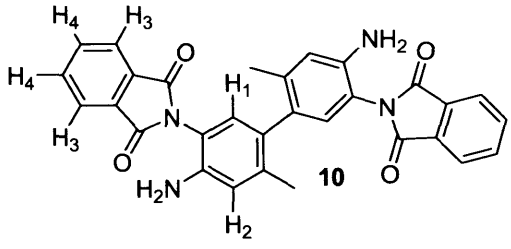

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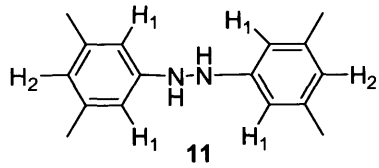

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Chapter 5- Binaphthyl-imines and their complexes

5.1 Introduction

Imines, or Schiff bases, were discovered in 1864 by Schiff[1] and since this time numerous studies have been performed. The work up to 1966 was reviewed by Holm *et al*[2] but of particular interest is the review of Hobday and Smith covering transition metal Salen complexes[3] of the kind shown in figure 5.1. Salen is a common abbreviation for N, N,-ethylenebissalicylideneimidate, a tetradentate di-anionic ligand with two nitrogen and two oxygen donors, which tends to form planar complexes with a wide range of transition metals. Many of these complexes bind small molecules such as CO, O_2 and NO making them possible models for biological systems. Dimers and bridged complexes are also formed to fill the vacant coordination sites of salen complexes of metals with a requirement for coordination number greater than four.

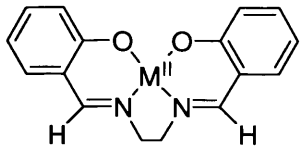

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Figure 5.1 Metal Salen complex.

Irie and co-workers used chiral [Ru(II)(salen)(NO)] to catalyze the oxidative coupling of 2-naphthols with moderate success, 33-71% e.e.[4] showing the use of chiral Schiff bases as asymmetric catalysts. Subsequently, Gong *et al* used a tetradentate ligand **2** with a biphenyl back-bone bound to vanadium, as a proficient catalyst for oxidative coupling of 2-naphthols with enantioselectivities of 90-97% and high yields.[5]

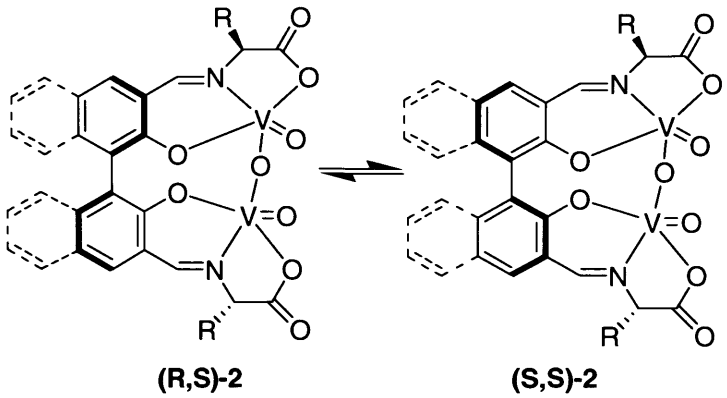

Figure 5.2 Oxovanadium biphenyl complex.

Binaphthyl schiff base complexes have been studied for their ability to catalyze asymmetric reactions. Somei *et al* extended the study of Gong's catalyst **2**, concentrating on binaphthyl based dual activation vanadium catalysts producing binaphthyl products of opposite absolute configurations.[6] Kozlowski and Dimauro used bimetallic Nickel(salen) complex **3** to perform the Michael addition of cyclohexenone to dibenzyl malonate resulting in dibenzyl-2-(3-oxocyclohexyl)malonate with a 90 % ee.[7]

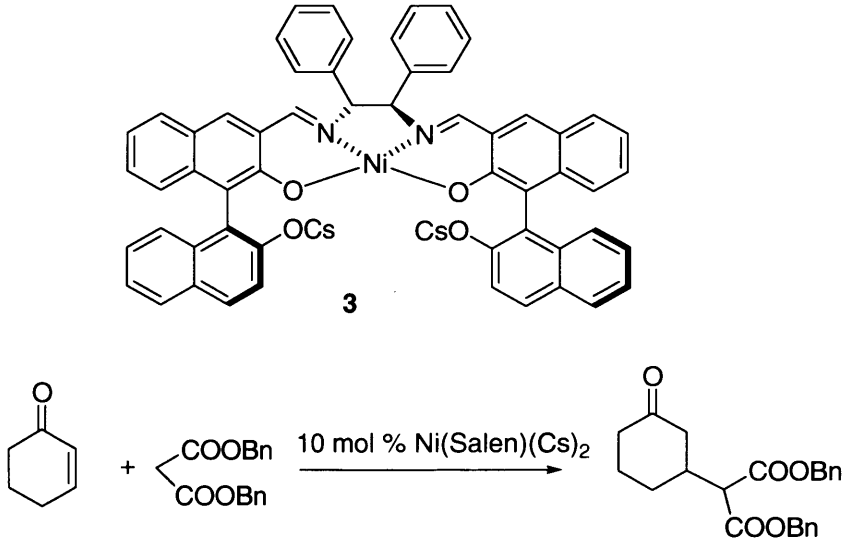

Figure 5.3 Michael catalysed addition with bimetallic nickel binapthyl derived imine complex.

Katsuki synthesised monometallic schiff base complexes similar to those produced by Kozlowski *et al* which also included two stereogenic centres. The aryl groups are brought in close to the binding site influencing the stereochemistry of the catalytic products.

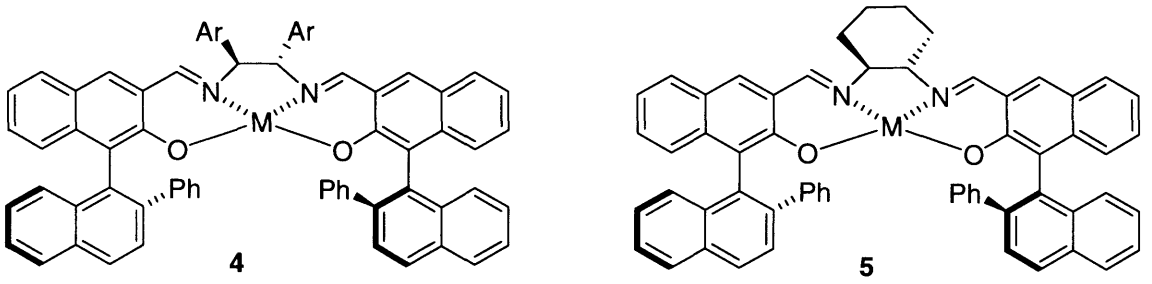

Figure 5.4 Monometallic binaphthyl-based imine complexes

Henri Brunner and Johann Goldbrunner synthesised a range of imines **6** and tested them as co-catalysts for the copper-catalyzed enantioselective cyclopropanation of styrene with ethyl diazoacetate. It is thought that the copper binds to the imino and hydroxy groups, in analogy to salen, but the exact binding site is not specified in this paper.[8]

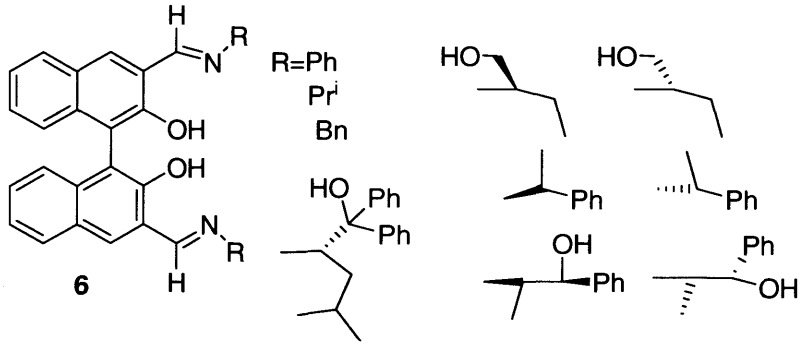

Figure 5.5 Binaphthyl derived imines

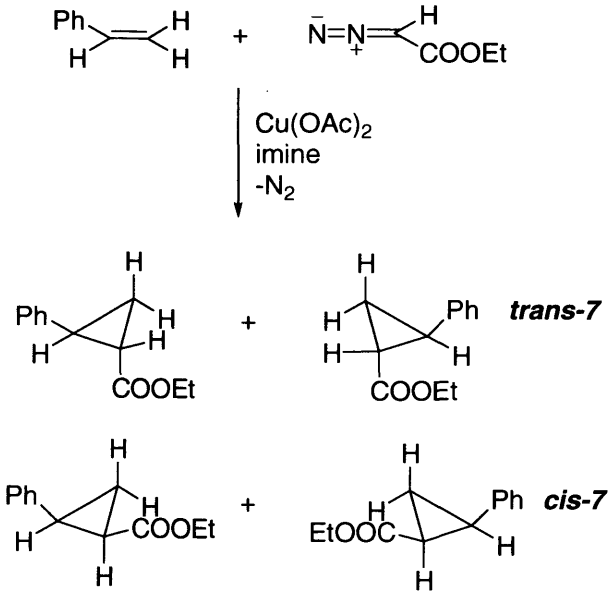

Figure 5.6 Copper-catalyzed enantioselective cyclopropanation of styrene with ethyl diazoacetate

A variation of the theme is to use a chiral bis-oxazoline as the binding site, instead of an imine, producing a rigid chiral environment around the metal; scandium in this case. Ohta and co-workers used this approach to catalyze the asymmetric 1,3-dipolar cycloaddition of N-benzylidenebenzylamine N-oxide to 3-((E)-2-butenoyl)-1,3-oxazolidin-2-one with their BINOL-Box-scandium complex.[9]

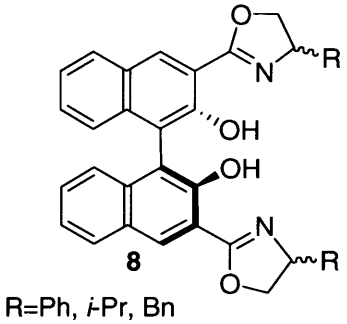

Figure 5.7 BINOL-Box ligand

This gave a yield of 94%, *endo:exo* ratio of 97:3 and 87% e.e. showing that this approach is highly effective.

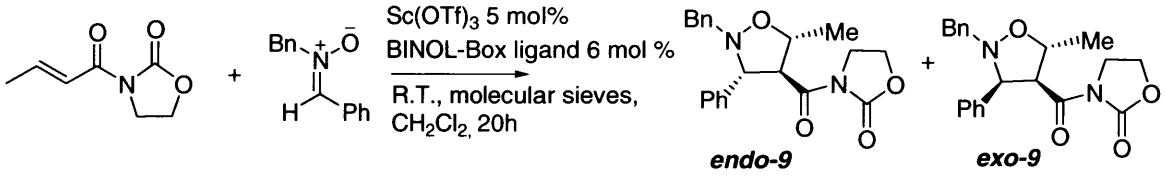

Figure 5.8 Asymmetric 1,3-dipolar cycloaddition of N-benzylidenebenzylamine N-oxide to 3-((E)-2-butenoyl)-1,3-oxazolidin-2-one.

There are other potential uses for chiral Schiff bases. Cram *et al* and Moneta *et al* incorporated binaphthyls functionalised with imines with crown ethers or imines in their macrocyclic structures used for chiral recognition.[10, 11] The chiral binaphthyl unit makes it possible to distinguish between enantiomers of guest molecule. Condensation of a simple diamine with a binaphthaldehyde was a facile route to macrocyclic host **10** which incorporates imine binding sites.

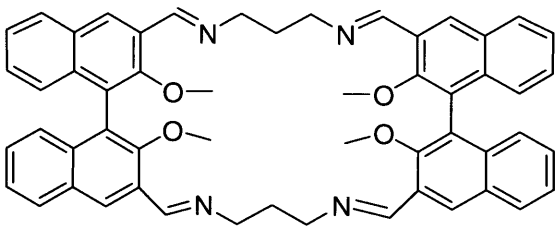

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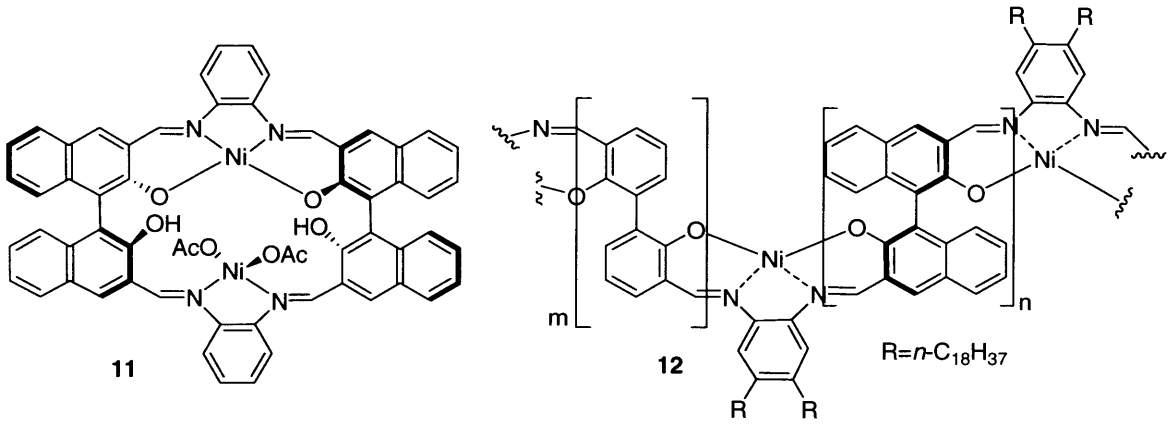
Figure 5.9 Macrocyclic host 10, synthesised by Moneta et al.

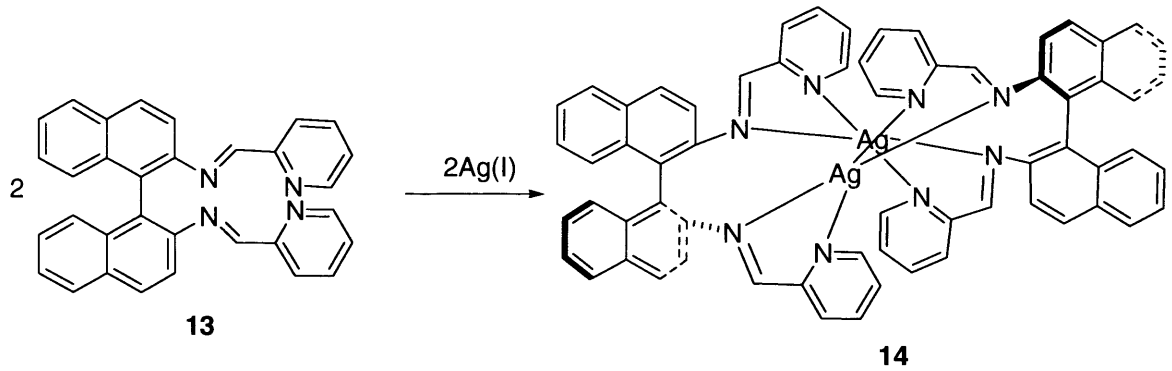
Lin Pu *et al* have also synthesised binaphthyl-based macrocyclic and polymeric complexes using the condensation of the 2,2'-binol-3,3'-carboxaldehyde with aryl diamines to form supramolecular structures **11** and **12**.[12]



11 **12** R=*n*-$C_{18}H_{37}$

Figure 5.10 Nickel supramolecular complexes

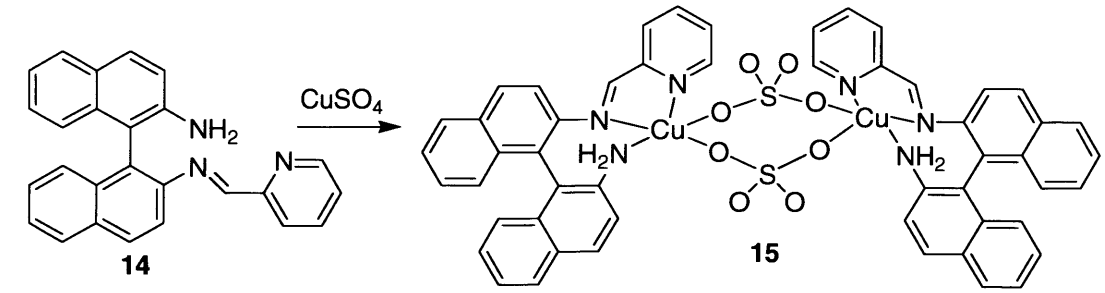
Salvadori *et al* characterised manganese and copper 2,2'-binol-3,3'-carboxaldehyde based imine complexes with ion-spray spectrometry.[13] Hannon and co-workers took a slightly different approach by condensing axially chiral amine BINAM with pyridine-2-carboxaldehyde to form ligand **13** and combined this with silver (I) or copper (I) in a one pot synthesis producing di-nuclear double stranded helicates.[14] It was found that the chirality of the binaphthyl spacer, and therefore the ligand, influenced the chirality of the helicates; the R ligand forming a P (right-handed) helix and the S ligand forming an M (left-handed) helix.



13 14

Figure 5.11 BINAM-based imine silver (I) complex 14

Telfer *et al* later tried to synthesise imino ligand **13** as a component in nickel, cobalt and copper complexes but discovered it was prone to hydrolysis and that there was a tendency to isolate complexes with asymmetric imino ligand **14.**[15] Complex **15** is an example of one of the complexes isolated by Telfer and co-workers.



14 15

Figure 5.12 [Cu((R)-10)(μ-SO4)]2

Thus, binaphthyl-based imines have interesting coordination chemistry and have a range of properties and there is proof of the possibility of helicate formation. There is also evidence that the chirality of the ligand can influence the chirality of the subsequent helicate. Formation could occur as shown in figure 5.13.

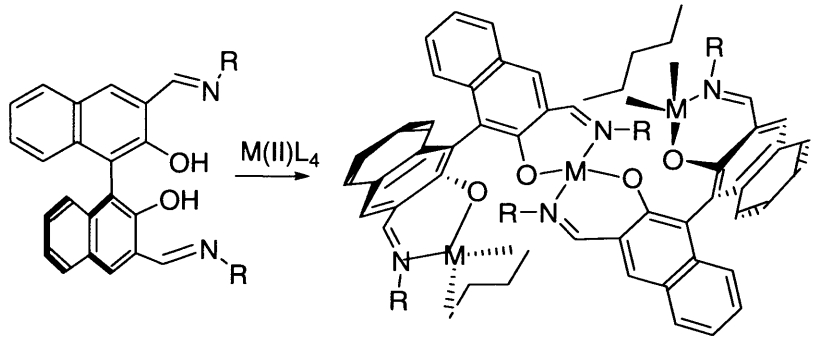


Figure 5.13 Imine helix formation

5.2 Results and Discussion

5.21 Ligand Synthesis

It has been shown that binapthyl-based imines can be synthesised from the corresponding binaphthaldehydes with a range of amines[8] and that these imines can form interesting complexes, including helicates. Therefore a route to imine formation was developed as shown in figure 5,14. To eliminate resolution problems commercial (*R*)-2,2'-dimethoxy-1,1'-binaphthylene was used as the starting material. A literature procedure was followed for the first step and (R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-dicarbaldhyde **16** was produced with a reasonable yield of 68% and with spectra and colour changes agreeing with the literature.[16] By TLC, all of the spots ran at the same place but dimeric aldehyde **16** showed as yellow under long wave light and the starting material was blue under short wave light. Imine formation followed as shown in figure 5.15, producing three different imines using three primary amines.

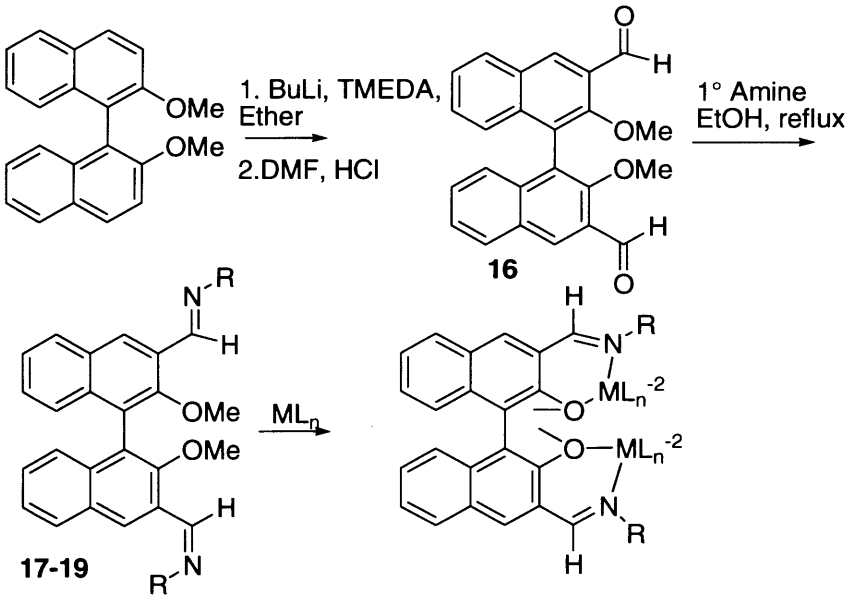


Figure 5.14 Route to synthesise metal complexes with imine ligands.

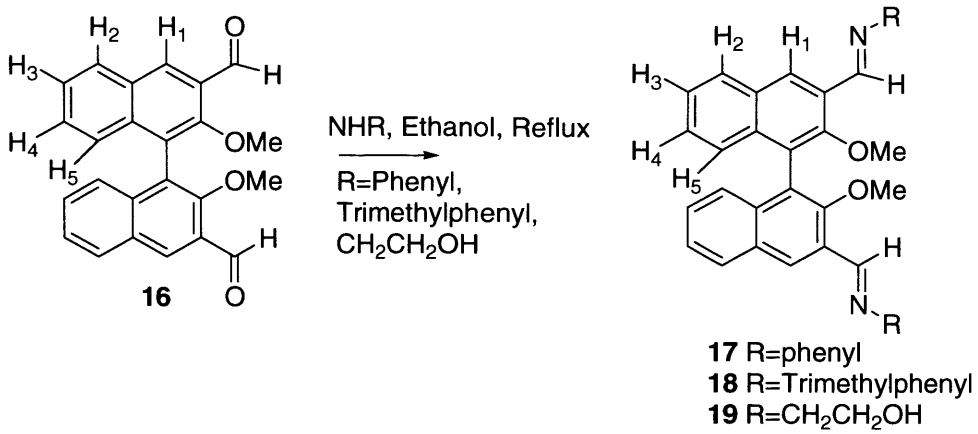


Figure 5.15 Dimeric Imine Syntheses

Imine **17** was synthesised by condensing aldehyde **16** with aniline, resulting in a yellow crystalline solid, with very few impurities. Recrystallisation was achieved by condensing the ethanol solution to ~10 ml and leaving it to cool. Once filtered, more solid was recovered from precipitation of the mother liquor with water. A high yield of 84% was obtained. Imine **18,** the product of aldehyde **16** condensed with trimethylaniline, was left to crystallise over the weekend, sufficient solvent had evaporated to form a good amount of yellow solid. This precipitate was filtered off and the mother liquor was precipitated with water. In general precipitation with water gave a slightly less pure product. Again a good yield of 89 % was obtained. Imine **19,** with its ethanol side chain, was slightly harder to purify. The reaction mixture did not crystallise so was evaporated to dryness, resulting in a yellow gum. This gum was dissolved in dichloromethane, dried over magnesium sulphate, filtered and evaporated; resulting in a yellow foamy solid. After scraping with a spatula, it was evident that the yellow solid was crystalline and shiny; the reaction yielded 71%.

All three of these reactions were difficult to follow by TLC as the spots ran at the same place. The main indicator that the reaction had worked was the shifting of the aldehyde peak in the NMR spectrum, from 10.4 to ~9 ppm for the imine. The carbonyl stretch absorption was no longer present in the infrared, the carbon nitrogen double bond stretch absorption came a lot lower, sometimes overlapping with carbon carbon double bond stretch.

The dimeric aldehyde **16** was deprotected with boron tribromide following a literature procedure with similar starting materials.[16] Once the boron tribromide was added the reaction mixture turned from yellow to purple, which was to be expected. Although

the product was virtually black, the NMR spectrum showed a peak for hydroxyl at 10.13 ppm, and there was no longer a methyl group peak at ~3.5 ppm. On closer inspection the black solid was shiny and crystalline and the yield was a high 93%. It is possible that the very dark colour is caused by a very small impurity which is very intensely coloured which occurs in similar compounds. When repeated the hydroxy aldehyde **20** was yellow/green but the NMR spectrum was identical to the previous reaction. Hydroxy aldehyde **20** was used to synthesise the analogues of imines **17, 18** and **19** using the same imine synthesis with similarly high yields. The hydroxy imines were more highly coloured than the methoxy imines, due to the added conjugation of the hydroxyl group. Imine **21** is a known compound and the characterisation matched with the literature.[8]

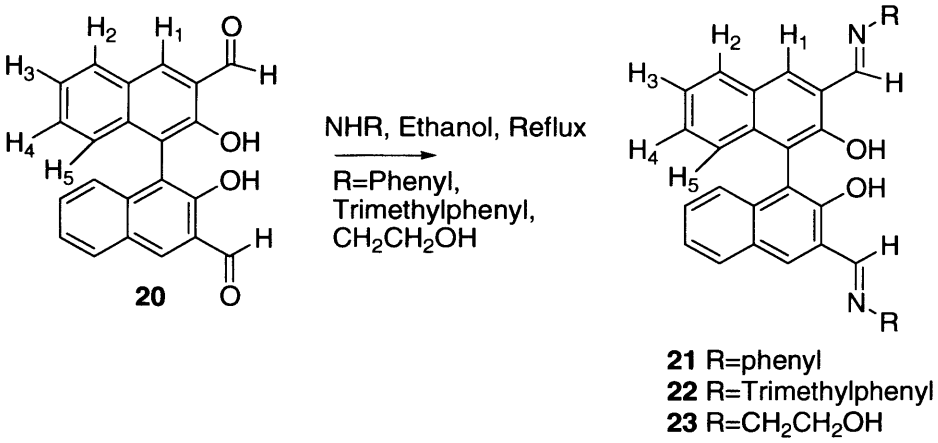


Figure 5.16 Dimeric hydroxyl imine syntheses

5.22 Complexes

Complexation with the imine ligands was initially attempted using palladium bis-acetonitrile dichloride. All of the methoxy-imines were complexed to palladium in a two palladiums to one ligand ratio resulting in yellow /orange precipitates of each complex.

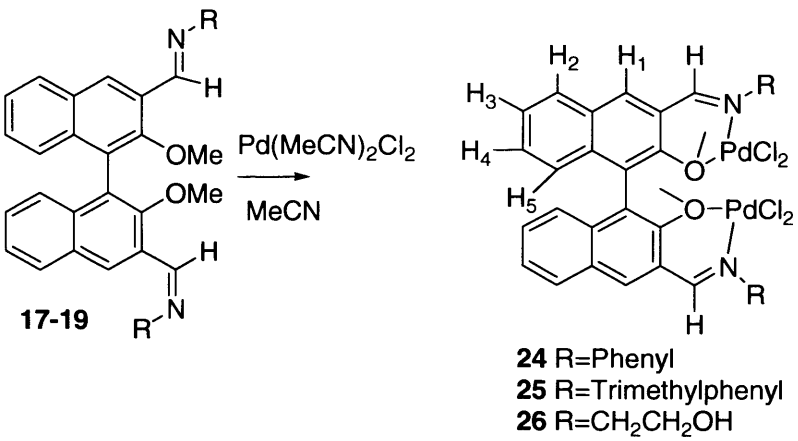


Figure 5.17 Palladium Complexation

It appears that palladium complex **24** formed from looking at the NMR spectra; H_1, H_2 and H_5 have shifted up field. This phenomenon was to be expected as H_1, H_2 are the closest to the binding site and H_5 can be affected depending on the orientation of the ligand. This result was confirmed through observation of the correct isotope pattern for Pd_2Cl_4(Imine **17**) in the mass spectrum. There was some starting imine **17** left, shown in the NMR spectrum. Palladium complex **25** also showed a Pd_2Cl_4(Imine **18**) isotope pattern but the NMR spectrum had a lot of broad peaks that are difficult to distinguish between, probably due to the tautomerism of the imine ligands. Another potential reason for the broad peaks which are observed in all of the methoxy complexes formed could be isomerism due to positioning of the methyl group up or down. Palladium complex **26** showed an isotope pattern of $PdCl_2$(Imine **18**) which can also be seen by the unsymmetrical nature of the NMR spectrum. H_3, H_4 and H_5 had the same environment on either side of the ligand but the protons nearer the binding site, H_2, H_1 and the imine proton showed two distinct peaks resulting from their significantly different environments.

The complexation reaction was repeated with the hydroxy imine analogues **22** and **23.**

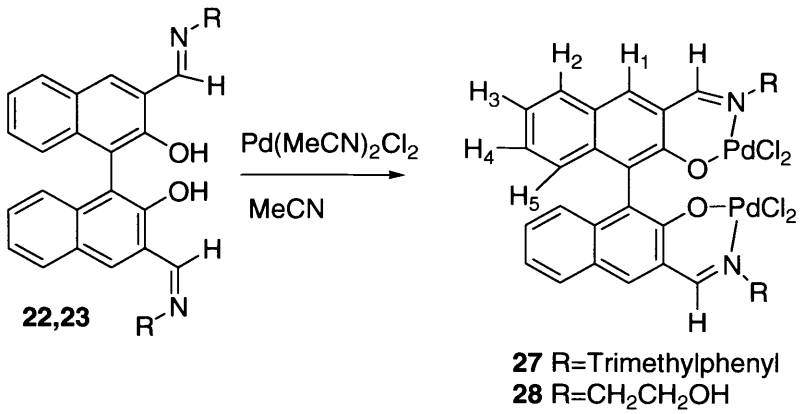


Figure 5.18 Hydroxy imine palladium complexes 27-28

These complexes **27-28** had very complicated NMR spectra and showed no palladium isotope patterns in the mass spectra so it is possible that the complexes did not form. Other two metals to one ligand complexes attempted were the reaction between imine ligand **17** with ruthenium (II) bisbipyridine chloride and rhenium (I) pentacarbonyl chloride. In the case of ruthenium (II) bisbipyridine chloride, silver tetrafluoroborate was added to remove the chlorides. The NMR spectrum was in-conclusive; the reaction seemed to work as there was a colour change from purple to red, producing an orange solid. The reaction with rhenium (I) pentacarbonyl chloride showed a colour change from yellow to red which is a common colour for rhenium complexes. The required isotope pattern for the complex minus methyl chloride was observed in the mass spectrum as well as the correct pattern for methyl and two chlorides or three carbonyls were observed.

One metal to two ligand complexes were synthesised using imine ligands **17** and **18** with palladium bisacetonitrile chloride as the metal reagent. Silver tetrafluoroborate was used to remove the chlorides from the complex before being added to the ligand

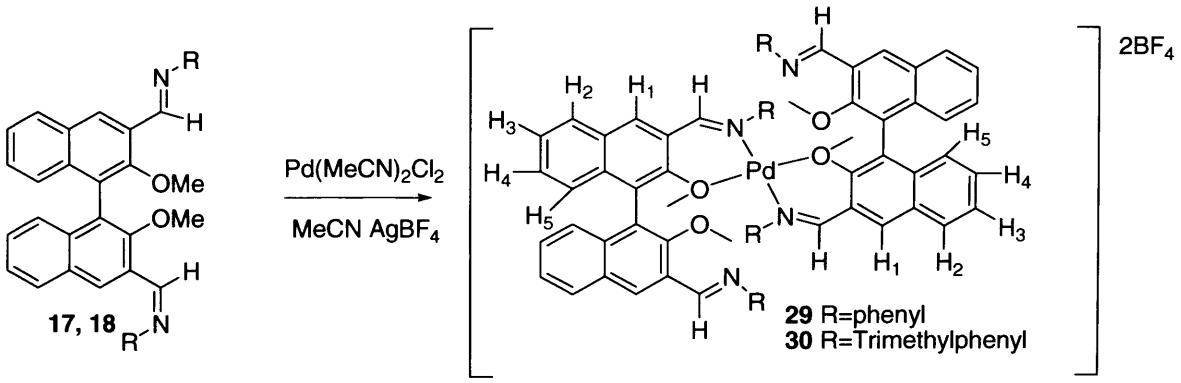


Figure 5.19 Two ligands to one palladium complexes.

solution. When a solution of the palladium complex was added, the reaction mixture turned from pale yellow to bright yellow. The NMR spectrum of both complexes showed two sets of binaphthyl peaks, those on the complexed half of the molecule and those on the free half, in a one to one ratio, after recrystallisation the ratio stayed the same so it could not be just starting material and complex. Unfortunately the mass spectra showed only ligand so it could be that the complexes are not stable under mass spectrometric conditions.

The palladium complexation with the hydroxyl analogue of imine **17** was first attempted with potassium t-butoxide to deprotonate the ligand but no reaction occurred so the reaction was repeated with no base.

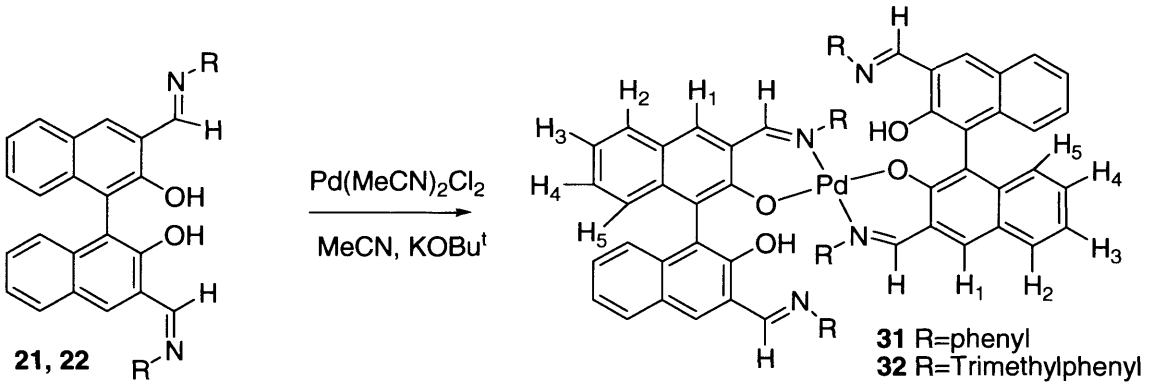


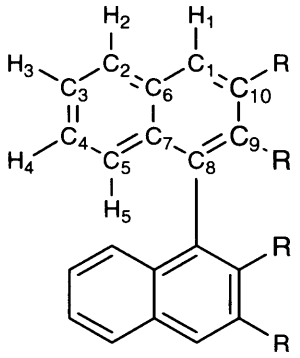
Figure 5.20 Two ligands to one palladium complexes.

After two hours the reaction mixture was pH 1 which is concurrent with hydrochloric acid formation. The NMR spectrum again showed two sets of peaks so the complex was a one to two ratio but also had lots of impurities which could be seen by TLC as different coloured spots. The complex would not recrystallise so was purified by column chromatography. The compound separated into several different coloured layers, each one only a few milligrams so the yield was very low. The mass spectrum was weak due to the very small amount of compound left to analyse but the required isotope pattern was observed. The reaction was repeated with ligand **21** but only starting material was seen in the NMR and mass spectra.

As imine ligand **22** had three binding sites on each end of the ligand it was thought that a metal which preferred octahedral geometry would be interesting to look at. Zirconium tetrachloride was reacted with ligand **22** in a two to one ratio, but no complex was formed according to NMR and mass spectrometry. Nickel chloride was also tried but again no reaction occurred.

A set of binaphthyl based imines have been successfully synthesised and complexed to palladium, ruthenium and rhenium to form 2:1 and 1:2 metal complexes which are precursors to helical structures. However the structure of the complexes was not wholly predictable and although the ligands were easily recrystallised the complexes were not and were often rather insoluble. Therefore structure elucidation via x-ray crystallography was not possible leaving the supermolecular structure of these complexes unknown. In order to find complexes suitable for x-ray crystal structure determination, the research moved on to synthesis of biquinazolinone ligands and complexes which would hopefully be more easily recrystallised.

5.3 Experimental



Synthesis of (R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-dicarbaldehyde 16.[16]

A solution of (R)-(-)-2,2'-dimethoxy-1,1'-binaphthylene (4.96g, 0.02 mol) and TMEDA (12.4 ml, 0.01 mol) in diethyl ether (240 ml) was cooled to 0°C under a nitrogen atmosphere. A 2.5M solution of n-BuLi in hexanes (28 ml, 0.07 mol) was added drop wise over a 10 minute period. The yellow mixture was stirred at 0°C for 1hr and was then slowly warmed to reflux. After being refluxed for 16hr the resulting pale brown suspension was cooled to 0°C and DMF (10 ml, 0.13 mol) was added. The mixture was stirred at 0°C for 90 min, and then 4 M HCl (48 ml, 0.19 mol) was added slowly under vigorous stirring. The resulting two-phase system was stirred for 30 min. The organic layer was separated, washed with 0.5 M HCl (80 ml), a saturated $NaHCO_3$ solution (80 ml) and brine (80 ml), dried ($MgSO_4$), and evaporated to give (R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-dicarbaldehyde **16** (3.95g, 68%) as a yellow solid; ν_{max} (nujol)/cm^{-1}: No OH, 2920 (C-H st), 1681 (C=O st), 1619 (C=C ar), 1587 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.4 (2H,s, O=CH), 8.5 (2H, s, H_1), 8.0 (2H,d *J=8 Hz*, H_2), 7.4 (2H, m, H_4), 7.3 (2H, m, H_3), 7.1 (2H, d *J=8 Hz*, H_5), 3.4 (6H, s, OMe).[16]

Synthesis of (R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-diimine 17,18,19.

Typical procedure:

(R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-dicarbaldehyde **16** (1g, 2.70 mmol) was added to a 100ml round-bottomed flask and partially dissolved in ethanol (50 ml). A primary amine (6 mmol) was added and the mixture was stirred at reflux for 2-3 hours. The yellow solution was left to cool overnight, crystallising or precipitating, filtered or condensed to <10ml and precipitated with H_2O or evaporated to dryness depending on the amount of solid produced.

N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17**, yellow needles (1.18g, 84%); mp 171-172 °C; (Found: C, 82.3; H, 5.42; N, 5.31 $C_{36}H_{28}N_2O_2.0.25CH_3CH_2OH$ requires C, 82.4; H, 5.59; N, 5.26 %); ν_{max} (nujol)/cm^{-1}: No OH, 2922 (C-H st), 1614 (C=N/C=C st), 1587 (C=C ar). Aromatic overtones present; δ_H (400 MHz, $CDCl_3$): 9.0 (2H,s, N=CH), 8.8 (2H, s, H_1), 8.0 (2H,d *J=8 Hz*, H_2), 7.4 (6H, m, H_3, H_m), 7.3 (6H, m, H_4, H_o), 7.2 (2H, t *J=7.2 Hz*, H_p), 7.2 (2H, d *J=8 Hz*, H_5), 3.4 (6H, s, OMe); δ_c (400 MHz, $CDCl_3$): 157.4 (N=*C*H), 156.3 (C_9), 152.7 (C=N-*C*), 136.0 (C_7), 131.0 (C_6) 130.1 (C_1), 129.7 (C_m) 129.5 (C_2), 129.3 (C_p), 128.5 (C_5), 126.7 (C_4), 126.0 (C_{10}, C_3), 125.2 (C_8), 121.6 (C_o), 63.0 (OMe); *m/z*(ES) 493 (100%, $[M+H]^+$).

N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18,** yellow powder (1.49g, 89%); mp 134-135 °C; (Found: C, 82.84; H, 6.76; N, 4.83 $C_{42}H_{40}N_2O_2.0.25CH_3CH_2OH$ requires C, 82.8; H, 6.79; N, 4.54 %); ν_{max} (nujol)/cm^{-1}: No OH, 2918 (C-H st), 1629 (C=N st), 1614 (C=C ar), 1590 (C=C ar) aromatic overtones present; δ_H (400 MHz, $CDCl_3$): 8.8 (2H,s, H_1), 8.6 (2H, s, N=CH), 8.0 (2H,d *J=8 Hz*, H_2), 7.4 (2H, t *J=8 Hz*, H_3), 7.3 (2H, t *J=8 Hz*, H_4), 7.1 (2H , d *J=8 Hz*, H_5) 6.8 (4H, s, H_6), 3.4 (6H, s, OMe) 2.2 (6H, s, Me), 2.1 (12H, s, 4Me); δ_c (400 MHz, $CDCl_3$): 159.7 (N=*C*H), 155.8 (C_9), 149.1 (C=N-*C*), 135.7(C_7), 133.2 (C_6) 130.6 (C_2) 130.0 (C_1), 129.7 (C_{10}) 128.9 (C_8), 128.8 (C_m), 128.7 (C_4), 128.0 (C_o), 127.1 (C_5), 125.7 (C_3), 125.0(C_p) 63.7 (OMe), 21.2 (Me), 18.9 (2Me); *m/z*(ES) 605.3 (100%, $[M+H]^+$), 488.0 ($[(M+O)-NPh(Me)_3]^+$).

2,2'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene)diethanol **19** yellow crystals (0.91g, 71%); mp 105 °C; (Found: C, 71.4; H, 6.38; N, 5.45 $C_{28}H_{28}N_2O_4.CH_3CH_2OH$ requires C, 71.7; H, 6.81; N, 5.57 %); ν_{max} (nujol)/cm^{-1}: 3354 (OH, st), 2922(C-H st), 1639 (C=N st), 1618 (C=C ar), 1591 (C=C ar); δ_H (400 MHz, $CDCl_3$): 8.8 (2H,s, N=CH), 8.6 (2H, s, H_1), 7.9 (2H, d *J=8 Hz*, H_2), 7.4 (2H, m, H_4), 7.2 (2H, m, H_3), 7.1 (2H, d *J=8 Hz*, H_5), 4.0 (4H, t *J=5 Hz*, C=NCH_2) 3.8 (4H, t *J=5 Hz* CH_2OH) 3.4 (6H, s, OMe) 1.7 (2H, s, OH); δ_c (400 MHz, $CDCl_3$): 160.2 (N=*C*H), 155.6 (C_9), 135.7 (C_7), 130.9 (C_6) 129.8 (C_1) 128.9 (C_{10}, C_2), 128.1 (C_4), 125.9 (C_3, C_5, C_8), 63.2(OMe), 63.0 (*C*H_2N=), 62.6 (*C*H_2OH); *m/z*(ES) 457 (100%, $[M+H]^+$), 414 ($[(M+O)-NCH_2CH_2OH]^+$).

Deprotection of (R)-(-)-2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-dialdehyde 16[16]

To a cooled (0°C) solution of dimeric aldehyde **16** (0.81g, 2.20 mmol) in DCM (50 ml) BBr_3 (0.83ml, 8.78 mmol, in 8ml DCM) was added drop wise. After the purple mixture was stirred at room temp for 4h a saturated $NaHCO_3$ solution (10 ml) was added. The purple mixture was poured into water (100 ml), turned dark brown and was extracted with DCM (3 x 75 ml). The organic layer was washed with 2M HCl (100ml), dried and evaporated to leave (R)-(-)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde **20** (0.70g, 93%) as a black/dark green crystalline solid; ν_{max} ($CDCl_3$)/cm^{-1}: 3434 (OH, st), 2924(C-H st), 1661 (C=O st); δ_H (400 MHz, $CDCl_3$): 10.5 (2H, s, O=CH), 10.1 (2H, s, OH), 8.3 (2H, s, H_1), 7.9 (2H, m, H_2), 7.4 (4H, m, H_3 and H_4), 7.3 (2H, m, H_3), 7.1 (2H, m, H_5).[8]

Synthesis of (R)-(-)-3,3'-bis((phenylimino)methyl)-1,1'-binaphthyl-2,2'-diol 21

(R)-(-)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde **20** (0.99g, 2.90 mmol) was added to a 100ml round bottomed flask and partially dissolved in chloroform and ethanol (50 ml). Aniline (1 ml) was added and the mixture was stirred at reflux for 3 hours. The orange solution was left to cool, filtered and dried leaving (R)-(-)-3,3'-bis((phenylimino)methyl)-1,1'-binaphthyl-2,2'-diol **21**(1.23 g, 86 %) as an orange solid; mp 214 °C; (Found: C, 79.8; H, 5.05; N, 5.38 $C_{34}H_{24}N_2O_2.1H_2O$ requires C, 80.0; H, 5.13; N, 5.49 %); ν_{max} ($CDCl_3$)/cm^{-1}: 3546.7 (OH), 1621 (C=O), 1590 (C=C), 1505 (C=C) aromatic overtones present; δ_H (400 MHz, $CDCl_3$): 13.2 (2H, s, NH), 8.9 (2H, s, N=CH), 8.1 (2H, s, H_1), 7.9 (2H, m, H_2), 7.3 (4H, m, H_3, H_4), 7.2 (12H, m, H_o, H_m, H_p, H_5); δ_c (400 MHz, $CDCl_3$): 162.6 (N=*C*H), 154.6 (C_9), 148.2 (C=N-*C*), 135.8 (C_7), 134.9 (C_1), 129.5 (C_m) 129.2 (C_2) 128.9 (C_p), 127.9 (C_6), 127.2 (C_4), 124.9 (C_5), 123.7 (C_3), 121.4 (C_8), 121.3 (C_o), 116.9 (C_{10}); *m/z*(ES) 493 (100%, $[M+H]^+$).

Synthesis of (R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol 22.

(R)-(-)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde **20** (1.07g, 3.12 mmol) was added to a 100ml round bottomed flask and partially dissolved in chloroform (50 ml). Trimethylaniline (1 ml) was added and the mixture was stirred at reflux overnight. The dark green solution was left to cool, evaporated and recrystallised from DCM and hexane resulting in (R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol **22** (1.67g, 92%) as a light green solid; mp 160 °C; ν_{max} ($CDCl_3$)/cm^{-1}: 3547 (OH), 1621

(C=O), 1590 (C=C), 1505 (C=C) aromatic overtones present; (Found: C, 78.4; H, 6.36; N, 4.38 $C_{40}H_{36}N_2O_2.2H_2O$ requires C, 78.4; H, 6.58; N, 4.57 %); δ_H (400 MHz, $CDCl_3$): 12.9 (2H, s, NH), 8.5 (2H, s, N=CH), 8.0 (2H, s, H_1), 7.9 (2H, m, H_2), 7.4 (6H, m, H_3, H_5 and H_4), 6.9 (4H, s, H_6), 2.1 (12H, s, CH_3) 2.1 (6H, s, CH_3); δ_c (400 MHz, $CDCl_3$): 166.9 (N=*C*H), 154.8 (C_9), 145.7 (C=N-*C*), 135.7 (C_p), 134.7 (C_7), 134.6 (C_1) 129.2 (C_m) 129.1 (C_2), 128.8 (C_4), 128.5 (C_o), 127.7 (C_8), 125.0 (C_5), 123.7 (C_3), 121.0 (C_{10}), 116.8 (*C*-C=N), 20.9 (Me), 18.7 (2Me); *m/z*(ES) 578 (100%, $[M+H]^+$), 577 (M^+), 460 ($[(M+O)-NPh(Me)_3]^+$).

Synthesis of 3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol 23

(R)-(-)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dialdehyde **20** (0.24g, 0.70 mmol) was added to a 100ml round bottomed flask and partially dissolved in chloroform (50 ml). Ethanolamine (84 µl) was added and the mixture was stirred at reflux for 5 hours. The dark orange solution was left to cool overnight and evaporated leaving 3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol **23** (0.30 g, 99%) as a red shiny solid; mp 89 °C; (Found: C, 67.3; H, 6.03; N, 5.98 $C_{26}H_{24}N_2O_4.2H_2O$ requires C, 67.2; H, 6.07; N, 6.03 %); ν_{max} ($CDCl_3$)/cm^{-1}: 3611 (OH), 1637 (C=O), 1576 (C=C), 1508 (C=C) aromatic overtones present; δ_H (400 MHz, $CDCl_3$): 13.2 (2H, s, OH), 8.55 (2H, s, N=CH), 7.9 (2H, s, H_1), 7.8 (2H, m, H_2), 7.3 (4H, m, H_3+H_4), 7.1 (2H, m, H_5), 3.7 (8H, m, $4CH_2$), 2.0 (2H, s, OH); δ_c (400 MHz, $CDCl_3$): 167.0 (N=*C*H), 154.5 (C_9), 135.2 (C_7), 133.5 (C_1) 129.0 (C_2) 128.5 (C_4) 127.6 (C_6), 124.7 (C_3), 123.5 (C_5), 120.8 (C_{10}), 116.6 (C_8), 61.9 (*C*H_2N=), 61.7 (*C*H_2OH); *m/z*(ES) 429 (100%, $[M+H]^+$), 386 ($[M+OH-(NHCH_2CH_2OH)]^+$).

Synthesis of Pd_2Cl_4(Imine17, 18 or 19)

Typical procedure:

The imine (0.125g, 0.240 mmol) and $PdCl_2(MeCN)_2$ (0.12 mg, 0.48 mmol) were partially dissolved in MeCN (10 ml) and heated at reflux for 2 hours. The orange solution was left to cool slowly overnight to precipitate. A precipitate formed and filtered off and washed with acetonitrile.

Pd_2Cl_4(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine) **24**: Recrystallised from dichloromethane and ethyl acetate, orange solid (0.13g, 78%); mp dec. 160 °C; ν_{max} (nujol)/cm^{-1}: No OH, 2924 (C-H st),

1690 (C=N), 1614, 1585 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.7 (2H,s, N=CH), 8.4 (2H, s, H_1), 7.7 (6H, m, H_2, H_o), 7.4 (6H, m, H_3, H_m), 7.3 (4H, m, H_4, H_p), 7.2 (2H, m, H_5), 3.4 (6H, m, OMe); *m/z*(ES) 841 ($[M-Cl]^+$), 823 ($[M-Cl-CH_3]^+$), 802 ($[M-2Cl]^+$), 698 ($M-2CH_3-2PhNH_2+2H_2O$), 521 (N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17**), 446 (N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17**- $PhNH_2$ +H_2O) 370 (N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17**- $2PhNH_2$ + $2H_2O$).

Pd_2Cl_4(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine)) **25:** Recrystallised from chloroform diffused with hexane, orange needles (0.21g, 89%); mp dec. 149 °C; ν_{max} ($CDCl_3$)/cm^{-1}: No OH, 2927 (C-H st), 1718 (C=N), 1613, 1591 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.5 (2H, s, N=CH), 8.5 (2H, s, H_1), 8.0 (2H, m, H_2), 7.4 (4H, m, H_3, H_4), 7.2 (6H, m, H_5, H_m), 3.4 (6H, m, OMe); *m/z*(FAB) 960 (M^+ correct isotope pattern), 923 ($[M-Cl]^+$), 887 ($[M-2Cl-1H]^+$), 851 ($[M-3Cl-2H]^+$).

Pd_2Cl_4(2,2'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene)diethanol) **26**: Recrystallised from chloroform diffused with hexane, orange needles (0.040g, 52%); mp dec. 116 °C; ν_{max} ($CDCl_3$)/cm^{-1}: 3155 (OH), 1644 (C=N), 1603, 1557 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.4 (1H, s, N=CH), 8.2 (3H, s, H_1), 7.9 (2H, m, H_2), 7.5 (2H, m, H_3), 7.35 (2H, m, H_4), 7.3 (2H, m, H_5) 4.8, 4.5, 3.9 (8H, m $4CH_2$) 3.3 (6H, m, OMe); *m/z*(ES) 674 ($[M-Pd-2CH_3]^+$).

Attempted synthesis of 2(Ru(bipy)$_2$)(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine)

Under a nitrogen atmosphere, N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17** (0.03g, 0.05 mmol) and $RuCl_2(bipy)_2$ (0.05g, 0.10 mmol) were dissolved in dry MeCN. This purple solution was surrounded in foil, $AgBF_4$ (0.07g, 0.03 mmol) was added and the solution was heated to reflux. After 20 minutes the solution had turned red and a precipitate of silver chloride had formed. The reaction was stopped after 1 hour, left to cool, filtered through celite and evaporated. The resultant orange solid was dissolved in MeCN and

put in the freezer to recrystallise. The resulting solid was a mixture of starting materials according to the NMR spectrum.

Synthesis of 2(Re(CO)$_3$Cl)(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine)

$Re(CO)_5Cl$ (0.15 g, 0.43 mmol) was added to a 10 ml round bottomed flask and under nitrogen dry toluene (2 ml) and N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17** (0.11 g, 0.21 mmol) were added. The yellow mixture was heated to reflux for 2.5 hours. After this time the reaction mixture had become dark red and was left to cool. The reaction mixture was precipitated with with pet. ether to produce $Re(CO)_3Cl$(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine) (0.13g, 55%) as an orange solid; mp dec. 149 °C; ν_{max} ($CDCl_3$)/cm^{-1}: No OH, 2984 (C-H st), 2026, 1922 (C≡O) 1642 (C=N), 1602, 1561 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.5 (2H,s, N=CH), 8.5 (2H, s, H_1), 8.0 (2H, d *J=8 Hz*, H_2), 7.2 (14H, m, H_3, H_4, H_p, H_o, H_m, H_5), 3.4 (6H, m, OMe); *m/z*(LSIMS) 1169 ([M+Cl]$^+$), 1140([M+Cl-CO-H]$^+$), 1124 ([M+CO-Cl]$^+$), 1083 [(M+Cl -3CO +H]$^+$), 1047 ([M-3CO]$^+$).

Synthesis of Pd_2Cl_4((R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol) 27

(R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol **22** (0.06g, 0.10 mmol) and $PdCl_2(MeCN)_2$ (0.05g, 0.19 mmol) were partially dissolved in MeCN (8ml) and heated at reflux for 2 hours under nitrogen. The red solution was left to cool evaporated and recrystallised from acetonitrile resulting in Pd_2Cl_4((R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol) **27** (0.05g, 57%) as a yellow/brown solid; ν_{max} (Nujol)/cm^{-1}: No OH, 2923 (C-H st), 1655 (C=N), 1611, 1595 (C=C ar); *m/z*(EI/FAB) only ligand visible.

Synthesis of Pd_2Cl_4(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol) 28

3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol **23** (0.09g, 0.22 mmol) was dissolved in warm MeCN (5 ml) and added to a solution of $PdCl_2(MeCN)_2$ (0.11 g, 0.44 mmol) in MeCN (5ml) and a orange/yellow precipitate

formed spontaneously resulting in Pd_2Cl_4(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol) **28** (0.17g, 52%) as a orange/yellow solid; ν_{max} (Nujol)/cm^{-1}: No OH, 1659 (C=N), 1613, 1580 (C=C ar); *m/z*(FAB) 960 (Pd(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$), 918 (Pd(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$-$NH_2CH_2CH_2OH$ + H_2O), 875.2(Pd(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$-$NH_2CH_2CH_2OH$ + H_2O).

Preparation of Bisacetonitrile palladium (II) chloride[17]

$PdCl_4$ (3.52g, 0.01 mol) was added to a 50 ml round bottomed flask with acetonitrile (25 ml) under nitrogen. This was left to stir for 4 hours. The reaction mixture turned form a brown suspension to an orange suspension. This was filtered producing an orange solid (3.67g, 100%).

Preparation of Pd(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine)$_2$(BF_4)$_2$ 29

$PdCl_2(MeCN)_2$ (0.06g, 0.22 mmol) was dissolved in dry MeCN (25 ml) under nitrogen. $AgBF_4$ (0.10g, 0.50 mmol) was added, turning the solution a cloudy yellow. The reaction mixture was heated to reflux for 3 hours in the dark and left to settle. N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine **17** (023g, 0.44 mmol) was dissolved in MeCN (25 ml) producing a pale yellow solution. The bright yellow palladium solution was transferred via canula into the imine solution producing a bright yellow solution. The reaction mixture was left to stir overnight, filtered through celite and evaporated leaving Pd(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)dibenzenamine)$_2$(BF_4)$_2$ **29** (0.28g, 96%); δ_H (400 MHz, $CDCl_3$): 10.5 (2H, d *J=4 Hz,* Pd-N=CH), 9.0 (2H, d, *J=5 Hz,* N=CH), 8.8 (2H, s, H_1), 8.6 (2H, s, $H_{1'}$), 8.0 (4H, m, H_2 + $H_{2'}$), 7.5-7.0 (32H, m, H_3, H_4, H_5, H_6, H_7, H_8 and attached), 3.45 (6H, s, OMe'), 3.40 (6H,s, OMe).

Preparation of Pd(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine))$_2$(BF_4)$_2$ 30

$PdCl_2(MeCN)_2$ (0.05g, 0.20 mmol) was dissolved in dry MeCN (25 ml) under nitrogen. $AgBF_4$ (0.10g, 0.49 mmol) was added, turning the solution a cloudy yellow. The reaction mixture was heated to reflux for 3 hours in the dark and left to settle. N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18** (023g, 0.44 mmol) was dissolved in dry MeCN (25 ml) producing a yellow solution. The bright yellow palladium solution was transferred *via* canula into the imine solution producing an orange solution. The reaction mixture was left to stir overnight, filtered through celite and evaporated leaving Pd(N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine))$_2$(BF_4)$_2$ **30** (0.20g, 96%) as an orange shiny solid; ν_{max} ($CDCl_3$)/cm^{-1}: 1689, 1644 (C=N), 1617, 1590, 1501 (C=C ar); δ_H (400 MHz, $CDCl_3$): 10.5 (2H, s, Pd-N=CH), 9.2 (2H, s, N=CH), 8.8 (2H, s, H_1), 8.6 (2H, s, $H_{1'}$), 8.0 (4H, m H_2 + $H_{2'}$), 7.4 (7.2 (8H, m, H_3, H_{6m}), 6.7 (4H, m, H_5), 3.4 (6H, m, OMe); *m/z*(ES) 815 (Pd_2 N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18**), 801 (Pd_2 N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18**-Me) 605 (N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18**) 488 ([N,N'-(2,2'-dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(methan-1-yl-1-ylidene)bis(2,4,6-trimethylbenzenamine) **18**-$NPh(Me)_3$]$^+$).

Preparation of Pd((R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$ 31

(R)-(-)-3,3'-bis((mesitylimino)methyl)-1,1'-binaphthyl-2,2'-diol **22** (0.177g, 0.307 mmol) was dissolved in DCM (30 ml) and $PdCl_2(MeCN)_2$ (0.038g, 0.152 mmol) was slowly added as a solid. The reaction mixture was stirred for 3 hours, becoming pH 1, a sample was taken for NMR, then the whole solution was evaporated (0.178g, 93% crude); mp dec. 240 °C. Product was starting material according to NMR spectrum and mass spectrum.

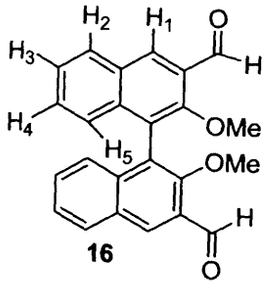
Preparation of Pd((R)-(-)-3,3'-bis((phenylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$ 32

(R)-(-)-3,3'-bis((phenylimino)methyl)-1,1'-binaphthyl-2,2'-diol **21** (0.19g, 0.38 mmol) was dissolved in MeCN (30 ml) with a little DCM with heating. $PdCl_2(MeCN)_2$ (0.05g, 0.19 mmol) was slowly added as a solid. The dark orange solution was stirred for 3 hours, becoming pH 1, a sample was taken for NMR spectroscopy, then the whole solution was evaporated to an orange solid. Reaction not complete so potassium t-butoxide (0.05g, 0.45 mmol) was added turning the reaction mixture red. This was left stirring overnight under nitrogen. TLC showed several compounds so a small column run with pet.ether, ethyl acetate and ethanol fractions. Only a few mgs of each compound came through, yellow, red, orange, pink.

Preparation of [(3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol)$_2$Zr]Cl$_2$

$ZrCl_4$ (0.03g, 0.13 mmol) in dry MeCN (5 ml) was slowly added to a solution of 3,3'-bis((2-hydroxyethylimino)methyl)-1,1'-binaphthyl-2,2'-diol **23** (0.07g, 0.15 mmol) in acetonitrile (20 ml) under nitrogen. A yellow solid formed instantly, was filtered off (0.05g, 68%) which was not very soluble. After addition of triethylamine and acetonitrile the solid was quite insoluble. δ_H (400 MHz, $CDCl_3$): very small peaks due to insolubility; *m/z*(FAB) 919.1 ($[M-H_2O]^+$), very small peak.

5.4 Compound List



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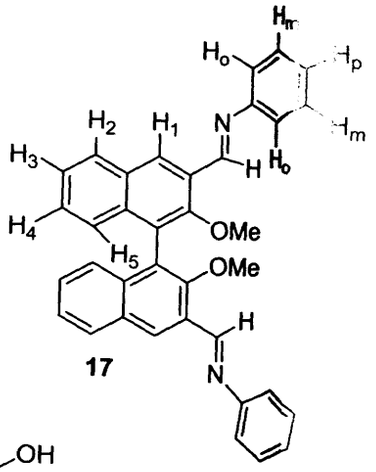

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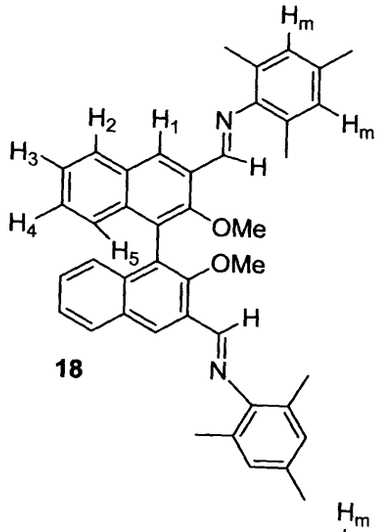

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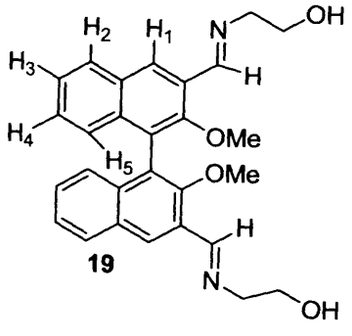

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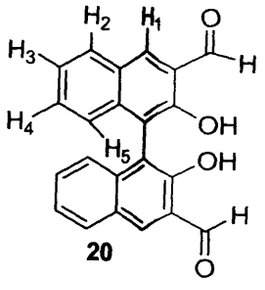

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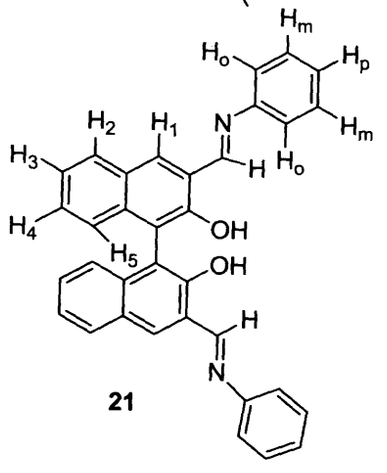

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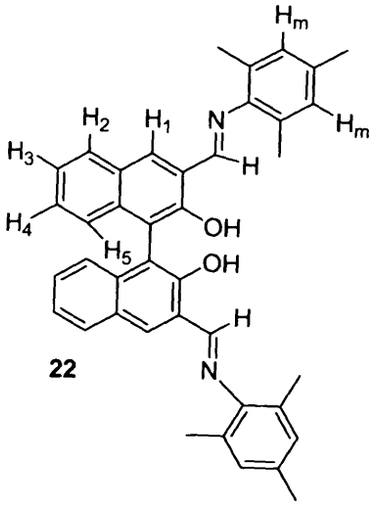

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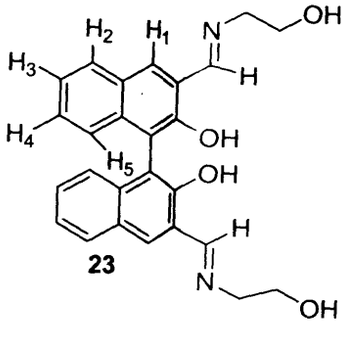

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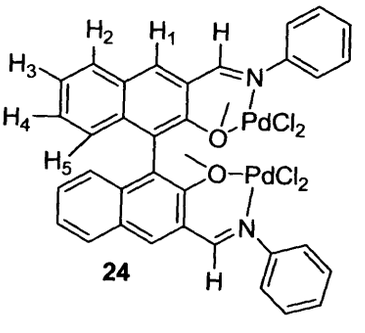

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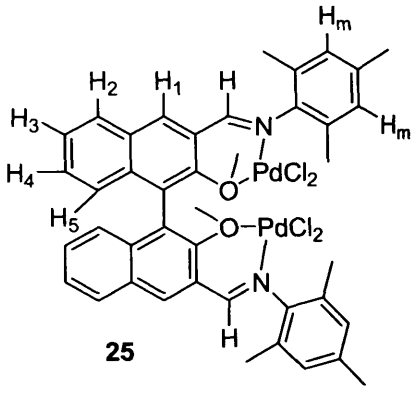

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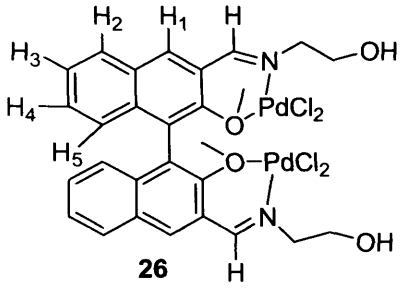

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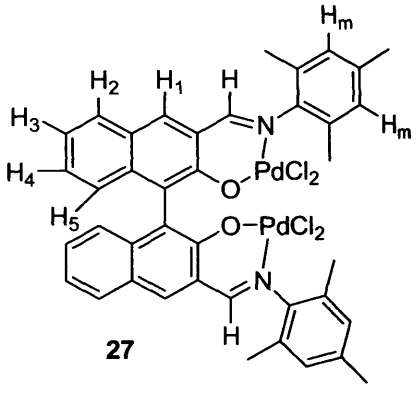

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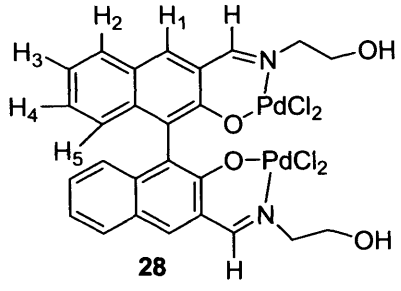

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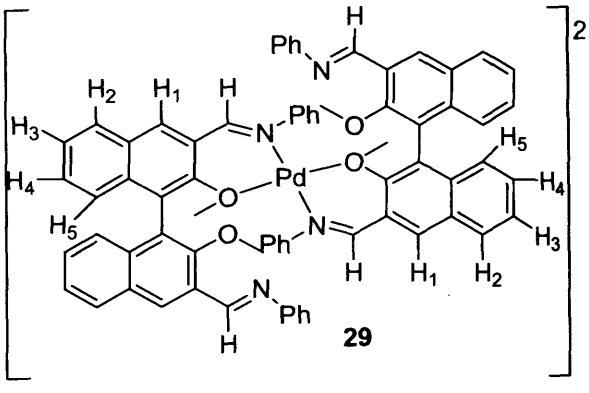

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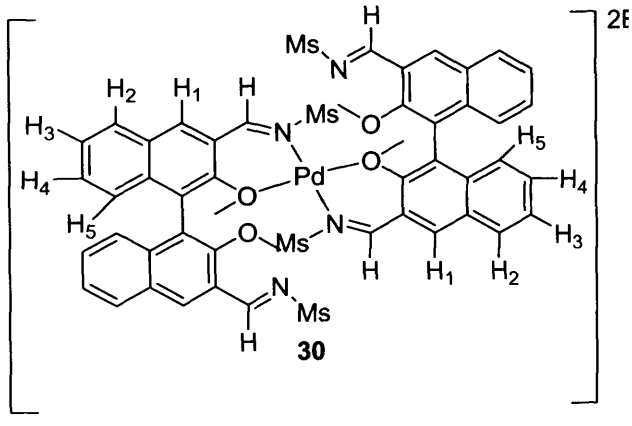

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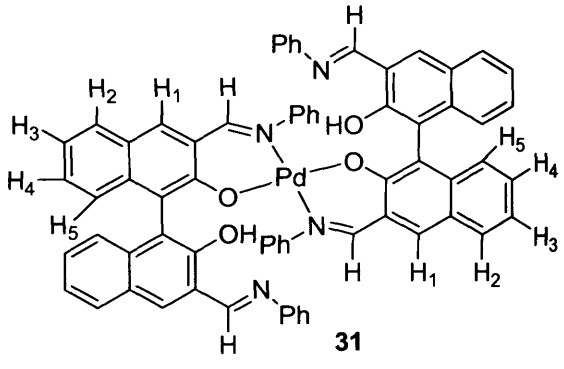

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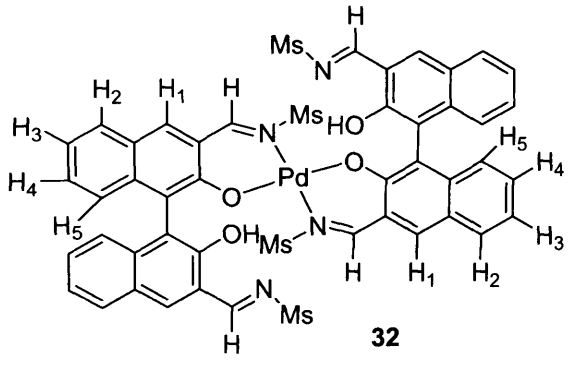

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Chapter 6 Biquinazolinones and Complexes

6.1 Introduction

6.11 Biquinazolinone Synthesis

3,3'-Biquinazoline-4'4'-diones are particularly interesting due to the restricted rotation around the N-N bond which causes axial chirality. Even so, few groups have seen the potential of these dimeric heterocycles and there are no reports of their application as ligands in coordination chemistry.

The first example of a 3,3'-biquinazoline-4'4'-dione was synthesised by Marston Taylor Bogert and Ellen Parmelee Cook in 1907.[1] They produced 6,6'-dinitro-2,2'-dimethylbiquinazoline-4,4'-one (figure 6.1) by taking hydrazine monohydrate and heating it to 160-180° for twenty minutes with 6-nitro-benzoxazine. Side products such as aminoquinoline and unchanged benzoxazine had to be removed and this resulted in a poor yield. They later went on to synthesise the 1,1' dinitro isomer.[2]

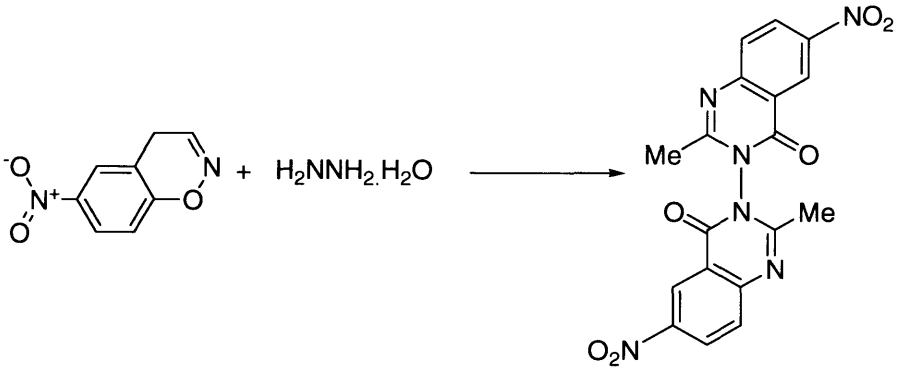


Figure 6.1. 6,6'-Dinitro-2,2'-dimethylbiquinazoline-4,4'-one

A use for this type of compound was not envisaged until 1974 when Hans Kohl *et al* patented the synthesis of six bis(tetrahydroquinazolinones) with varying substituents on the phenyl ring and at the 2,2' position and found them to be useful as bactericides.[3]

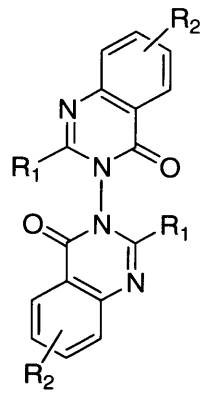


Figure 6.2. Bis(tetrahydroquinazolinones)
R_1=PhCH$_2$, 4-ClC$_6$H$_4$ or 5-nitro-2-furyl
R_2=H, Cl or 2Cl

The synthesis of 2,2'-dimethyl-3,3'-biquinazoline-4,4'-one was first achieved by Nagahara *et al* in 1977 from a condensation of bisanthranoyl hydrazine and triethoxyethane.[4] Bisanthranoyl hydrazine was first obtained from the reaction of isatoic anhydride with hydrazine monohydrate.[5]

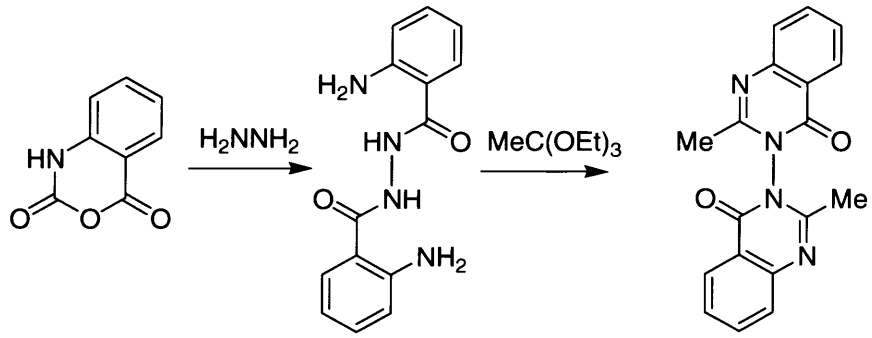


Figure 6.3. Synthesis of 2,2'-dimethyl-3,3'-biquinazoline-4,4'-one

Substituted biquinazolinones were further studied for their antimicrobial activity by various scientists at the Al-Azhar Universtiy in Cairo.[6-8] P. S. N Reddy *et al* have synthesized a number of biquinazolinones with R_1= H, Me, Et, n-Pr, $CHMe_2$, n-Bu, n-pentyl, 2-$O_2NC_6H_4$, 2-ClC_6H_4, Ph, 2-furyl, 4-MeC_6H_4 for their possible use as a source of quinazolinoyl radicals, significant in physiological processes in organisms.[9] This group has also produced triketyl biquinazolinones[10] and biquinazolinones linked through a methine group.[11]

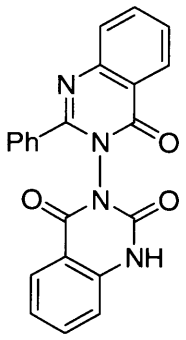


Figure 6.4. 3-(4-oxo-2-phenylquinazolin-3(4H)-yl)quinazoline-2,4(1H,3H)-dione

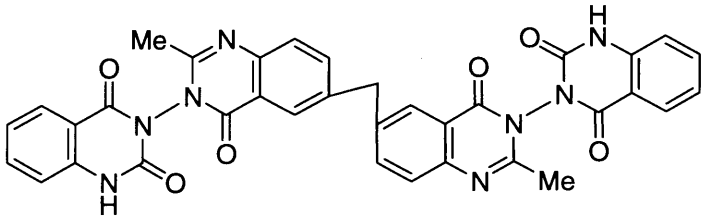


Figure 6.5. A tetraquinazolinone

Synthesis of the disulphone dione (figure 6.6) was achieved by H.K Gakhar *et al* in 1982 by reacting isatoic anhydride with 3-amino-2-thioxo-2,3-dihydroquinazolin-4(1H)-one and carbon disulphide. [12] This could potentially be a good ligand for soft metals.

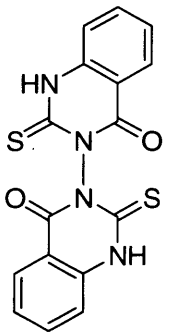


Figure 6.6-Disulphone dione

Peter Langer *et al* synthesised the first 2,2' biquinazolin-4,4'-ones in 2001 by the treatment of substituted methyl 2-aminobenzoate with substituted oxalimidoyl dichloride which resulted in quite low yields, [13] so the isatoic anhydride method is probably the best to get high yields.

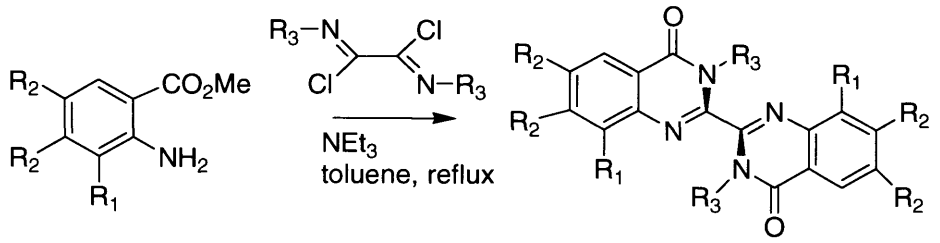


Figure 6.7 Synthesis of 2,2' biquinazolin-4,4'-diones

The MPC group is interested in these molecules for their application as ligands in supramolecular structures, the focus of this work, and in asymmetric catalysis, which is currently being investigated. Previous work in our group has verified the presence of chirality in biquinazolinones by calculating the barrier to rotation and has developed methods for deracemisation through asymmetric transformation, an example is shown in figure 6.8.[14]

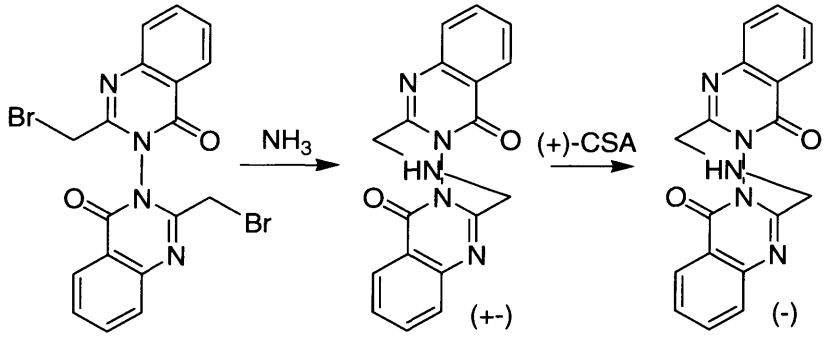


Figure 6.8 Asymmetric transformation

Novel symmetrical and unsymmetrical biquinazolinones have also been synthesised using various methods.[15]

6.12 Coordinaton Chemistry of Quinazolinones

The complexation of biquinazolinones has yet to be reported but can be predicted from the literature on quinazolinone complexes. K. Verra Reddy *et al* synthesised a range of quinazolinones and formed ruthenium complexes starting with $RuCl_2(DMSO)_4$ as shown in figure 6.9.[16] This shows binding at the carbonyl oxygen and on the O or N donor in the 3 position.

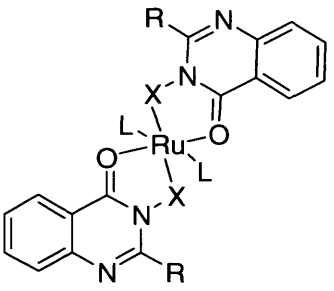


Figure 6.9 Ruthenium quinazolinone complex where X=various O and N donors, R= Me or Ph, L= Cl with neutral ligands or DMSO with charged ligands.

Copper complexes of 2-methyl-3-amino-9-(3H)-quinazolin-4-one with various counter ions showed similar binding modes and the complexes also displayed biological activity.[17] A thiolate in the 2 position has been shown to bind to gold phosphines and arsines by Mariano Laguna *et al* as shown in figure 6.10.[18]

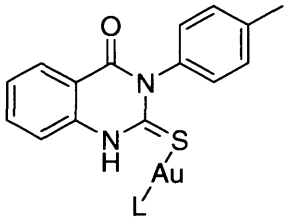
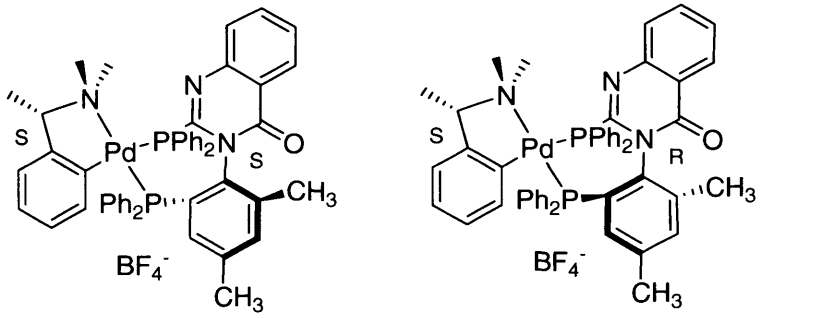


Figure 6.10 3-tolyl-4-oxo-2-thioxo-1,2,3,4-tetrahydro-quinazoline gold complex.

Resolution of an atropisomeric quinazolinone was achieved by complexation with S-(-)-di-μ-chlorobis[1-naphthylethyl)-aminato-C^2,N]dipalladium showing palladium binding to a phosphine in the 2 position and a phosphine on the 3-aryl ring in analogy to BINAP.[19]



(S,S)-complex, precipitation (S,R)-complex, mother liquor

Figure 6.11 Resolution of an atropisomeric quinazolinone

Imine binding has been reported by Peter Langer *et al*, where they showed that these ligands would coordinate to nickel through an N-O binding mode. The N-donor was part of the quinazolinone ring and the O-donor an exocyclic amide[13]

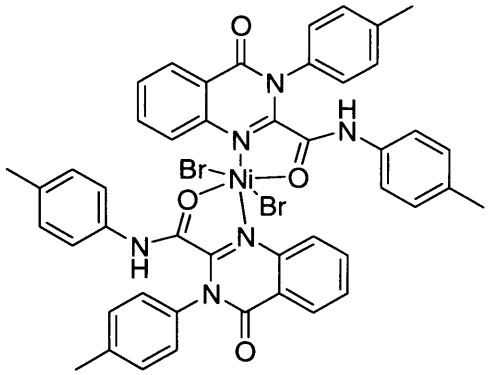


Figure 6.12 Quinazolinone-nickel binding

Most recently, Kalagouda B. Gudasi *et al* synthesised an interesting novel ligand, 2-pyridine-2-yl-3(pyridine-2-carboxylideneamino)quinazolin-4(3H)-one (PPCAQ) and studied it's complexation behaviour.[20] Varying the metal showed two types of complexation, shifting between amide or pyridine binding, as shown in figure 6.13. The metals bound to the pyridine are softer in character and therefore prefer the softer nitrogen donor whereas nickel and manganese (II) prefer the harder amide carbonyl. Some of the complexes were also found to have enhanced antibacterial activity compared to the free ligand.

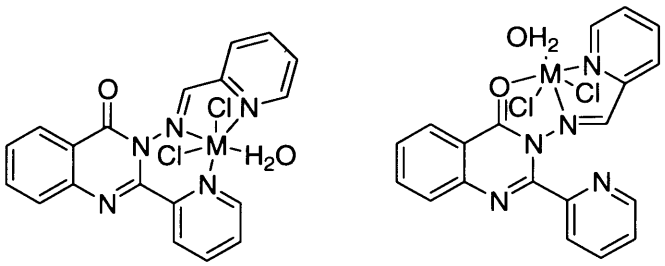


Figure 6.13 PPCAQ complexes

6.13 Prospects for Biquinazolinones as Ligands.

From the literature therefore various binding sites could be predicted for the ligands synthesised in this chapter as shown in figure 6.14. Binding mode I would be preferred by softer metals such as palladium (II) whereas nickel (II) would probably prefer binding mode III. Binding mode II might occur when synthesising heterometallic species.

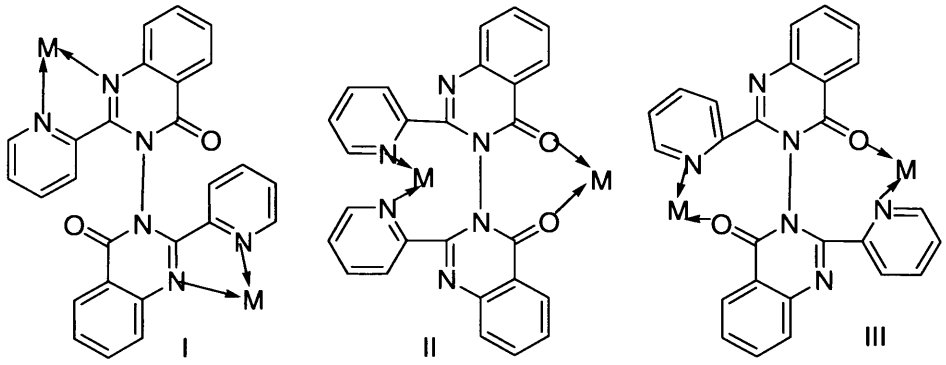


Figure 6.14 Possible metal binding sites

If binding mode I could be achieved then it would be possible to build up a polymer that would have a built in twist due to the axial chirality and therefore could be helical.

6.2 Results and Discussion

6.21 Ligand Synthesis

As shown earlier, a possible route to obtain biquinazolinones is to start with the condensation of isatoic anhydride with hydrazine monohydrate to form bisanthranoyl hydrazine **1**.[5] Then in turn this could be condensed with various species to form the second ring necessary in a biquinazolinone. The first step is very straight forward, and can be done on a large scale using only cheap starting materials with a good yield of 79%. There was no need to further purify this material as it was essentially pure. To form chelating ligands with a twist, pyridine -2-carboxaldehyde was condensed under reflux with hydrazine **1** as shown in figure 6.15. Again, this was a facile reaction; hydrazine **1** was suspended in ethanol, pyridine-2- carboxaldehyde was added and the mixture was refluxed for one hour. Once cooled a white solid, 2-pyridyl-tetrahydrobiquinazolinone **2** (tetrahydro BiQpy), was obtained; the NMR spectrum of

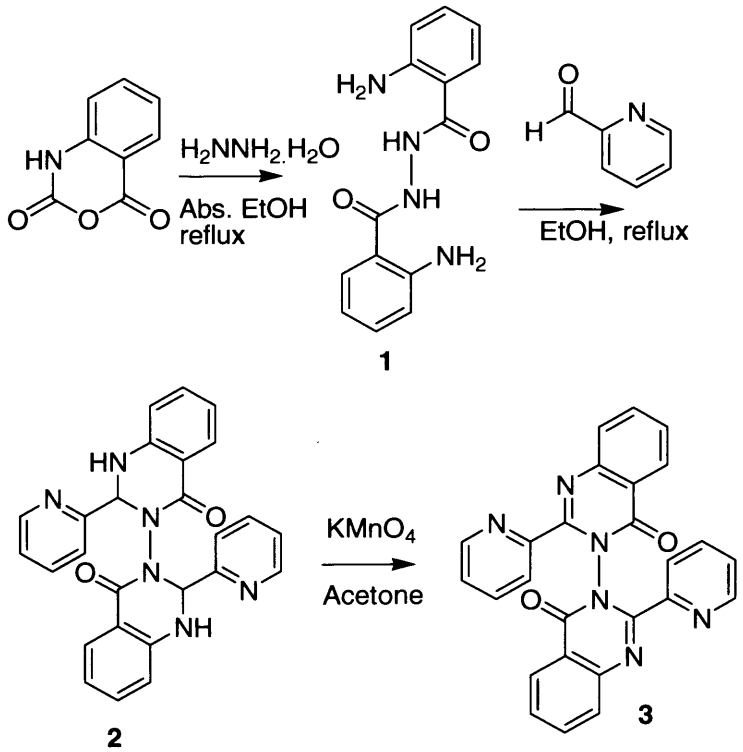


Figure 6.15 Biquinazolinone synthesis

this solid was complicated due to tautomerism in the product but it was proven to be pure material through combustion analysis. A 93 % yield was obtained of pure material without the need for recrystallisation. In order to form the fully aromatic system it was necessary to oxidise tetrahydro-BiQpy **2.** This reaction was achieved by

suspending **2** in acetone and adding potassium permanganate. After stirring for five hours the reaction was complete (as indicated by TLC) so dichloromethane was added and the reaction mixture was filtered to remove inorganic solids. After aqueous work up a pale yellow solid production of 2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one **3** (henceforth BiQpy) was left and recrystallised from chloroform and ethanol giving a 60% yield. The BiQpy ligand was varied by substituting pyridine-2-carboxaldehyde with 6-methylpyridine-2-carboxaldehyde to form 2,2'-di-6-methylpyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one (tetrahydro-BiQMepy) **4** then 2,2'-di-6-methylpyridyl-3,3'-biquinazolin-4,4'-one (BiQMepy) **5** and 2-quinolinecarbaldehyde to form 2,2'-diquinolyl-tetrahydro-3,3'-biquinazolin-4,4'-one (tetrahydro-BiQQu) **6** then 2,2'-diquinolyl-3,3'-biquinazolin-4,4'-one (BiQQu) **7.** The steps were kept the same and produced high yields and pure compounds. Crystal structures of BiQMepy **5** and BiQQu **7** were also obtained.

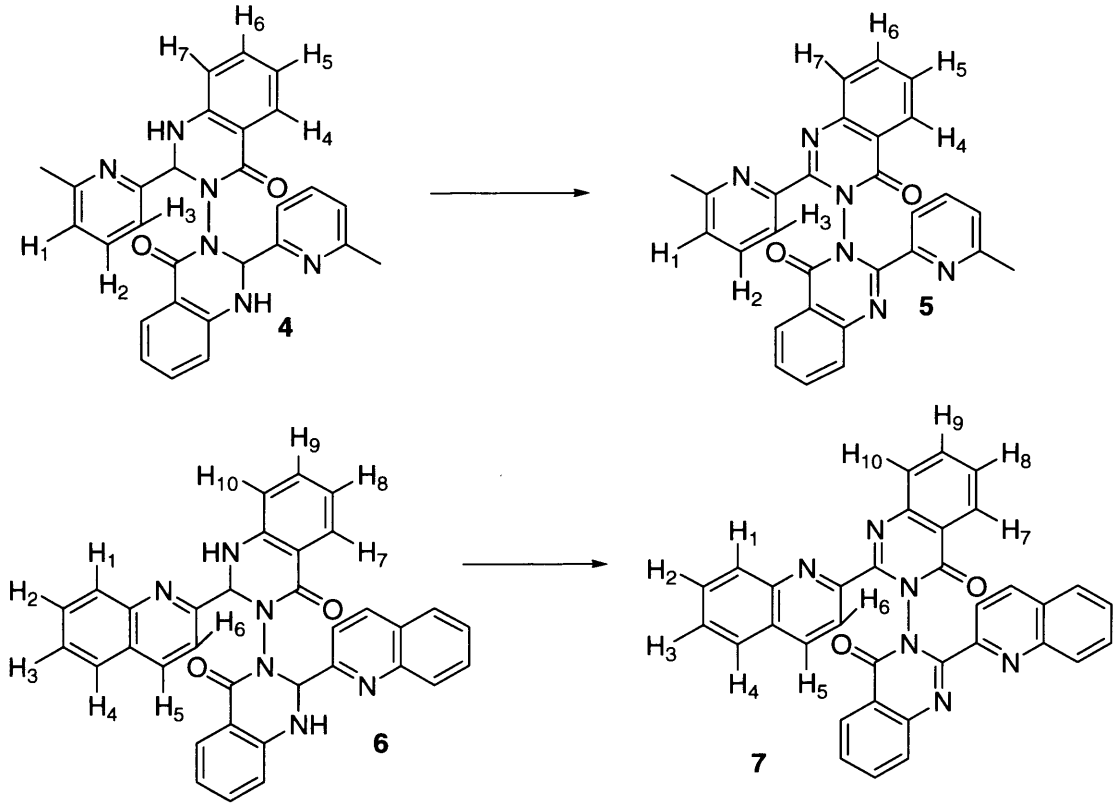


Figure 6.16 Other pyridyl based biquinazolinone ligands

The variations in the ligands are interesting as the methyl group adds more steric hindrance but also donates electron density to the pyridine making it a stronger sigma donor than the un-substituted pyridine. Substituting a quinoline increases the conjugation in the system leading to more π-backbonding, but also an increase in

delocalisation could lead to decreased electron density on the nitrogen making it a poorer sigma donor.

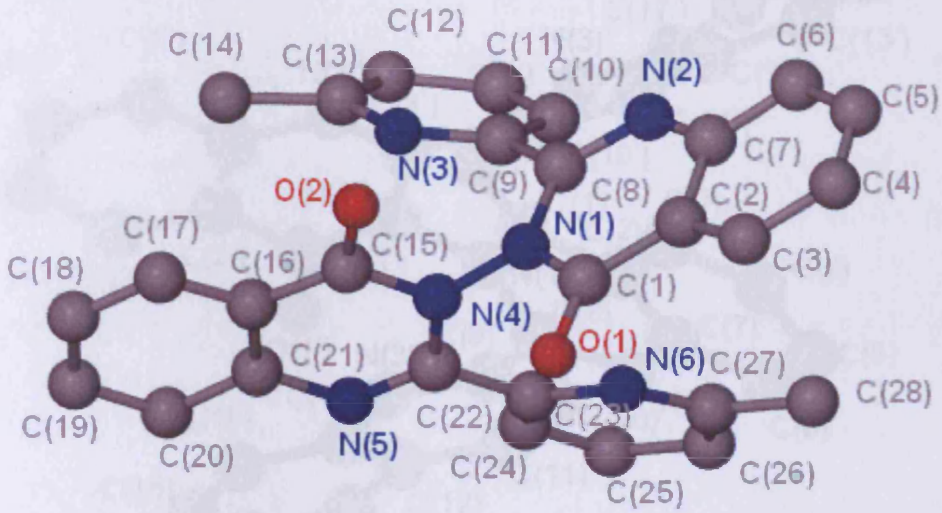


Figure 6.17 Crystal structure of BiQMepy 5.

Table 6.2 Crystallographic details for BiQMepy 5

Compound	5
Formula	$C_{28}H_{20}N_6O_2$
M	472.50
***a* (Å)**	11.4447(2)
***b* (Å)**	17.0917(3)
***c* (Å)**	11.5133(3)
***α*(°)**	90.000
***β*(°)**	92.2014(7)
***γ*(°)**	90.000
V (Å^3)	2250.45(8)
T (K)	150
Crystal system	Monoclinic
Space group	P 21/n
Z	4
μ (mm^{-1})	0.092
Reflections collected	36126
Independent reflections (R_{int})	5150[R(int)=0.1178]
Final R indices (all data)	R_1=0.0534, wR_2=0.1368

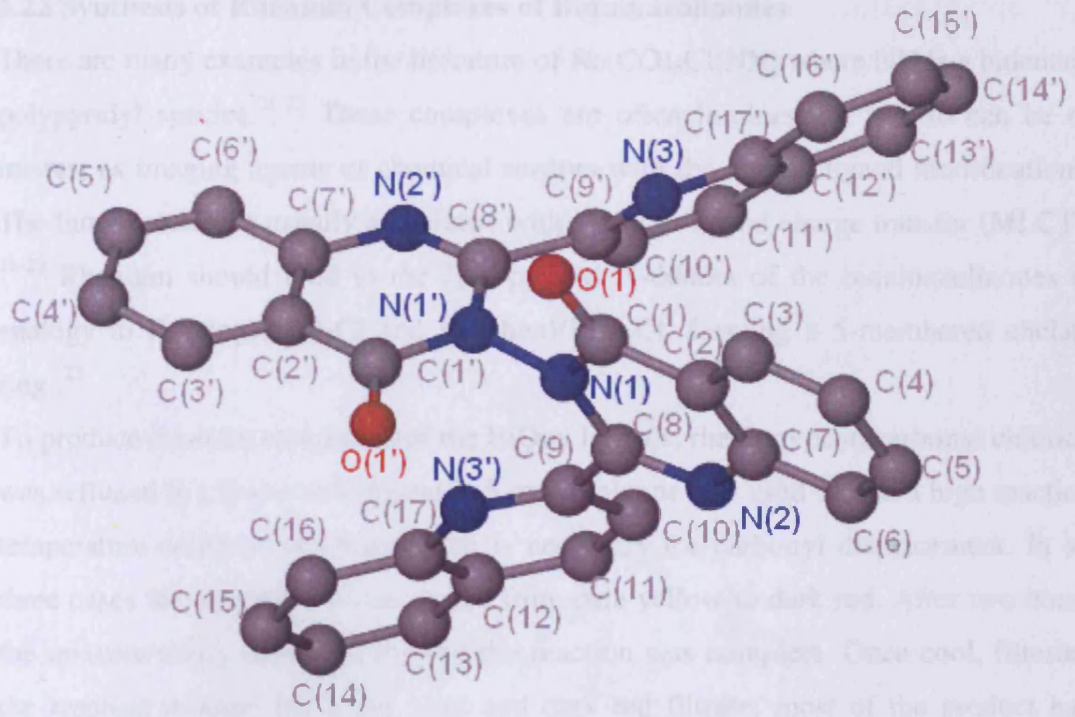


Figure 6.18 Crystal structure of BiQQu 7.

Table 6.3 Crystallographic details for BiQQu 7

Compound	7
Formula	$C_{34}H_{20}N_6O_2$
M	544.56
***a* (Å)**	10.3349(3)
***b* (Å)**	11.6951(3)
***c* (Å)**	12.6075(4)
α(°)	100.099(2)
β(°)	101.1624(18)
γ(°)	109.4835(12)
V (Å^3)	1361.16(7)
T (K)	150
Crystal system	Triclinic
Space group	P -1
Z	2
μ (mm^{-1})	0.086
Reflections collected	21771
Independent reflections (R_{int})	6214[R(int)=0.0996]
Final R indices (all data)	R_1=0.0752, wR_2=0.2130

It was necessary to SQUEEZE the data for BiQQu **7** to remove the problems associated with solvent disorder.

6.22 Synthesis of Rhenium Complexes of Biquinazolinones

There are many examples in the literature of $Re(CO)_3Cl(NN)$ where NN is a bidentate polypyridyl species.[21-23] These complexes are often luminescent and so can be of interest as imaging agents or chemical sensors with the correct ligand modifications. The luminescence is usually associated with metal to ligand charge transfer (MLCT). [21-23] Rhenium should bind to the four pyridyl N-donors of the biquinazolinones in analogy to $Re(bipy)(CO)_3Cl$ and $Re(phen)(CO)_3Cl$, forming a 5-membered chelate ring .[22]

To produce rhenium complexes of the BiQpy ligands, rhenium pentacarbonyl chloride was refluxed in toluene with ligand **3, 5** or **7.** Toluene was used so that a high reaction temperature could be reached, which is necessary for carbonyl displacement. In all three cases the reaction mixture turned from pale yellow to dark red. After two hours the mixture was a very dark red and the reaction was complete. Once cool, filtering the reaction mixture left a red solid and dark red filtrate; most of the product had crystallised out.

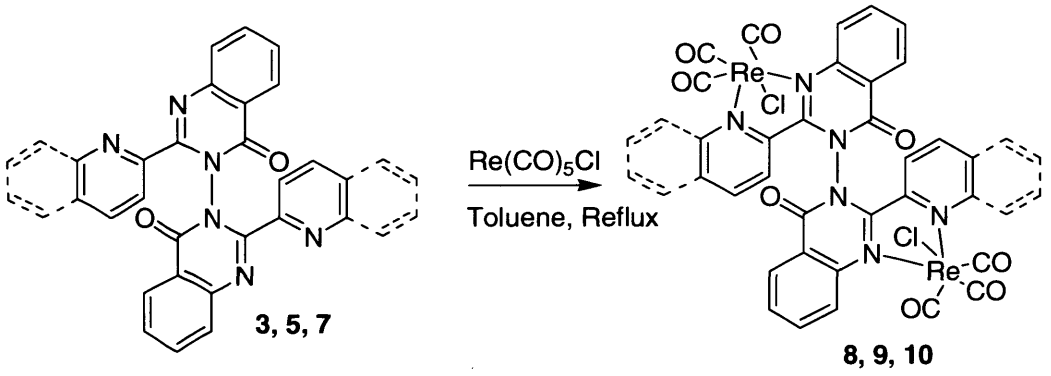


Figure 6.19 Rhenium complex formation.

Rhenium BiQpy complex **8** was easily recrystallised by slow diffusion of methanol into a chloroform solution producing x-ray quality crystals. A crystal structure was obtained as shown in figure 6.20. This is the first reported crystal structure of a biquinazolinone complex. The unit pictured crystallised with three molecules of chloroform. It is possible to see the way that the pyridine twists round to help chelate rhenium and the twist in ligand, leading to axial chirality. The ligand binds to rhenium in analogy to bipyridine rather than to the amide carbonyl donors. Rhenium is a relatively soft metal so prefers binding to the softer pyridyl N-donors rather than the harder amide O donors. The N N chelate size is comparable to Bipy so was likely to bind Rhenium (I) successfully. This type of binding is preferable for helicate

formation as it incorporates the twist of the ligand along the helical chiral axis. This complex would make a poor asymmetric catalyst due to the metal binding site being too far from the chiral axis.

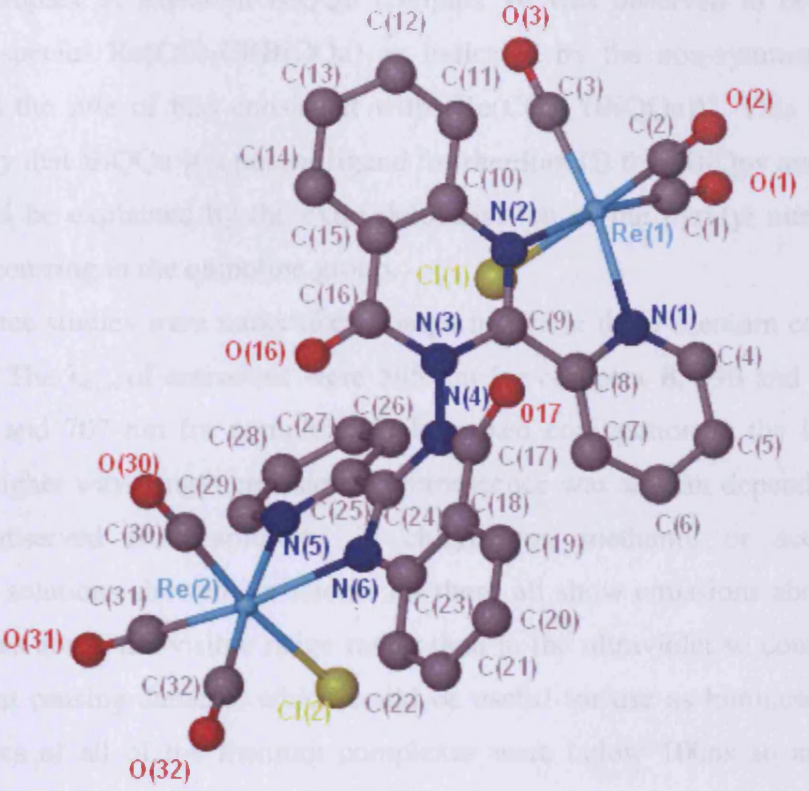


Figure 6.20 Crystal structure of rhenium BiQpy complex 8

Table 6.4 Crystallographic details for rhenium BiQpy complex 8

Compound	8
Formula	$C_{35}H_{19}N_6O_8Re_2$
M	1413.91
***a* (Å)**	15.889(5)
***b* (Å)**	14.114(5)
***c* (Å)**	20.776(5)
***α*(°)**	90.000(5)
***β*(°)**	105.214(5)
***γ*(°)**	90.000(5)
V (Å^3)	4496(2)
T (K)	150
Crystal system	Monoclinic
Space group	P 21/n
Z	4
μ (mm^{-1})	6.090
Reflections collected	74910
Independent reflections (R_{int})	10298[R(int)=0.1434]
Final R indices (all data)	R_1=0.0455, wR_2=0.1007

Crystals of rhenium BiQMepy complex **9** were grown in the same way but after several attempts it was not possible to obtain data good enough to solve the x-ray crystal structure but all of the spectroscopic data confirmed formation of the desired rhenium complex **9.** Rhenium BiQQu complex **10** was observed to be the mono-metallated species $Re(CO)_3Cl(BiQQu)$ as indicated by the non-symmetrical NMR spectra and the m/z of 856 consistent with $(Re(CO)_3\ (BiQQu))^+$. This information would imply that BiQQu is a poorer ligand for rhenium (I) than BiQpy and BiQMepy which could be explained by the extra delocalisation of the pyridyl nitrogen donor electrons occurring in the quinoline group.

Luminescence studies were undertaken comparing these three rhenium complexes to each other. The λ_{max} of emissions were 595 nm for complex **8**, 590 and 602 nm for complex **9** and 707 nm for complex **10**. Increased conjugation in the latter ligand leads to a higher wavelength emission. Luminescence was solvent dependant with no emission observed from solutions in chloroform, methanol or acetone, only acetonitrile solutions showed emissions. As these all show emissions above 400 nm the emissions are in the visible range rather than in the ultraviolet so could penetrate cells without causing damage, which could be useful for use as luminescent agents. The lifetimes of all of the rhenium complexes were below 100ns so are short for $NNReCO_3Cl$ complexes; this is probably due to the ligands having numerous vibrational modes for the energy to be dissipated non-radiatively. The λ_{max} of emissions were 450 nm for BiQpy **3**, 447 nm.for BiQMepy **5** and 446nm for BiQQu **7.** These are lower than the complexes but still within the visible range. The lifetime of emission for BiQpy **3** was recorded using a nanoLED exciting at 372 nm, measuring emission at 450 nm and calculated at 0.43 ns (54%) and 2.78 ns (46%). The lifetime of emission for Biqumepy **5** was calculated at 0.55 ns (59%) and 2.36 ns (41%) and for BiQQu **7** at 0.46 ns (77%) and 1.94 ns (23%). These lifetimes are all very short which is typical for most ligands.

The synthesis of a one to one complex of rhenium with BiQpy **3** was attempted; it seemed that two red/orange complexes were formed. One recrystallised out of solution as a dark orange solid **11a** and the second, **11b,** was precipitated from the filtrate with petroleum ether. From further analysis it is possible to conclude that **11a** was in fact the 1:1 complex required as indicated by the 16 peaks in the NMR spectrum and the required isotope pattern in the mass spectrum, m/z 750. Complex

11b was a mixture of this complex and the partially protonated complex $Re(BiQpy)(CO)_3Cl+H$; m/z 751.

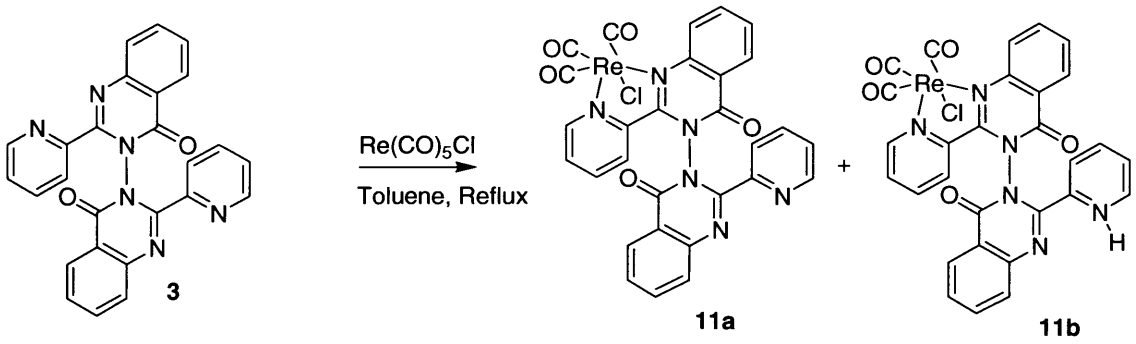


Figure 6.21 1:1 Rhenium complex formation

In order to build helicates it is necessary to join the rhenium complexes together. Therefore one must remove the chloride and replace it with a linker molecule (such as 4,4-bipy) as shown in figure 6.22.

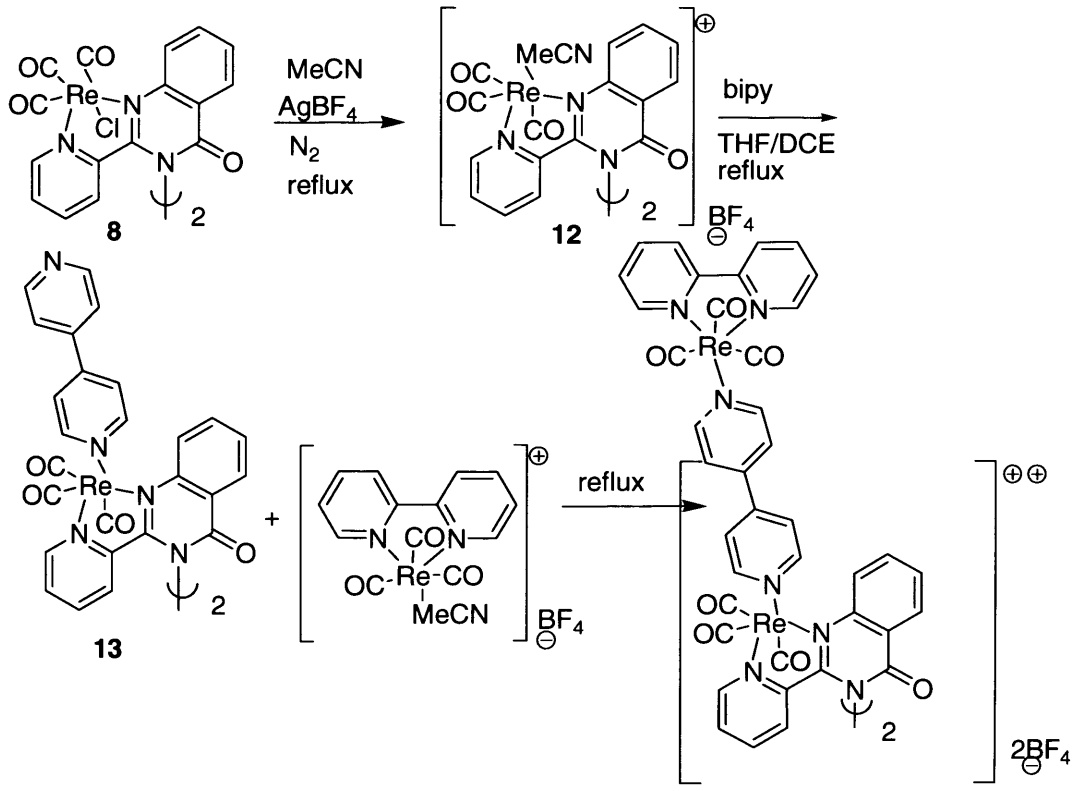


Figure 6.22 Route to a rhenium complex that could be incorporated in a helicate.

Chloride extraction was achieved by refluxing rhenium complex **8** in acetonitrile with silver tetrafluoroborate, to produce the rhenium acetonitrile complex **12.** The reaction mixture turned from red to yellow after refluxing for two days. This was filtered

through celite to remove silver chloride and evaporated to leave a yellow solid. The infrared spectrum showed a carbonyl absorbtion shift of 20 cm^{-1}, possibly due to change in structure, and a carbon nitrogen triple bond stretch was visible, showing the presence of an acetonitrile ligand. This structure was confirmed by the NMR spectrum, which also showed aromatic protons that had shifted, implying a change in the complex. The compound was recrystallised several times from acetonitrile and ethyl acetate and two different types of crystals formed, big and smaller crystals. A unit cell determination of the large crystals showed they were $[Re(CO)_3(MeCN)_3]BF_4$, so it is possible that either the starting material had some rhenium pentacarbonyl chloride in it or the acetonitrile displaced the ligand. The smaller crystals were the required complex **12** as shown in the NMR and IR spectra, but were recovered in a low yield. For the next stage in the synthesis 4,4'-bipyridine was added to the rhenium complex **12**. Several solvents were tried but the only solvent that would dissolve complex **12** was acetonitrile so the acetonitrile solution of 4,4'-bipyridine and complex **12** was refluxed for two and a half hours. The NMR spectrum appeared to be a mixture of starting materials and upon recrystallisation the ratios of the peaks changed confirming that the product was a mixture of starting materials. This could be because the excess of acetonitrile present prevented the acetonitrile leaving the complex.

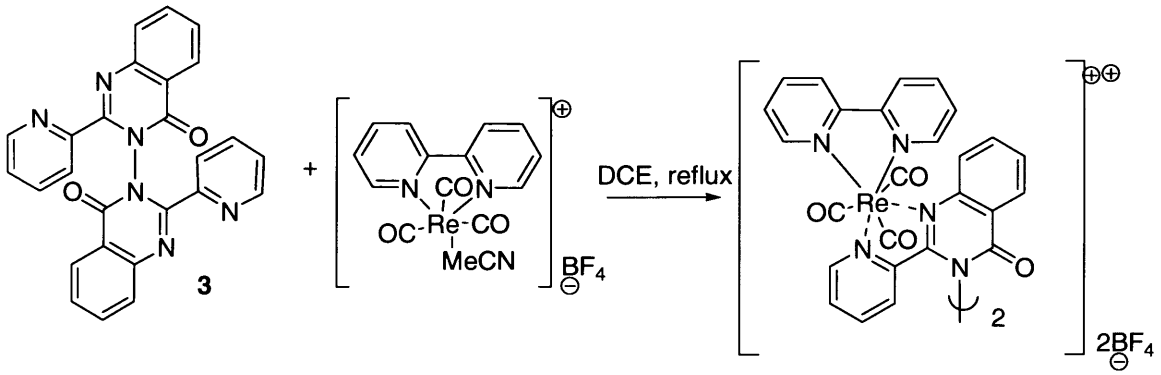


Figure 6.23 Complexation of $[Re(CO)_3MeCN]BF_4$ to BiQpy 3

Out of curiosity BiQpy **3** was reacted with [ReBipy $(CO)_3(MeCN)]BF_4$ to see if a carbonyl would be removed to from a chelated complex. Analogous bis-bipy compounds are known.[21] As in the previous example the yellow product appeared to be a mixture of starting materials and upon recrystallisation the ratio of ligand to rhenium complex changed in the NMR spectra. This was confirmed by the mass

spectrum which showed m/z 468 $(Re(Bipy)(CO)_3(MeCN))^+$, 445 (BiQpy) and 427 $(Re(Bipy)(CO)_3)$ but no mass for the combined complex.

6.23 Synthesis of Palladium Complexes of Biquinazolinones

Palladium (II) tends to form square planar complexes and prefers soft donors so would be one of the best metals to bind to biquinazolinones to form predictable helical structures. To produce a palladium complex with the BiQpy **3** ligand palladium bisacetonitrile dichloride was refluxed in acetonitrile with ligand **3.**

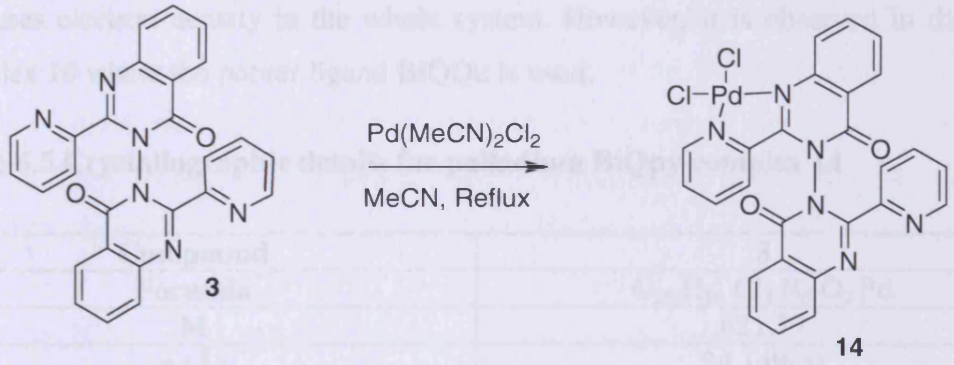


Figure 6.24 Palladium BiQpy complex

It was obvious from the number of inequivalent protons in the proton NMR spectrum of palladium complex **14** that an asymmetrical complex was formed, which was thought to be the mono-metallated complex **14.** This was confirmed by the crystal structure as shown in figure 6.25. The crystals were grown from slow evaporation of the palladium complex **14** acetonitrile solution.

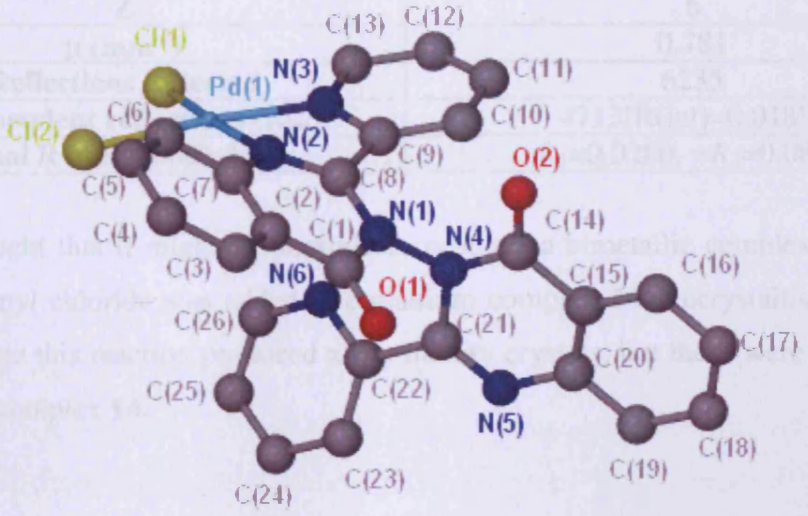


Figure 6.25 Crystal structure of palladium BiQpy complex 14

The palladium is bound in a distorted square planar geometry. Binding causes the pyridine moiety to rotate to face the palladium, whereas on the other half of the ligand the pyridine twists in the opposite direction so the nitrogens are facing in opposite directions. Binding of one palladium must make the second site less desirable to a second palladium, although it is not obvious why this occurs from the structure. It is possible that binding decreases the electron density in the entire system making the nitrogen donors less electron rich and therefore less likely to bind to a second palladium. This is not seen in the analogous rhenium complex **8** as the carbonyl ligands π-back bond, increasing the electron density on the metal which in turn increases electron density in the whole system. However, it is observed in rhenium complex **10** where the poorer ligand BiQQu is used.

Table 6.5 Crystallographic details for palladium BiQpy complex 14

Compound	8
Formula	$C_{26}H_{16}Cl_2N_6O_2Pd$
M	621.77
***a* (Å)**	24.149(5)
***b* (Å)**	11.110(2)
***c* (Å)**	18.009(4)
α(°)	90.00
β(°)	99.17(3)
γ(°)	90.00
V (Å^3)	4770.0(17)
T (K)	150
Crystal system	Monoclinic
Space group	C2/c
Z	6
μ (mm^{-1})	0.781
Reflections collected	6235
Independent reflections (R_{int})	4713[R(int)=0.0188]
Final R indices (all data)	R_1=0.0280, wR_2=0.0810

It was thought that it might be possible to produce a bimetallic complex if rhenium pentacarbonyl chloride was added to palladium complex **14.** Recrystallisation of the product from this reaction produced x-ray quality crystals, but these were found to be palladium complex **14.**

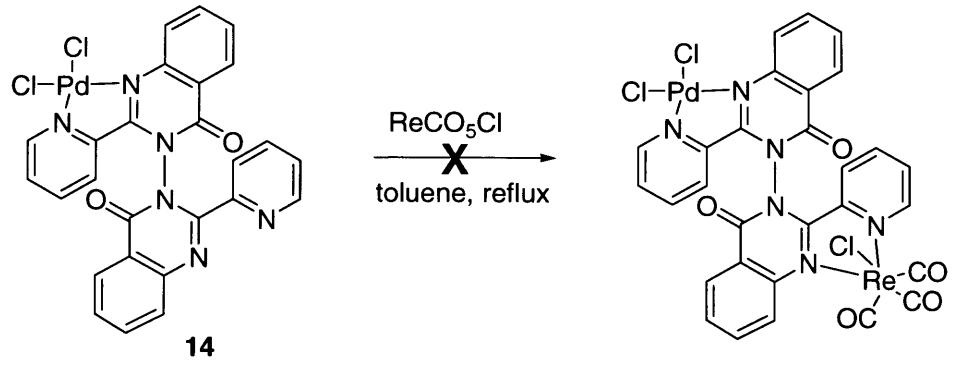


Figure 6.26 Attempted synthesis of a mixed metal BiQpy complex

When the palladium (II) bisacetonitrile chloride was added to BiQMepy **5** ligand, an orange symmetrical complex **15** was formed as implied by the symmetrical NMR spectrum which shows peaks shifted compared to BiQMepy **5.** The EI mass spectrum confirms a bimetallic structure and reveals the isotope pattern for $(Pd_2(BiQMepy)O_2)^{+\cdot}$ centred on m/z 718. Chloride ions are easily removed under ionisation but it is not possible to explain the presence of oxygen in this complex. BiQMepy **5** has two electron donating methyl groups which must counteract the electron-withdrawing effect of the bound palladium, facilitating the coordination of a second palladium.

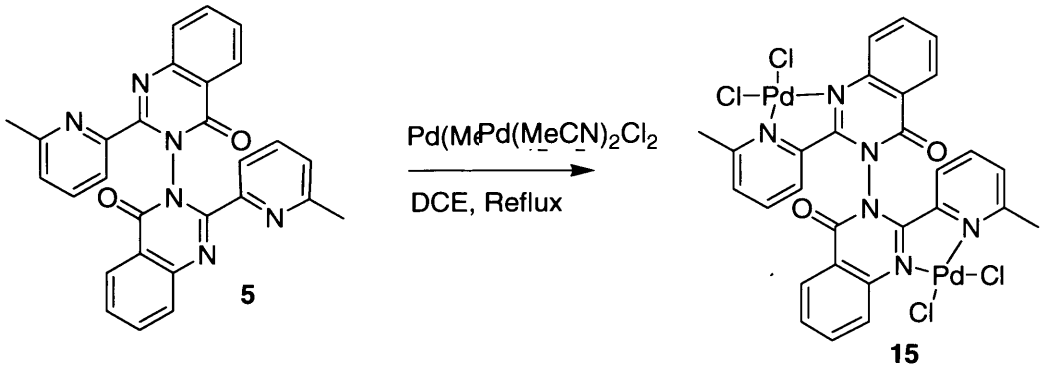


Figure 6.27 Palladium BiQMepy complex

After this discovery it was thought that BiQMepy **5** might be the best candidate for helix formation so $Pd(BiQMepy)_2$ synthesis was attempted. Two equivalents of ligand **5** were refluxed in acetonitrile with silver tetrafluoroborate and one equivalent of palladium bisacetonitrile chloride. The mass spectrum indicated the isotope patterns for $Pd_2(BiQMepy)O_2$ and Pd(BiQMepy)O m/z 718 and 594 respectively; although it can not be explained where the oxygens are bound. The NMR spectrum suggested a

symmetrical compound that was not ligand by itself but was also different to complex **15** so it is possible that the complex is actually $[Pd_2(BiQMepy)(MeCN)_4](BF_4)_4$. The acetonitriles would be lost easily under EI conditions. A C≡N stretch is also visible in the IR spectrum showing presence of acetonitrile.

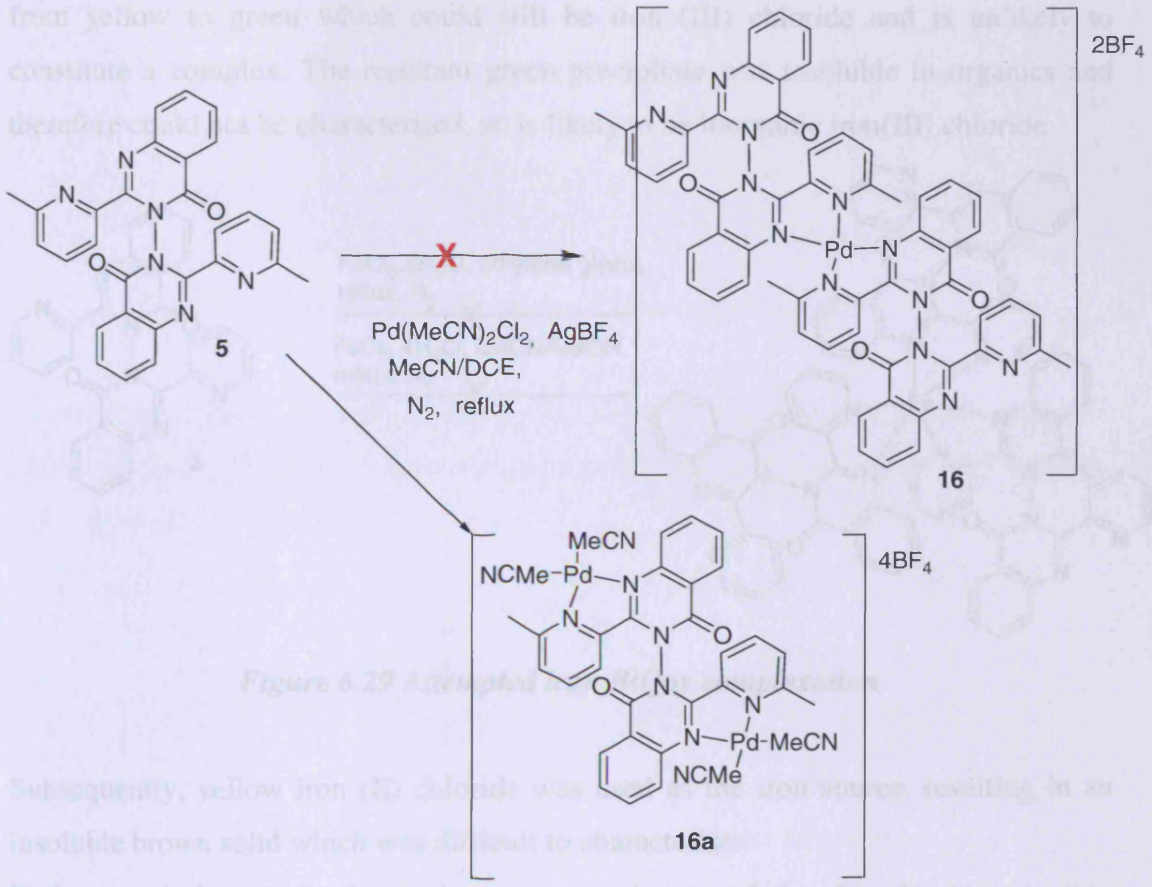


Figure 6.28 Attempted synthesis of a $[Pd(BiQMepy)_2](BF_4)_2$ 16 complex, resulting in $[Pd_2(BiQMepy)(MeCN)_4](BF_4)_4$ 16a

It is possible that there is too much steric hindrance to fill the coordination sphere of palladium with ligand **5** alone. The methyl group adds to the steric bulk increasing the problem. This problem could be resolved by adding a linker molecule with less steric bulk to join together the palladium BiQMepy moieties, but this would also reduce the control over the geometry around the metal.

6.24 Synthesis of RutheniumComplexes of Biquinazolinones

It was thought that other interesting structures could be formed with alternative metals so complexation with iron and ruthenium was studied. Initially attention focused upon the attempted reaction of BiQpy **3** with iron (III) salts. The reaction mixture turned from yellow to green which could still be iron (III) chloride and is unlikely to constitute a complex. The resultant green precipitate was insoluble in organics and therefore could not be characterised, so is likely to be inorganic iron(III) chloride

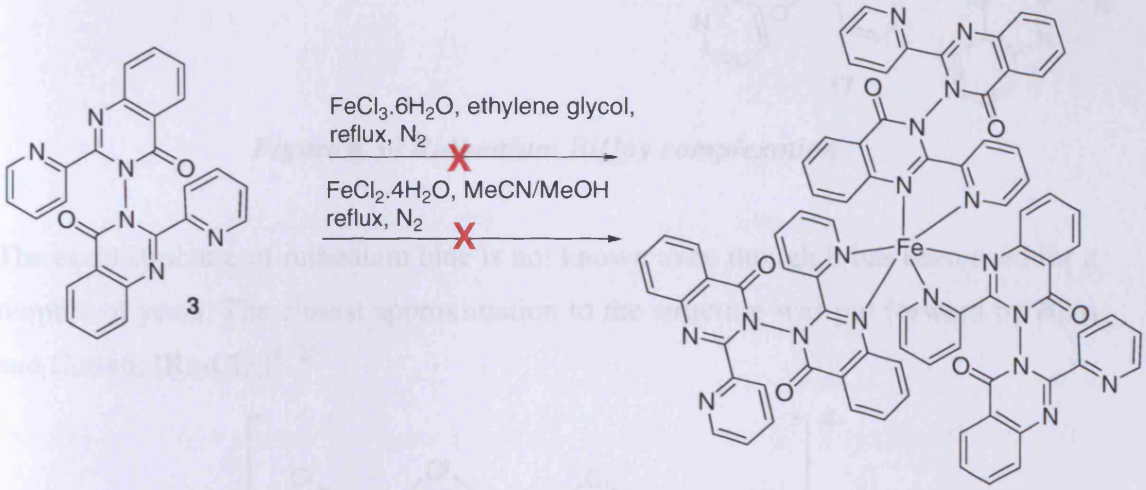


Figure 6.29 Attempted iron BiQpy complexation

Subsequently, yellow iron (II) chloride was used as the iron source, resulting in an insoluble brown solid which was difficult to characterise.

Ruthenium is known for its luminescent complexes and therefore is an interesting metal to study. Ruthenium biquinazolinone complex synthesis was initiated by the attempted reaction between $RuCl_3.3H_2O$ and BiQpy **3** to form dendrimer **17.** A colour change took place but the proton NMR indicated the compound was very impure so the reaction was repeated using ruthenium blue, prepared by the literature procedure.[24]

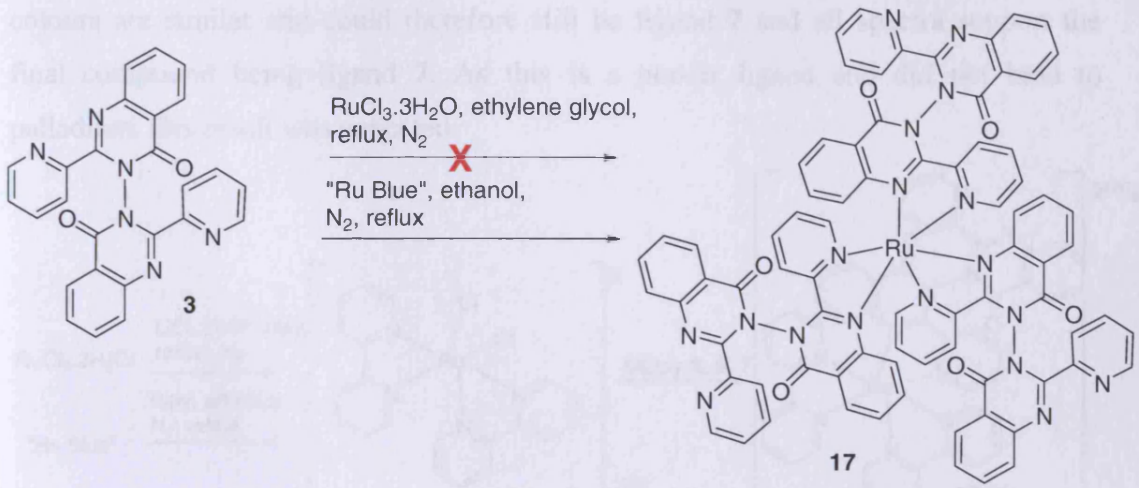


Figure 6.30 Ruthenium BiQpy complexation

The exact structure of ruthenium blue is not known even though it has been used for a number of years. The closest approximation to the structure was put forward by Bino and Cotton; $[Ru_3Cl_{12}]^{4-}$.[25]

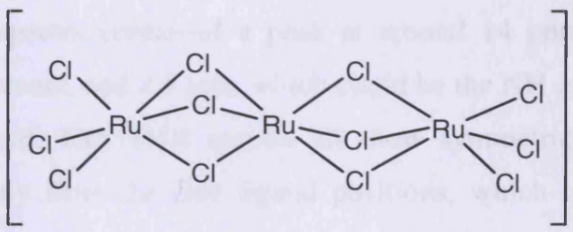


Figure 6.31 The dodecachlorotriruthenate (4 -) ion

Ruthenium blue ethanol solution was generated *in situ* and refluxed with a suspension of ligand **3, 5**or **7** in ethanol. The ruthenium BiquMepy complex was extremely insoluble in water and organic solvents and so characterisation was not feasible. The formation of ruthenium BiQpy complex **17** is not certain but there is evidence in its favour. It is purple and therefore can not be ligand or ruthenium blue. The NMR spectrum indicates a symmetrical species containing ligand **3** which is not consistent with the tris-BiQpy complex shown in figure 6.30, but the peaks have shifted and are broader indicating ruthenium binding. There is no indication of complex **17** in the mass spectrum but there are several high m/z peaks that look like they contain ruthenium species. A possible symmetrical structure could be $Ru_2Cl_2(H_2O)_4$BiQpy or a continuous ruthenium BiQpy polymer. The only evidence to support Ruthenium BiQQu complex **18** is the colour change in the reaction from green to yellow. These

colours are similar and could therefore still be ligand **7** and all spectra support the final compound being ligand **7**. As this is a poorer ligand and did not bind to palladium, this result was expected.

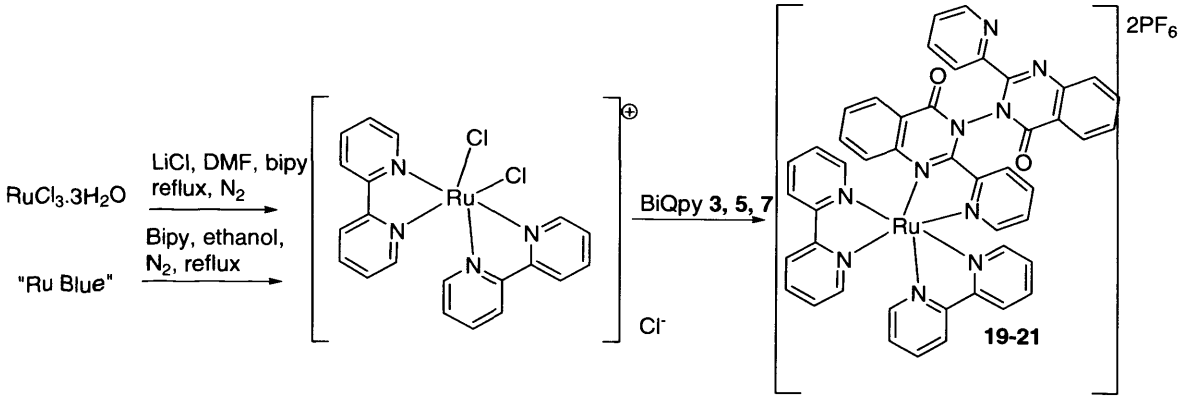
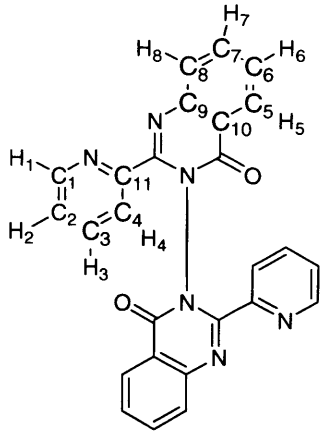


Figure 6.32 Ruthenium bis bipy BiQpy complexes.

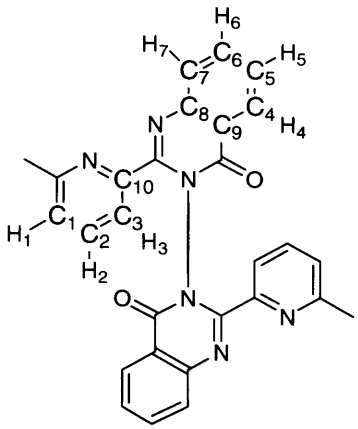
$[Ru(bipy)_2Cl_2]Cl.2H_2O$ was synthesised similarly to the trisBiQpy complexes, from ruthenium blue. Once isolated $[Ru(bipy)_2Cl_2].Cl.2H_2O$ was refluxed with BiQpy **3, 5** or **7.** All reactions afforded a red product with a UV-vis absorption at 550 nm. All of the proton NMR spectra contained a peak at around 14 ppm consistant with HCl which should be present, and 9.5 ppm which could be the NH of a pyridine protonated by hydrochloric acid. The NMR spectra all show symmetrical BiQ ligands which have shifted slightly from the free ligand positions, which could be explained by protonation. No bipy ligand was observed in the NMR spectra but this could be because the bipy containing ruthenium species were not soluble in the NMR solvent. The mass spectra of complex **20** and **21** showed only $Ru(bipy)_2Cl_2$, $Ru(bipy)_2Cl$ and free ligand so the red colour is attributed to $Ru(bipy)_2Cl_2$ but the mass spectrum of complex **19** shows M-PF_6 and M-PF_6+H_2O so some of the required BiQpy complex **19** must have formed but was insoluble in the NMR solvent. An attempt at capping the BiQpy ligand with two $Ru(bipy)_2$ moieties resulted in the same spectroscopic data as complex **19** so capping did not occur.

A range of novel biquinazolinone ligands were successfully synthesised. The first examples of biquinazolinone complexes were reported, including x-ray structure determination of palladium and rhenium complexes. As of yet the formation of a helical chain has not been achieved but interesting coordination compounds have been formed none-the-less. In future work it would be necessary to resolve the biquinazolinone ligands and try to build a helical chain.

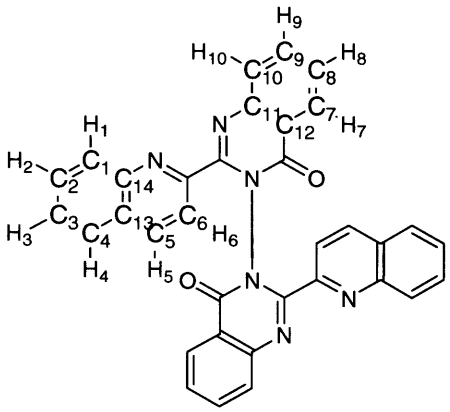
6.3 Experimental



BiQpy compounds



BiQMepy compounds



BiQQu compounds

Preparation of 1,2- diantharaniloylhydrazine 1.[5]

Isatoic anhydride (76.53g, 0.47 mol) was suspended in ethanol (250 ml) in a 1L round bottomed flask, and the reaction mixture was stirred. The hydrazine was added slowly and CO_2 evolution occurred. The reaction needed some manual stirring as well magnetic. Once all the hydrazine was added the reaction mixture was brown and could hardly stir, this was heated to reflux which made the brown solid more mobile. The reaction was refluxed overnight and then left to cool. The reaction mixture was filtered leaving a light brown solid and a red/brown filtrate. The filtrate was evaporated, refluxed in ethanol and left to cool then re-filtered and dried. The brown solids were washed with diethyl ether and dried under suction producing 1,2-diantharaniloylhydrazine **1**(49.80g, 79%) as a light brown solid; δ_H (400 MHz, DMSO): 10.1 (2H, br s, 2NH), 7.7 (2H, d *J=8 Hz*, H_4), 7.2 (2H, t *J=8 Hz*, H_2), 6.8 (2H, d *J=8 Hz*, H_1), 6.6 (2H, t *J=8 Hz*, H_3), 6.4 (4H, br s, $2NH_2$).[5]

Preparation of 2,2'-dipyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one 2

1,2- diantharaniloylhydrazine **1** (10.84g, 0.04 mol) was suspended in ethanol (200ml) and pyridine carboxaldehyde (8ml, 0.08 mol) was added. This light brown reaction mixture was stirred at reflux for 1 hour. The suspension started to turn yellow almost instantly. After 20 minutes the reaction mixture had turned white and stayed white. The reaction was left to cool and filtration produced a white solid and an orange filtrate. The solid was washed with diethyl ether and dried under suction leaving 2,2'-dipyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one **2** (16.68g, 93%); mp 245°C; (Found: C, 69.4; H, 4.50; N, 18.5 $C_{26}H_{20}N_6O_2$ requires C, 69.6; H, 4.49; N, 18.7 %);

ν_{max}(nujol)/cm^{-1} 3260 (NH), 1670 (C=O), 1648 (C=N), 1615 and 1503 (C=C); δ_H (400 MHz, DMSO): 8.1 (2H, d *J=4 Hz,* H_1), 7.7 (2H, m, H_5), 7.4 (2H, d *J=3 Hz,* NH), 7.4 (2H, m, H_3), 7.2 (2H, m, H_7), 7.0 (2H, t *J=8Hz,* H_2), 6.9 (2H, d *J=8 Hz,* H_4), 6.7 (2H, t *J=8 Hz,* H_6), 6.6 (2H, d *J=8 Hz,* H_8), 6.1 (2H, d *J=3 Hz,* CH); δ_C (DMSO): 162.3 (*C*=O), 157.9 (py*C*=N), 148.3 (C_1), 146.3 (HN-*C*Ar), 136.8 (C_3), 134.0 (C_7), 128.2 (C_5), 123.3 (C_4), 121.0 (C_2), 117.7 (C_6), 115.1 (*C*-C=O), 115.0 (C_8), 73.8 (N-C-N); *m/z* (ES) 487 ([M+K]$^+$), 449 (100%, [M+H]$^+$).

Preparation of 2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one 3

2,2'-dipyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one **2** (16.54g, 0.04 mol) was suspended in acetone (200ml) and, while stirring, $KMnO_4$ (58.26g, 0.37 mol) was slowly added over 30 minutes. This turned the reaction mixture from white to purple to a brown/purple colour. After 4 hours the reaction was stopped, DCM (250ml) was added and the mixture was filtered to remove inorganic solids. The reaction mixture was washed with lots of water and brine and checked with starch-iodide paper. The yellow organic layer was dried over magnesium sulphate, filtered and evaporated leaving 2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one **3** (12.68g, 77%) as a pale yellow solid, recrystallised from DCM and ethanol (9.19g, 60%); mp 263°C; (Found: C, 70.1; H, 3.61; N, 18.8 $C_{28}H_{16}N_6O_2$ requires C, 70.3; H, 3.13; N, 18.9 %); λ_{max}^{em}(MeCN)/nm 450; lifetime/ns 0.43 (54%), 2.78 (46%);ν_{max}($CDCl_3$)/cm^{-1} 1699 (C=O), 1595, 1568(ArC=C); δ_H (400 MHz, $CDCl_3$): 8.2 (2H, d *J=8 Hz,* H_1), 8.1 (2H, d *J=5 Hz,* H_5), 8.0 (2H, d *J=8 Hz,* H_4), 7.8 (4H, m, H_8, H_7), 7.7 (2H, m, H_2), 7.5 (2H, m, H_6), 7.1 (2H, m, H_3); δ_C ($CDCl_3$): 159.6 (*C*=O), 151.5 (N-*C*=N), 151.1 (py*C*=N), 148.0 (C_1), 146.6 (*C*-N=C), 136.7 (C_3), 135.0 (C_7), 128.1 (C_5), 127.7 (C_6, C_2), 125.3 (C_8), 124.7 (C_4), 121.6 (*C*-C=O); *m/z* (ES) 445 (100%, [M+H]$^+$).

Preparation of 2,2'-di-6-methylpyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one 4

1,2- diantharaniloylhydrazine **1** (5.57g, 0.02 mol) was suspended in ethanol (50ml) and 6-methylpyridine-2-carboxaldehyde (5.20g, 0.04 mol) was added. This brown suspension was stirred at reflux for 1 hour. On heating the reaction mixture turned yellow within 5 minutes. After 15 minutes the reaction mixture had turned an off-white colour. After 1 hour the reaction was left to cool and filtered producing an off-white solid and an orange filtrate. The solid was washed with diethyl ether and dried

under suction. The filtrate was evaporated and recrystallised from ethanol producing more white solid, 2,2'-di-6-methylpyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one **4** (8.30g, 89%); mp 246°C; (Found: C, 67.9; H, 4.83; N, 17.1 $C_{28}H_{24}N_6O_2.H_2O$ requires C, 68.0; H, 5.30; N, 17.0 %); ν_{max}(nujol)/cm^{-1} 3277 (NH), 1666 (C=O), 1650 (C=N), 1618 and 1505 (C=C); δ_H (400 MHz, DMSO): 7.7 (2H, d *J=8 Hz,* H_4), 7.6 (2H, d *J=3 Hz,* NH), 7.3 (2H, t, *J=8 Hz,* H_2), 7.2 (2H, t *8 Hz,* H_6), 6.85 (4H, d *J=3 Hz,* H_1, H_3), 6.7 (2H, t *J=8 Hz,* H_5), 6.6 (2H, d *J=8 Hz,* H_7), 6.1 (2H, d, *J=3 Hz,* CH), 2.2 (6H, s, CH_3); δ_C (DMSO): 162.1 (*C*=O), 157.6 (py*C*=N), 156.4 (C-Me), 146.4 (HN-CAr), 136.9 (C_2), 134.0 (C_6), 128.2 (C_5), 122.3 (C_1), 117.7 (C_3), 117.6 (C_5), 115.1 (*C*-C=O), 115.0 (C_7), 73.9 (N-C-N), 24.112 (Me); *m/z*(ES) 515 ([M+K]$^+$), 477 (100%, [M+H]$^+$).

Preparation of 2,2'-di-6-methylpyridyl-3,3'-biquinazolin-4,4'-one 5

2,2'-di-6-methylpyridyl-tetrahydro-3,3'-biquinazolin-4,4'-one **4** (8.18g, 0.02 mol) was suspended in acetone (100ml) and, while stirring, $KMnO_4$ (19.959g, 0.126 mol) was slowly added over 30 minutes turning the reaction mixture from white to purple to a brown/purple colour. The reaction was left stirring overnight, DCM (150ml) was added and the mixture was filtered to remove inorganic solids. The reaction mixture was washed with lots of water and brine and checked with starch-iodide paper. The yellow organic layer was dried over magnesium sulphate, filtered and evaporated leaving a pale yellow solid (6.32g, 78%) recrystallised from DCM and ethanol producing 2,2'-di-6-methylpyridyl-3,3'-biquinazolin-4,4'-one **5** (6.14g, 76%); mp 218°C; (Found: C, 70.9; H, 4.26; N, 17.8 $C_{28}H_{20}N_6O_2$ requires C, 71.1; H, 4.26; N, 17.9 %); λ_{max}^{em}(MeCN)/nm 450; lifetime/ns 0.55 (59%), 2.36(41%);ν_{max}($CDCl_3$)/cm^{-1} 1699 (C=O), 1597, 1570 (ArC=C); δ_H (400 MHz, $CDCl_3$): 8.3 (2H, d *J=8 Hz,* H_4), 7.8 (6H, m, H_2, H_3, H_6), 7.5 (4H, m, H_5, H_7), 6.9 (2H, d *J=8 Hz,* H_1) 1.8 (6H, s, CH_3); δ_C ($CDCl_3$): 159.9 (*C*=O), 157.0 (N-*C*=N), 150.7 (*C*-Me), 150.6 (py*C*=N), 146.7 (*C*-N=C), 136.8 (C_2), 134.9 (C_6), 128.0 (C_4), 127.6 (C_5), 127.5 (C_1), 124.3 (C_7), 122.3 (C_3), 122.0 (*C*-C=O), 23.3 (Me); *m/z* (ES) 473 (100%, [M+H]$^+$).

Preparation of 2,2'-diquinolyl-tetrahydro-3,3'-biquinazolin-4,4'-one 6

1,2- diantharaniloylhydrazine **1** (0.86g, 3.18 mmol) was suspended in ethanol (50ml) and 2-quinoline carboxaldehyde (1.00g, 6.36 mmol) was added. This yellow suspension was stirred at reflux for 1 hour. On heating the reaction mixture went

bright yellow. After 2 hours the reaction mixture had turned white and stayed white. The reaction was left to cool and filtered producing a white solid and an orange filtrate. The solid was washed with diethyl ether and dried under suction leaving 2,2'-diquinolyl-tetrahydro-3,3'-biquinazolin-4,4'-one **6** (1.52g, 89%) as a white solid; mp 208°C; (Found: C, 73.8; H, 4.70; N, 15.2 $C_{34}H_{24}N_6O_2$ requires C, 74.4; H, 4.41; N, 15.3 %); ν_{max}(nujol)/cm^{-1} 3263 (NH), 1665 (C=O), 1636 (C=N), 1614 and 1505 (ArC=C); δ_H (400 MHz, DMSO): 7.7 (4H, m, H_1, NH), 7.6 (4H, m, H_5, H_4), 7.5 (4H, m, H_2, H_7), 7.2 (2H, m, H_3), 7.2 (2H, m, H_9), 7.0 (2H, d *J=8 Hz,* H_6), 6.7 (2H, t *J=7 Hz,* H_8), 6.6 (2H, d, *J=8 Hz,* H_{10}), 6.6 (2H, d *J=4 Hz*, CH); δ_C (DMSO): 163.9(*C*=O), 158.2 (py*C*=N), 146.0 (HN-CAr), 145.6 (C_{14}), 136.3 (C_5), 134.1 (C_9), 129.4 (C_2), 128.8 (C_1), 128.4 (C_7), 127.6 (C_4), 127.0(C_{13}) 126.7 (C_3), 118.5 (C_6), 118.0 (C_8), 115.4 (C_{10}), 115.1 (*C*-C=O), 73.7 (N-C-N); *m/z* (ES) 549 (100%, $[M+H]^+$), 274 (M^{2+}) or monomer.

Preparation of 2,2'-diquinolyl-3,3'-biquinazolin-4,4'-one 7

2,2'-diquinolyl-tetrahydro-3,3'-biquinazolin-4,4'-one **6** (1.44g, 2.62 mmol) was suspended in acetone (50ml) and, while stirring, $KMnO_4$ (4.17g, 2.63 mmol) was slowly added over 30 minutes. This turned the reaction mixture from white to purple to a brown/purple colour. After 4 hours the reaction was stopped, DCM (50ml) was added and the mixture was filtered to remove inorganic solids. The reaction mixture was washed with water and brine and checked with starch-iodide paper. The yellow organic layer was dried over magnesium sulphate, filtered and evaporated leaving a pale yellow solid (1.31g, 92%) recrystallised from DCM and ethanol to produce 2,2'-diquinolyl-3,3'-biquinazolin-4,4'-one **7** (0.94g, 66%); mp 264°C; (Found: C, 74.6; H, 3.71; N, 15.4 $C_{36}H_{20}N_6O_2$ requires C, 75.0; H, 3.70; N, 15.4 %); λ_{max}^{abs}(MeCN)/nm 326, 312 and 246 (ε/dm^3 mol^{-1} cm^{-1} 19367, 19480 and 44237); λ_{max}^{em}(MeCN)/nm 460; lifetime/ns 0.46 (77%), 1.94(23%); ν_{max}($CDCl_3$)/cm^{-1} 1698 (C=O), 1590, 1563 (C=C); δ_H (400 MHz, $CDCl_3$): 8.4 (2H, d *J=8 Hz,* H_5), 8.3 (2H, d *J=9 Hz,* H_7), 8.1 (2H,d *J=9 Hz,* H_1), 7.8 (4H, m, H_4, H_6), 7.7 (2H, m, H_9), 7.5 (2H, m, H_2), 7.4 (4H, m, H_{10}, H_3), 7.1 (2H, m, H_8); δ_C ($CDCl_3$): 160.1(*C*=O), 150.9 (N-C=N), 150.4 (py*C*=N), 146.7 (*C*-N=C), 146.3 (C_{12}), 136.6 (C_5), 135.0 (C_9), 129.7 (C_2), 129.4 (C_1), 128.3 (C_7), 127.9 (C_4), 127.8 (C_8), 127.7 (*C*-C=O), 127.3 (C_3), 122.1 (C_{10}), 121.8 (C_6); *m/z* (ES) 545 (100%, $[M+H]^+$).

Preparation of $(Re(CO)_3Cl)_2$(BiQpy) 8

$Re(CO)_5Cl$ (0.11g, 0.31 mmol) was added to a 10 ml round bottomed flask and dry toluene (2 ml) and 2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one **3** (0.07 g, 0.16 mmol) were added under nitrogen. The yellow mixture was heated to reflux for 2.5 hours. After this time the reaction mixture had become dark red and was left to cool and filtered or evaporated. The red solid was recrystallised from chloroform diffused with methanol producing red crystals of $Re(CO)_3Cl$(BiQ) **8** (0.11 g, 65%); mp dec. 248°C; (Found: C, 33.6; H, 1.74; N, 6.72 $Re_2C_{32}H_{16}N_6O_8Cl_2.CDCl_3$ requires C, 33.7; H, 1.54; N, 7.15 %); λ_{max}^{em}(MeCN)/nm 595; lifetime/ns 60; $\nu_{max}(CDCl_3)/cm^{-1}$ 2032, 1940, 1915 (C≡O), 1725 (C=O), 1594 (C=C); δ_H (400 MHz, $CDCl_3$): 9.2 (2H, d *J=5 Hz,* H_1), 8.7 (2H, d *J=9 Hz,* H_5), 8.4 (2H, d *J=9 Hz,* H_4), 8.2 (2H, m, H_8), 8.1 (2H, m, H_6), 8.0 (2H, m, H_3), 7.7 (2H, m, H_7) 7.6 (2H, m, H_2); δ_C ($CDCl_3$): 196.1, 195.3, 188.3 (C≡O), 158.6(*C*=O), 157.3 (N-C=N), 155.1 (C_1), 149.2 (C_{11}), 145.6 (C_9), 141.5, 138.2, 131.3, 131.2, 129.2, 128.8, 128.6, 119.5(ArC); *m/z* (ES) 1074 ($[M-Cl+2CO]^+$), 1021 ($[M-Cl]^+$), 906 ($[M-Cl-4CO]^+$).

Preparation of $(Re(CO)_3Cl)_2$(BiQmepy) 9

$Re(CO)_5Cl$ (0.11 g, 0.29 mmol) was added to a 10 ml round bottomed flask and under nitrogen dry toluene (2 ml) and 2,2'-di-6-methylpyridyl-3,3'-biquinazolin-4,4'-one **5** (0.07 g, 0.16 mmol) were added. The yellow mixture was heated to reflux for 2.5 hours. After this time the reaction mixture had become red and was left to cool and filtered leaving a dark orange solid (0.13 g, 77%). The orange solid was recrystallised from chloroform diffused with methanol producing red crystals of $(Re(CO)_3Cl)_2$(BiQmepy) **9** (0.11g, 68 %); mp 293 °C; (Found: C, 39.4; H, 2.42; N, 6.83 $Re_2C_{34}H_{20}N_6O_8Cl_2.0.5\ C_6H_5CH_3$ requires C, 39.9; H, 2.14; N, 7.44 %); λ_{max}^{em}(MeCN)/nm 590, 602; lifetime/ns 48; $\nu_{max}(CDCl_3)/cm^{-1}$ 2029, 1936, 1907 (C≡O); δ_H (400 MHz, $CDCl_3$): 8.7 (2H, d *J=8 Hz,* H_4), 8.4 (2H, d *J=8 Hz,* H_3), 8.1 (4H, m, H_2, H_7), 7.8 (2H, t *J=8 Hz,* H_6), 7.7 (2H, t *J=8 Hz,* H_5), 7.5 (2H, d *J=8 Hz,* H_1), 3.1 (6H, s, CH_3); *m/z* (ES) 1049 ($[M-Cl]^+$).

Preparation of $(Re(CO)_3Cl)_2$(BiQqu) 10

$Re(CO)_5Cl$ (0.11 g, 0.29 mmol) was added to a 10 ml round bottomed flask and under nitrogen dry toluene (2 ml) and 2,2'-diquinolyl-3,3'-biquinazolin-4,4'-one **7** (0.09 g, 0.16 mmol) were added. The yellow mixture was heated to reflux for 2.5 hours. After this time the reaction mixture had become dark red and was left to cool and evaporated. The red solid was recrystallised from chloroform producing $Re(CO)_3Cl)_2$(BiQqu) **10** (0.16 g, 96%) as a red solid; mp 292°C; λ_{max}^{em}(MeCN)/nm 707; lifetime/ns <10; ν_{max}(KBr)/cm^{-1} 2024, 1933 br s (C≡O), 1729 br s (C=O); 1587, 1523, 1505 (C=C); δ_H (400 MHz, $CDCl_3$) 9.0 (1H, d *J=8 Hz,* H_5), 8.9 (1H, d *J=7 Hz,* H_7) 8.8 (1H, d *J=7 Hz,* H_1) 8.4 (1H, d *J=8Hz,* $H_{5'}$), 8.3 (1H, d *J=8 Hz,* $H_{7'}$) 8.2 (2H, m, $H_{1'}$,H_6), 8.2 (1H, d *J=8Hz,* $H_{6'}$), 8.0 (2H, m, H_4, $H_{4'}$), 7.9 (1H, m, H_9), 7.8 (2H, m, H_2, $H_{2'}$) 7.7 (1H, m, $H_{9'}$) 7.5 (4H, m, H_{10}, $H_{10'}$, H_3, $H_{3'}$) 7.1 (2H, m, H_8, $H_{8'}$); *m/z* (ES) 856 ([$Re(CO)_3$(BiQqu)]$^+$), 545 (BiQqu$^+$)

Preparation of $(Re(CO)_3Cl)$(BiQpy) 11a/11b

$Re(CO)_5Cl$ (0.11 g, 0.29 mmol) was added to a 10 ml round bottomed flask and under nitrogen dry toluene (2 ml) and 2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one **3** (0.13 g, 0.29 mmol) were added. The yellow mixture was heated to reflux for 3 hours. After this time the reaction mixture had become dark red and was left to cool and filtered and washed with diethyl ether leaving $(Re(CO)_3Cl)$(BiQ) **11a** (0.10g, 46%) as a dark orange solid; mp 207°C; ν_{max}($CDCl_3$)/cm-1 2029, 1929, 1908(C≡O), 1710 (C=O), 1603 (C=C); δ_H (400 MHz, $CDCl_3$): 9.2 (1H, d *J=5 Hz,* H_1), 8.6 (1H, d *J=9 Hz,* H_5), 8.3 (1H, d *J=8 Hz,* H_4), 8.2 (3H, m, $H_{1'}$, H_8, $H_{5'}$), 8.1 (1H, d *J=9 Hz,* $H_{4'}$), 8.0 (6H, m, H_3, H_6, $H_{8'}$, $H_{7'}$, H_7, $H_{2'}$), 7.6 (3H, m, H_2, $H_{3'}$, $H_{6'}$)); *m/z* (FAB) 750 (100%, M^+)

The filtrate was precipitated with petroleum ether producing $(Re(CO)_3Cl)$(BiQ)H **11b** as a red/orange solid (0.095g, 44%) mp 200°C; ν_{max}($CDCl_3$)/cm-1 2029, 1929, 1908(C≡O), 1709 (C=O), 1601 (C=C); δ_H (400 MHz, $CDCl_3$): 9.2 (1H, d *J=5 Hz,* H_1), 8.7 (1H, d *J=9 Hz,* H_5), 8.5 (1H, d *J=8 Hz,* H_4), 8.5 (1H, d, $H_{1'}$) 8.2 (1H, d, *J=8* Hz, H_8) 8.2 (1H, d, *J=8 Hz,* $H_{5'}$), 8.1 (1H, d *J=9Hz,* $H_{4'}$), 8.0 (1H, m, H_6) 7.9 (2H, m, $H_{8'}$, $H_{7'}$) 7.8 (2H, m, H_3, $H_{2'}$), 7.6 (3H, m, H_2, H_7, $H_{6'}$) 7.3 (1H, m, $H_{3'}$); δ_C ($CDCl_3$): 159.6(*C*=O), 157.22(N-C=N), 154.0 (C_1), 150.3 (C_{11}), 148.9 (C_9), 145.4, 138.8, 137.6, 136.8, 136.6, 130.4, 130.1, 129.1, 128.9, 128.8, 128.5, 128.2, 127.9, 125.8,

125.3, 124.9, 120.9, 119.8(ArC), 40.4 (CH); *m/z* (FAB) 751 (100%, $[M+H]^+$), 750 (98, M^+).

Preparation of $[(Re(CO)_3(MeCN))_2(BiQpy)][(BF_4)_2]$ 12.

$Re(CO)_3Cl(BiQpy)$ **8** (0.57g, 0.54 mmol) was dissolved in acetonitrile (30ml) under nitrogen in a side arm 100ml round bottomed flask. $AgBF_4$ (0.23g, 1.16 mmol) was added and the reaction was heated to reflux overnight in the dark. NMR showed the reaction had not gone to completion so more $AgBF_4$ was added and left to reflux again overnight. The reaction was left to cool, filtered through celite, the filtrate was evaporated and recrystallised from acetonitrile and ethyl acetate in the freezer. Orange precipitate and large yellow crystals formed. The large crystals were $[Re(MeCN)_3(CO)_3][BF_4]$ as seen by X-ray crystallography, and the precipitate was $[(Re(CO)_3(MeCN))_2(BiQpy)][(BF_4)_2]$ **12.** The large crystals redissolved at room temperature (0.10g, 15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2053, 1949 (C≡O), 1702 (C=O), 1600, (C=C); δ_H (400 MHz, $CDCl_3$): 8.8 (2H, d *J=4 Hz,* H_1), 8.4 (2H, d *J=8 Hz,* H_5), 7.9 (2H, d *J=8 Hz,* H_4), 7.8 (4H, m, H_8, H_6), 7.7 (2H, t *J=8 Hz,* H_3), 7.5 (2H, t *J= 6 Hz,* H_7) 7.3 (2H, t *J=8 Hz,* H_2), 2.45 (6H, s, MeCN).

Preparation of $[(Re(CO)_3(bipy))_2(BiQpy)][(BF_4)_2]$

4,4'-Bipyridine (0.03g, 0.19 mmol) was dissolved in THF (10 ml) added to a suspension of $[Re(CO)_3(MeCN)(BiQpy)][BF_4]$ (0.07g, 0.06 mmol) in THF and left to reflux for 6 hours. The complex did not dissolve and no colour changed occurred so DCE (10 ml) was added but the complex still did not dissolve. Acetonitrile was added and the reaction mixture dissolved and was left to reflux for 2.5 hours. The solution was evaporated leaving $[(Re(CO)_3(bipy))_2(BiQpy)][BF_4]$ (0.05g, 64%) as a yellow solid; $\nu_{max}(CDCl_3)/cm^{-1}$ 2047 2028, 1982 (C≡O), 1731, 1699 (C=O), 1594 (C=C); NMR shows a mixture of bipy and starting rhenium complex.

Preparation of $(BiQpy)PdCl_2$ 14

2,2'-dipyridyl- 3,3'-biquinazolin-4,4'-one **3** (0.53g, 1.20 mmol) and $Pd(MeCN)_2Cl_2$ (0.31g, 1.20 mmol) were partially dissolved in acetonitrile (40 ml) and DCM (10ml) in a 100ml round bottomed flask. This was heated to reflux for 4 hours and left to cool overnight producing $(BiQpy)PdCl_2$ **14** (0.65 g, 88%) as orange crystals; mp dec.

258°C; (Found: C, 47.5; H, 2.49; N, 12.4 $PdC_{26}H_{16}N_6O_2Cl_2.0.5CH_2Cl_2$ requires C, 47.9; H, 2.58; N, 12.7 %); ν_{max}(KBr)/cm^{-1} 1700 (C=O), 1591, 1564 (ArC=C); δ_H (400 MHz, $CDCl_3$): 9.5 (1H, d *J=5 Hz,* H_1) 9.3 (1H, d *J=5 Hz,* H_1), 8.7 (1H, d *J=9 Hz,* H_5), 8.4 (1H, d *J=9 Hz,* H_5), 8.2 (1H, d *J=9 Hz,* H_4), 8.0 (1H, m, H_8), 8.1 (2H, m, H_6), 8.0 (2H, m, H_3), 7.7 (2H, m, H_7) 7.6 (2H, m, H_2); δ_C ($CDCl_3$): 196.1, 195.3, 188.3 (C≡O), 158.6(*C*=O), 157.3 (N-C=N), 155.1 (C_1), 149.2 (C_{11}), 145.6 (C_9), 141.5, 138.2, 131.3, 131.2, 129.2, 128.8, 128.6, 119.5(ArC); *m/z*(ES) 1031 ($[L_2PdCl]^+$), 585 ($[LPdCl]^+$), 540 ($[LPd]^+$), 443 ($[L-H]^+$).

Attempted preparation of $Re(CO)_3Cl(BiQpy)PdCl_2$

$Re(CO)_5Cl$ (0.09 g, 0.25 mmol) was added to a 10 ml round bottomed flask and, under nitrogen, dry toluene (2 ml) and $(BiQpy)PdCl_2$ (0.15 g, 0.24 mmol) were added. The orange mixture was refluxed for 4 hours and left to cool overnight. The reaction mixture turned a dark orange. Recrystallisation produced orange crystals of $(BiQ)PdCl_2$.as shown by the x-ray structure. ν_{max}(KBr)/cm^{-1} 1701 (C=O), 1592, 1564 (ArC=C)

Preparation of $(BiQMepy)(PdCl_2)_2$ 15

2,2'-di-6-methylpyridyl-3,3'-biquinazolin-4,4'-one **5** (0.18g, 0.39 mmol) and $Pd(MeCN)_2Cl_2$ (0.20g, 0.76 mmol) were partially dissolved in DCE (25 ml) 50ml round bottomed flask. This was heated to reflux overnight, cooled, filtered and evaporated leaving $(BiQMepy)(PdCl_2)_2$ (0.29g, 95%) as a dark orange solid; mp>330°C; ν_{max}(nujol)/cm^{-1} 1716 (C=O), 1603 (C=C); δ_H (400 MHz, CD_3CN): 8.2 (2H, d *J=8 Hz,* H_4), 7.9 (6H, m, H_2, H_3, H_6), 7.8 (2H, d *J=7 Hz,* H_7), 7.6 (2H, t *J=8 Hz*, H_5), 7.3 (2H, d *J=6 Hz,* H_1), 3.7 (6H, s, CH_3); *m/z* (EI) 718 (Pd_2(BiQMepy)+O_2).

Preparation of $(BiQqu)(PdCl_2)_2$

2,2'-diquinolyl-3,3'-biquinazolin-4,4'-one **7** (0.16g, 0.30 mmol) and $Pd(MeCN)_2Cl_2$ (0.15g, 0.59 mmol) were partially dissolved in DCE (40 ml) in a 50ml round bottomed flask. All solids dissolved on heating. The solution was heated to reflux overnight. An orange precipitate started to form. The reaction was left to cool; filtered and evaporated orange precipitate (0.18g) The NMR, UV and IR spectra looked like a mixture of starting materials.

Preparation of $[Pd(BiQMepy)_2][(BF_4)_2]$ 16/16a

$Pd(MeCN)_2Cl_2$ (0.11g, 0.44 mmol) was mostly dissolved in acetonitrile (25ml) in 100 ml side arm round bottomed flask, under nitrogen. $AgBF_4$ (0.20g, 1.01 mmol) was added and the mixture was stirred at reflux for 2 hours, in the dark. BiQMepy **5** (0.41g, 0.88mmol) was partially dissolved in acetonitrile and the palladium solution was added by filter canula to the BiQMepy **5** mixture. The reaction was refluxed for two hours, left to cool and filtered through celite leaving a yellow/orange solution. This was evaporated and recrystallised from acetonitrile and ethyl acetate giving $[(Pd(MeCN)_2)_2BiQMepy][(BF_4)_4]$ **16a** (0.17g, 65% based on available palladium); m.p. >330°C; $\nu_{max}(CDCl_3)/cm^{-1}$ 2256 (C≡N), 1614(C=C); δ_H (400 MHz, CD_3CN): 8.2 (2H, t *J=8 Hz,* H_2), 8.1 (2H, d *J=8 Hz,* H_4), 8.0 (2H, m, H_3), 7.9 (2H, m, H_6), 7.8 (2H, d *J=8 Hz,* H_7), 7.6 (2H, d *J=8 Hz,* H_1), 7.5 (2H, t *J=7 Hz,* H_5), 2.5 (6H, s, CH_3); δ_C ($CDCl_3$): 168.4, 156.9, 146.1, 137.8, 135.8, 134.1, 129.4, 128.3, 126.9, 124.6,124.5, 121.5, 120.8 (ArC); *m/z* (EI) 718 (Pd_2(BiQMepy)O_2), 594.1 (Pd(BiQMepy)O).

Preparation of $[Fe(BiQpy)_3]Cl_2$

Ethylene glycol (5ml) had N_2 bubbled through for 15 minutes in a 100ml schlenk. $FeCl_3.6H_2O$ (0.09g, 0.33 mmol) and. BiQpy **3** (0.42g, 0.95 mmol) were added to the schlenk and the solution was heated to reflux overnight. The reaction mixture went from yellow to green and once evaporated the green compound was insoluble. This reaction was repeated starting with $FeCl_2.4H_2O$ (0.08g, 0.39 mmol) in degassed acetonitrile and methanol and molecular sieves to remove water produced. The reaction turned from yellow to brown. The brown solid was very insoluble and could not be characterised

Preparation of Ruthenium Blue[24]

$RuCl_3.3H_2O$ (0.40g, 1.54mmol) was dissolved in a mixture of ethanol (12ml) and water (8ml) and reflued for 4 hours. The reaction mixture turned dark green the dark blue with a small amount of black deposit around the sides. The characteristic blue solution was ruthenium blue and was used in situe.

Preparation of $Ru(Bipy)_2Cl_2.2H_2O$[24]

As literature procedure. λ_{max} (H_2O)/nm 370 nm, 310 nm, (lit[26] 370, 315nm); δ_H (400 MHz, D_2O): 8.7 (4H, d *J=4 Hz,* H_1), 8.5 (2H, br m, H_3), 8.3 (2H, br d *J=8 Hz,* H_4), 8.2 (2H, br t *J=7 Hz,* H_2).[26]

Attempted preparation of $[Ru(BiQpy)_3]$ $[(PF_6)_2]$ 17

Ethylene glycol (5ml) had N_2 bubbled through for 15 minutes, then $RuCl_3.6H_2O$ (0.10g, 0.38 mmol) was dissolved in it in a 100ml schlenk. Biquinazolinone (0.66g, 1.48 mmol) was added and the brown solution was heated to reflux overnight. The reaction was left to cool, NH_4PF_6 was added and the product was extracted into DCM and washed with water. The DCM was evaporated leaving a purple solid. The solid was recrystallised from DCM and petroleum ether leaving a purple solid and green solution. The purple solid was very impure so the reaction was repeated.

Ruthenium blue (0.15g, 0.58 mmol) in ethanol/water solution (7.5ml) was added to a suspension of BiQpy **3** (1.02g, 2.30 mmol) in ethanol (7ml). The reaction mixture was refluxed overnight and it turned from blue to purple/brown. The reaction solution was precipitated with saturated NH_4PF_6 producing a ruthenium BiQpy species **17** (0.41g) as a purple solid λ_{max} (MeCN)/nm 371, 313, 221; ν_{max}(nujol)/cm^{-1} 3575, 3483, 3209 (OH) 1672 (C=N) 1581, 1519(ArC=C); δ_H (400 MHz, DMSO): broad complicated peaks typical of ruthenium complexation, unable to elucidate. *m/z* (ES) 943 (?) 445 (BiQpy)

Attempted preparation of $[Ru(BiQQu)_3][(PF_6)_2]$ 18

Ruthenium blue (0.05g, 0.20 mmol) in ethanol/water solution(2.5ml) was added to a suspension of BiQQu **7** (0.42g, 2.32 mmol) in ethanol (7ml). DCE was added to ais ligand salvation. The reaction mixture was refluxed overnight and it turned from blue to dark green. The reaction solution was evaporated and dissolved on heating with acetone. This solution was precipitated with saturated NH_4PF_6 producing BiQQu **7** (0.23g) as a green crystalline solid; λ_{max} (MeCN)/nm 352, 315, 252; ν_{max}(nujol)/cm^{-1} 3154 (OH) 1698 (C=O) 1590, 1562(ArC=C); δ_H (400 MHz, $CDCl_3$): looks identical to ligand *m/z* (ES) 545 (BiQQu)

Preparation of $[Ru(Bipy)_2(BiQpy)][(PF_6)_2]$ 19

$[Ru(Bipy)_2Cl_2].Cl.2H_2O$ (0.10g, 0.18 mmol) was dissolved in methanol and was added to a suspension of BiQpy (0.09g, 0.19 mmol) in methanol starting as an orange mixture. After heating at reflux for 1.5 hours the reaction mixture darkened and after 4 hours a sample showed only ligand in the proton NMR so chloroform was added to the reaction mixture to increase ligand solubility. After a subsequent 3 hours at reflux the reaction solution had turned red. The chloroform was evaporated and the mixture filtered to remove unreacted ligand. Saturated NH_4PF_6 solution was added and most of the methanol was removed leaving $[Ru(Bipy)_2(BiQpy)][(PF_6)_2]$ **19** (0.18g, 90%) as a red solid m.p. dec. 269°C; λ_{max} (MeCN)/nm 550, 375, 294, 228, 203; ν_{max}(nujol)/cm^{-1} 3330 (NH) 1721, (C=O), 1696 (C=N) 1606, 1568(ArC=C); δ_H (400 MHz, CD_3CN): broad peaks 14.0(1H, s br, HCl) 9.5 (2H, s, NH), 8.2 (2H, d *J=8 Hz,* $H_{1,}$), 8.1 (2H, s, H_5), 7.9 (2H, m, H_4, H_8,), 7.8 (4H, m,H_7, H_2), 7.5 (2H, m, H_6), 7.1 (2H, m, H_3); *m/z* (ES)1021 (M-PF_6 +H_2O) 1003 ($[M\text{-}PF_6]^+$).

Attempted preparation of $[Ru(Bipy)_2(BiQMepy)][(PF_6)_2]$ 20

$[Ru(Bipy)_2Cl_2].Cl.2H_2O$ (0.10g, 0.17 mmol) was dissolved in methanol and was added to a chloroform solution of BiQpy (0.08g,0.18 mmol) starting as an orange mixture. After heating at reflux for 3.5 hours the reaction mixture had turned red. The chloroform was evaporated and the mixture filtered to remove unreacted ligand. Saturated NH_4PF_6 solution was added and most of the methanol was removed possibly leaving a mixture of $Ru(Bipy)_2Cl_2$ and BiQMepy(0.13g) as a red/orange solid m.p. dec. 228°C; λ_{max} (MeCN)/nm 550, 421, 381, 296, 210; ν_{max}(nujol)/cm^{-1} 1696 (C=N) 1579, 1563 (ArC=C); δ_H (400 MHz, CD_3CN): 14.2 (1H, s br, HCl) 9.5 (2H, s, NH), 8.2 (2H, d *J=8 Hz,* H_4), 7.9 (2H, m,H_6),7.7 (2H, d *J=8 Hz* H_3) 7.7 (2H, d *J=8 Hz,* H_7)7.5 (4H, m, H_5, H_2), 7.1 (2H, d *J=8 Hz,* H_1) 1.8 (6H, s, CH_3); *m/z* (ES) 484 ($(Ru(Bipy)_2Cl_2$) 473 (BiQMepy), 449 ($(Ru(Bipy)_2Cl$)

Attempted preparation of $[Ru(Bipy)_2(BiQQu)][(PF_6)_2]$ 21

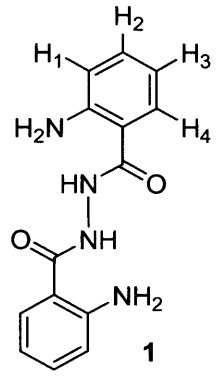
$[Ru(Bipy)_2Cl_2].Cl.2H_2O$ (0.06g, 0.10 mmol) was dissolved in methanol and was added to a chloroform solution of BiQQu (0.05g,0.10 mmol); starting as an orange mixture. After heating at reflux for 3.5 hours the reaction mixture had turned red. The chloroform was evaporated and the mixture filtered to remove unreacted ligand.

Saturated NH_4PF_6 solution was added and most of the methanol was removed possibly leaving a mixture of $Ru(Bipy)_2Cl_2$ and BiQQu **7** (0.08g,) as a red solid m.p. dec. 247°C; λ_{max} (MeCN)/nm 548, 371, 297, 238, 207; ν_{max}(nujol)/cm^{-1} 1703 (C=O), 1686 (C=N) 1604, 1502 (ArC=C); δ_H (400 MHz, CD_3CN): 14.2 (1H, s br, HCl) 9.5 (2H, s, NH), 8.4 (2H, d *J=8 Hz,* H_5), 8.3 (2H, d *J=9 Hz,* H_7), 8.2 (2H,d *J=9 Hz,* H_1), 8.0 (2H, m, H_9),7.8 (4H, m, H_4, H_6), 7.5 (2H, m, H_2), 7.4 (4H, m, H_{10}, H_3), 7.1 (2H, m, H_8); *m/z* (ES) 484 ($(Ru(Bipy)_2Cl_2)$ 473 (BiQMepy), 449 ($(Ru(Bipy)_2Cl)$, 545 ($[M+H]^+$).

Preparation of $[(Ru(Bipy)_2)_2(BiQpy)][(PF_6)_4]$

$[Ru(Bipy)_2Cl_2].Cl.2H_2O$ (0.10g, 0.18mmol) was dissolved in methanol and was added to a chloroform solution of BiQpy (0.04g,0.09 mmol) starting as an orange mixture. After heating at reflux for 3.5 hours the reaction mixture had turned red. The chloroform was evaporated and the mixture filtered to remove unreacted ligand. Saturated NH_4PF_6 solution was added and most of the methanol was removed leaving $[(Ru(Bipy)_2)_2(BiQpy)][(PF_6)_4]$ (0.13g, 73%) as a red solid mp dec. 269°C; spectroscopic data identical to $[Ru(Bipy)_2(BiQpy)][(PF_6)_2]$

6.4 Compound List



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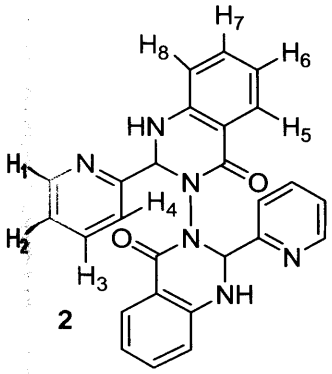

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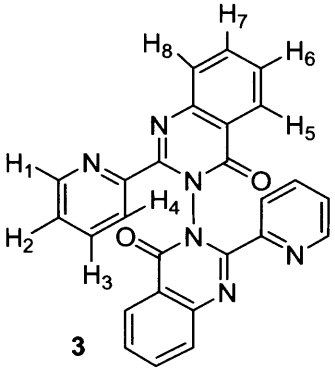

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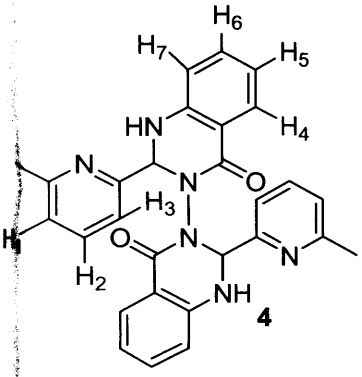

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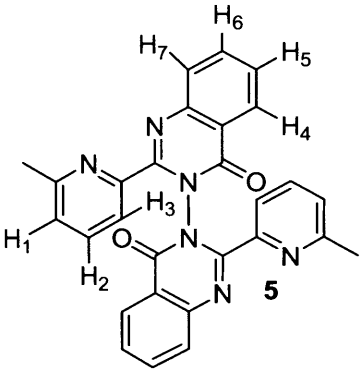

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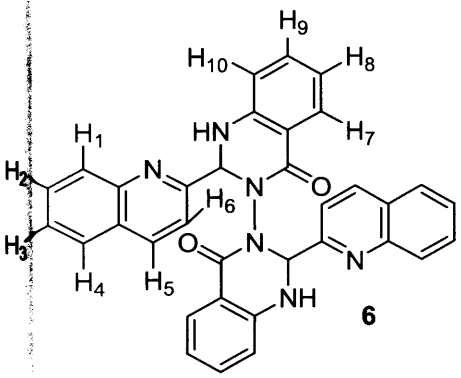

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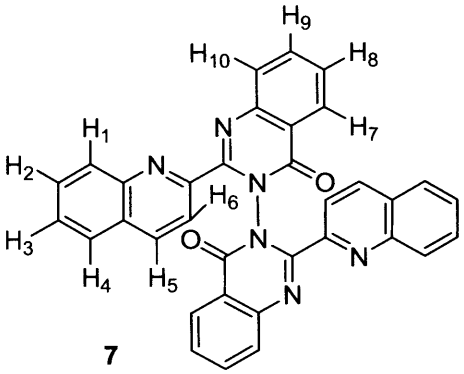

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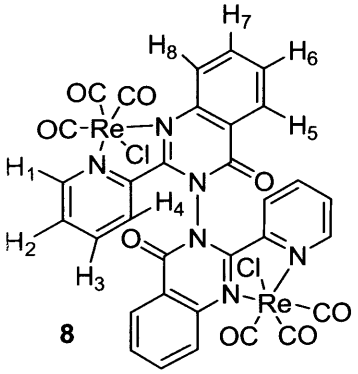

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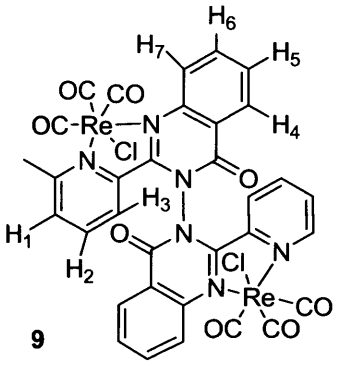

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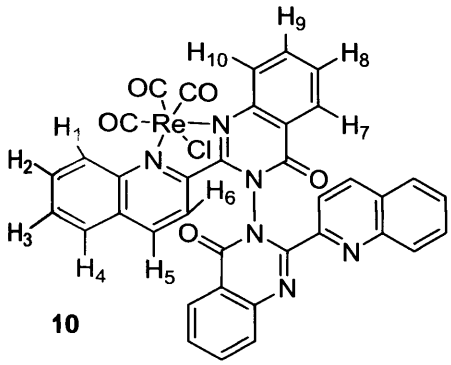

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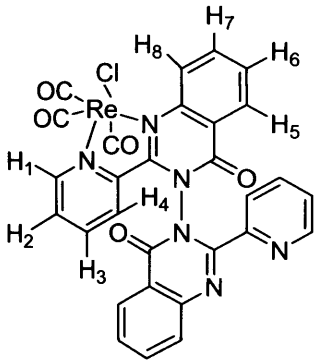

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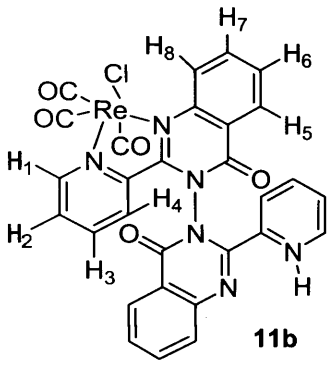

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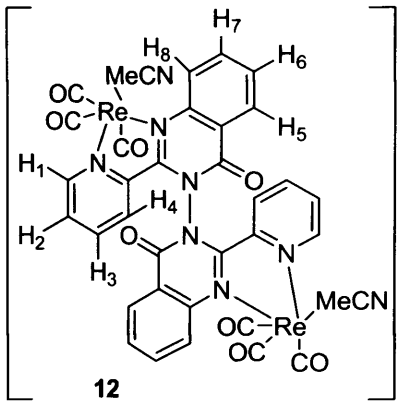

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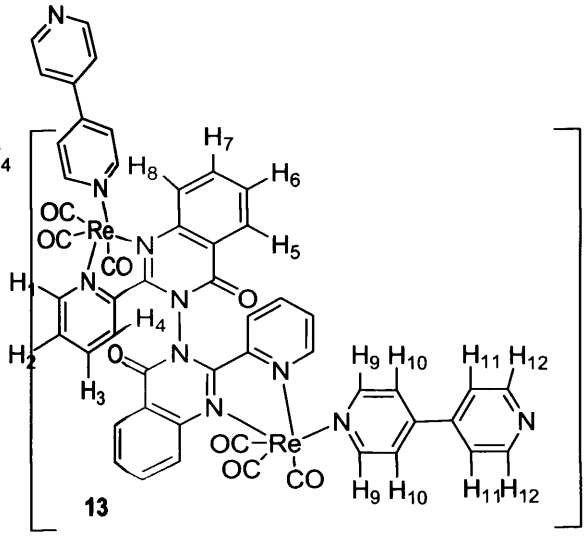

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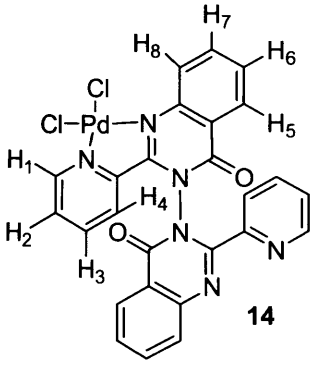

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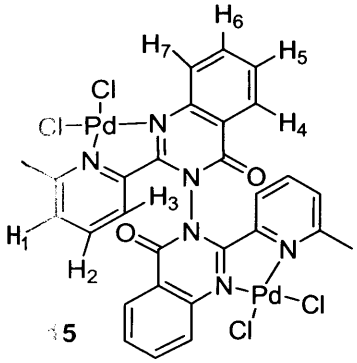

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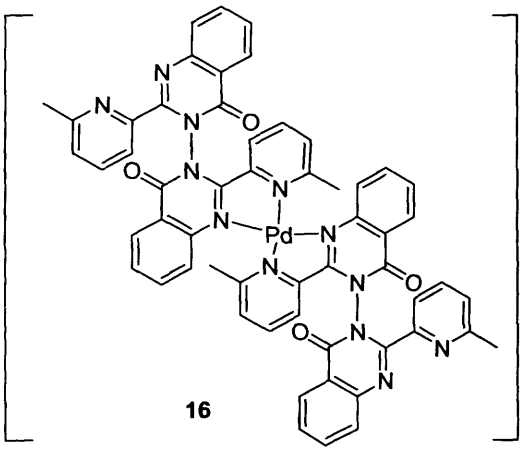

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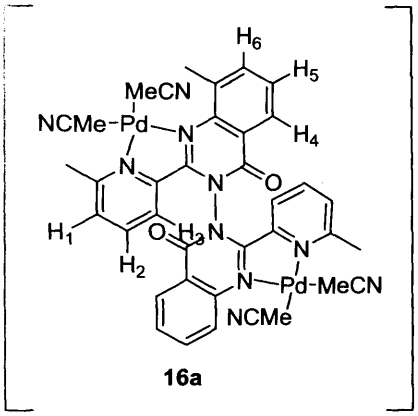

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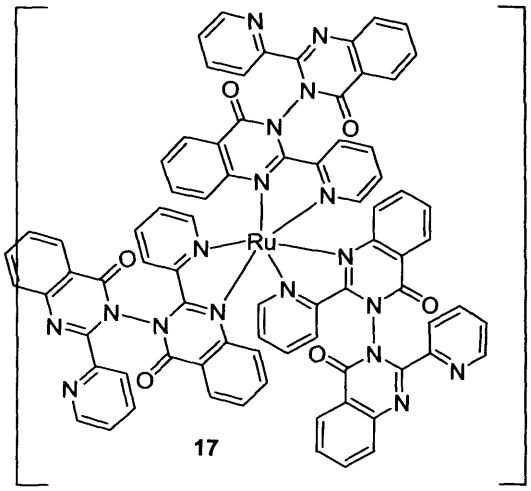

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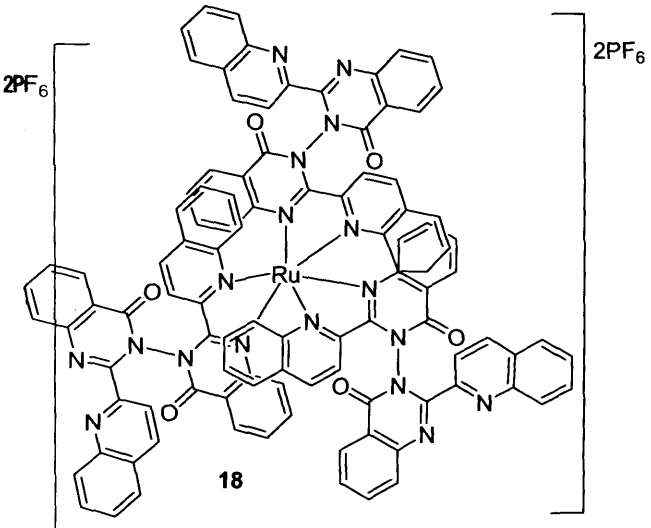

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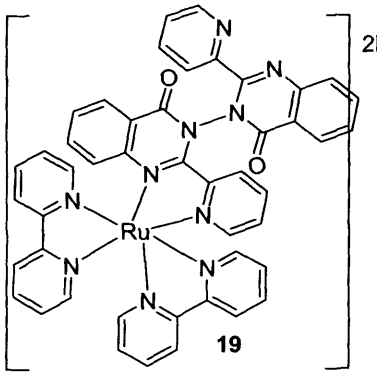

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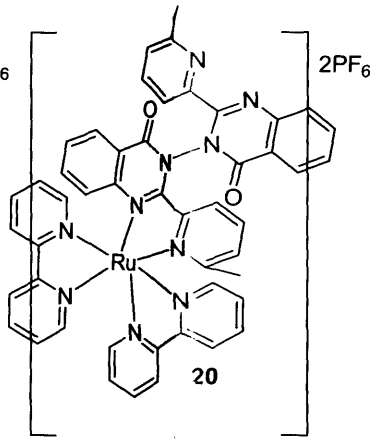

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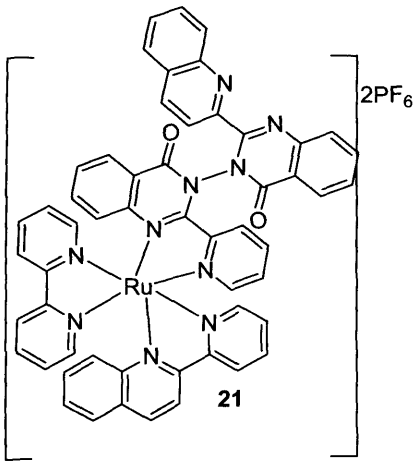

21

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