Synthesis and Study

of

New Nitrogen-Containing Ligands

A thesis submitted in partial fulfilment

of the requirements for the Degree

of

Doctor of Philosophy in Chemistry

at the

University of Canterbury

by

Chris M. Hartshorn

University of Canterbury, Christchurch, New Zealand

1996

Acknowledgements

I wish to express my gratitude to Dr. Peter Steel for his encouragement and supervision over the last four years stemming right back to my Honours research, and also for the odd beer or hundred at the Staff Club. All of these factors helped to maintain the productivity as well as the state of mind over this time. Thanks also to Prof. Ward Robinson and Dr. Mark Turnbull for their help with crystallographic messes in Peter's absence. Similarly, thanks also to Bruce Clarke for coping with some "less than satisfactory" mass spectrometric samples.

Special thanks to my parents for their support and encouragement, and also to the rest of my family who have provided great amounts of motivation over a long period of time.

Finally, full credit to Canterbury Draught and to all those who have partaken in this beverage with me over the years....cheers.

Contents

Abstract

Thirty new nitrogen-containing ligands have been synthesised and the coordination chemistry of the majority of these has been investigated. The coordination chemistry of previously reported ligands related to these has also been investigated. The ligands contain a central benzene ring to which nitrogen-containing heterocycles have been appended via one or two linking atoms. In this manner, between two and six such groups have been attached to a benzene ring to give ligands which display a great variety of modes of coordination to transition metals.

These complexes have been characterised by combinations of N.M.R. spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography - the X-ray crystal structures of thirty one complexes have been determined. Among these thirty one structures are chelated and macrocyclic complexes containing monochiral ligands, a supramolecular ten-component cage containing a guest molecule, a new N_3(arene) mode of coordination, as well as a number of complexes in which arene-arene and metal-arene interactions are observed. Cyclometallated complexes of some of these ligands have also been prepared, the dynamic N.M.R. processes of which have been investigated by variable temperature ^{1}H N.M.R. methods.

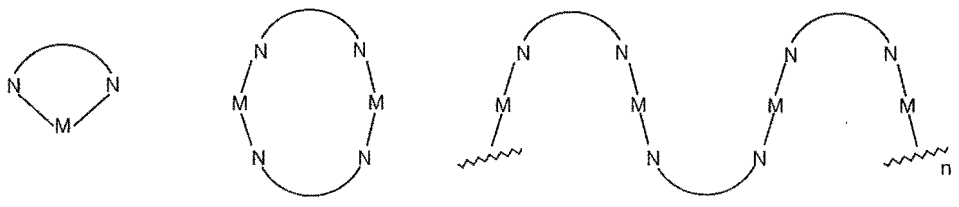
Chapter 1

Overview

Overview

Extensive investigation of poly-heterocyclic ligands and their metal complexes has given rise to a vast array of applications for these compounds.[1,2] One such class of compounds, those incorporating aromatic nitrogen-containing heterocycles, has been particularly well studied as a result of both the number of heterocycles available and the interesting and varied properties that their complexes display.[3-10]

A ligand containing two monodentate nitrogen heterocycles has a range of modes of metal coordination available to it (fig. 1.1a-c).[11] A number of factors contribute to which type of coordination is adopted in a particular complex: the specific heterocycle used, the flexibility of the link between the two heterocycles and the stereochemical preferences of the coordinating metal ion each contribute to the type of complex that assembles.[12] For a ligand incorporating a third heterocycle, combinations of the bis-heterocyclic modes of coordination are possible - for example two can be chelating to one metal, while the third bridges to a second metal - or triply-chelating or trinuclear bridging dimeric complexes are possible (fig. 1.1d,e). As increasing numbers of heterocycles are contained in a ligand, more combinations of the above, as well as new modes of coordination, become possible. Current research in coordination chemistry is focused, in part, on predicting and controlling which mode of coordination is adopted in a complex, as well as expanding and investigating the range of modes of coordination that are known.[13-20] In this respect, an area of coordination chemistry that is receiving much current attention is in its applications to supramolecular chemistry.



1.1a : Chelating **1.1b** : Bridging Dimeric **1.1c** : Bridging Polymeric

1.1d : Triply-Chelating **1.1e** : Trinuclear Bridging Dimeric

Fig. 1.1

Supramolecular chemistry is defined as "chemistry beyond the molecule, bearing on the organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces".[21] Early investigations of supramolecular self-assembly revolved around the use of hydrogen bonds to assemble supramolecular structures from individual molecular components, primarily because of the role of this type of interaction in biological systems.[22] However, in the last two decades the advantages of coordination chemistry in self-assembly processes have become apparent.[23] By selecting a metal, which will typically have a preferred coordination number and geometry, and choosing a ligand with the desired type, number and spatial arrangement of coordinating atoms, the self-assembly of a metallosupramolecular structure can be controlled to give useful and interesting architectures.[24-29]

1.2a **1.2b**

Fig. 1.2

A second type of interaction that has been exploited in supramolecular structures is that between two aromatic rings.[29,30] The two strongest aromatic interactions observed involve different orientations of the two aromatic rings: the π-stacked interaction wherein the rings are coplanar (1.2a); and a face-to-edge arrangement where the two rings are orthogonal (1.2b). A number of recent reports have discussed whether charge transfer or electrostatics lead to such aromatic interactions.[31-33] Such interactions between aromatic rings have been identified as being a major factor in the assembly of many supramolecular structures in chemistry as well as in biology and materials science.[33,34] The stereochemistry of organic reactions and binding affinities in host-guest chemistry are also areas where these interactions have significant influence.[31]

This thesis describes the synthesis and complexes of new nitrogen-containing heterocyclic ligands. These ligands, represented by the general structure shown (fig. 1.3), incorporate nitrogen-containing heterocycles attached through linking groups, X, to a central benzene ring. The use of a benzene allows for up to six heterocycles to be appended to the core of the ligand; and when two to four such groups are used, different spatial arrangements of the coordinating groups can be obtained by varying the substituent pattern on the benzene ring. By varying the number and arrangement of

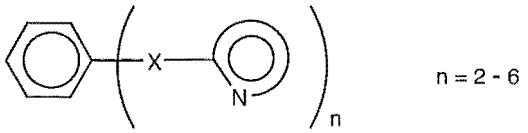


Fig. 1.3

heterocycles in this way the coordinating properties of the ligand can be controlled.

Other modifications to the ligand allow for further control of the coordination to a metal. The linking group, X, can be varied, both in the number of atoms linking the benzene to the heterocycle - one or two atoms are used in this work - and also in the type of atom used - carbon, oxygen, sulphur have been incorporated. Different heterocycles can be used, which will also vary the properties of the complexes obtained; pyridine and pyrazole have been used in the course of this work. The use of other heterocycles is currently being investigated by other workers.

By varying the design of the ligands in these ways, the metallosupramolecular structures characterised - thirty one of them crystallographically - display a range of different coordinating interactions. Metal-heterocycle chelating, bridging dimeric and polymeric structures, structures containing metal-metal bonds, metal-benzene σ-bonds and metal-benzene π-interactions, have all been observed, depending on the specific heterocycle, linking groups and benzene substituent pattern incorporated. Many complexes also contain π–π stacked aromatic rings which has allowed conclusions to be drawn about the preferred ring orientations in such interactions.

Chapter 2

Complexes of Polypyridyl Ligands

Complexes of Polypyridyl Ligands

2.1 Introduction.

Ligands containing more than one pyridine group have been known for over a century.[35] In particular, the coordination chemistry of 2,2'-bipyridine (2,2'-bpy, fig. 2.1) has been and continues to be intensely studied, and stable complexes are known for almost all metals in the periodic table.[36] Current interest in complexes containing 2,2'-bpy stems from their interesting electrochemical, photophysical and photoelectrochemical properties.[37]

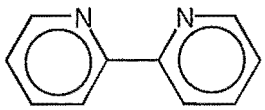


Fig. 2.1

The mode of coordination of 2,2'-bpy to a metal is typically chelation, where the two nitrogen donors coordinate to the same metal.[36,37] Coordination in this manner results in a favourable five-membered chelate ring system. If, instead of a direct link between the two pyridine groups, there are linking atom(s) joining the two heterocycles, chelation would lead to larger, less favourable ring sizes, or other modes of coordination may result.

A number of complexes containing bispyridyl ligands with one linking atom (2.2a) have been structurally characterised.[38-46] Despite the use of a variety of linking atoms (C, N, P, S) and an even wider variety of metals (Pd, Cu, Co, W, Mo, Cr, Cd, Ag), chelation to the metal to give a six-membered chelate ring is the dominant mode of coordination. Exceptions to this include a molybdenum complex, where a ligand comprised of two pyridine rings linked by a nitrogen atom is only monocoordinate,[47] and a metallopolymeric silver complex where the ligand (two pyridines linked by a carbonyl carbon) bridges two metal centres.[48] The same predominance of chelated structures is also observed for ligands containing a two atom pyridine bridge (2.2b),[49-56] although, for example, a metallopolymeric structure is observed for a mercury complex.[57] On extending the pyridine linkage still further, a different type of complex is observed from those of the shorter-linked ligands. A copper complex of 1,3-bis(2-pyridyl)propane (2.2c) is a discrete [2+2] macrocyclic system, where a 16-membered

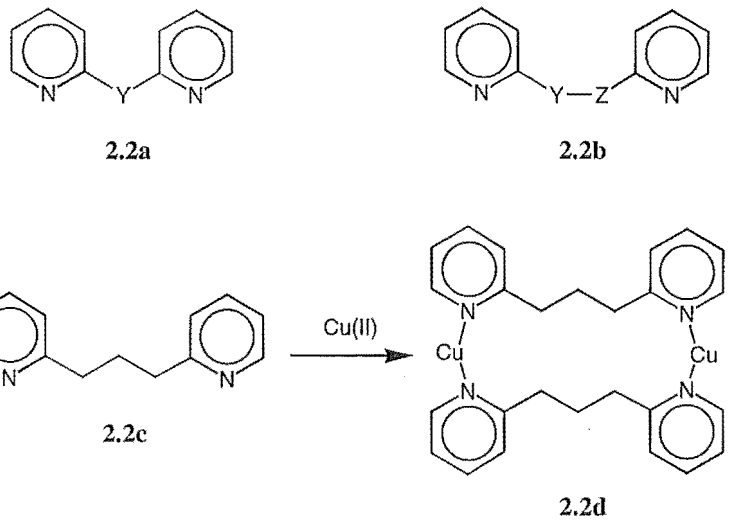


Fig. 2.2

ring is formed, the backbone of which contains two copper atoms bridged by two ligands (2.2d).[58] As discussed in the previous chapter, the self-assembly and properties of such compounds are the subject of much current investigation. Examples of further extensions of the organic linkage between two 2-substituted pyridines are limited, and typically incorporate extra donor atoms either in the linkage or branching out from it.

The coordination chemistry of two linked 4-substituted pyridines has, however, been more thoroughly investigated, without the presence of extra donor atoms in, or around, an extended linking chain. In contrast to 2,2'-bpy, 4,4'-bipyridine (2.3a) can not chelate to a metal. However, the rigid linearity of this ligand has allowed for its incorporation into macrocyclic tetranuclear coordination compounds.[59,60] The series of

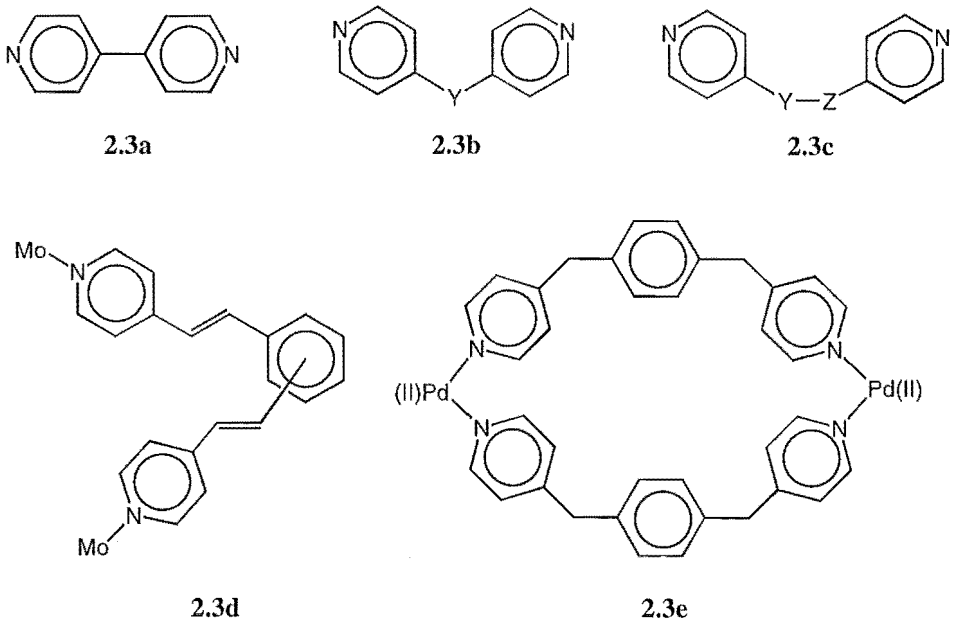


Fig. 2.3

bis-4-substituted pyridyl ligands ranges through compounds with one linking atom (2.3b), where [2+2] macrocyclic complexes are common, to those with two (2.3c), where again [2+2] systems are typical,[61] although monodentate,[62] metallopolymeric[63] and macrocyclic tetranuclear[61] structures have also been observed. The linked 4,4'-bpy system has been further expanded to include aromatic rings linking the two pyridine groups. The complexes of such ligands have been used both in studies of long range metal-metal interactions (eg. 2.3d),[7] and significantly, in a number of studies where a rich array of supramolecular coordination compounds have been constructed. Structures such as catenanes, interpenetrating molecular ladders and bricks, as well as standard [2+2] macrocycles have been characterised using a benzene ring as part of the pyridine linkage (eg. 2.3e).[26,64-66]

Given the interesting coordination compounds involving an aromatic linking group, and the precedent for macrocycle formation involving 2-substituted pyridines, it is surprising that the coordination chemistry of ligands containing both these structural features has not been examined. The first part of this chapter discusses the syntheses and complexes of ligands matching this description (fig. 2.4) with the specific aim of characterising macrocyclic structures. Included in this are six X-ray structure determinations: a chelated palladium complex, one palladium and two silver [2+2] macrocyclic complexes, and two metallopolymeric silver complexes.

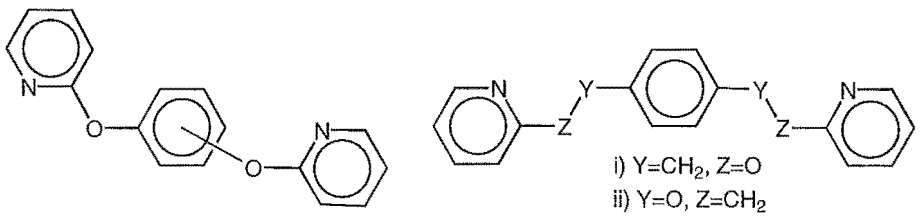
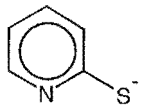


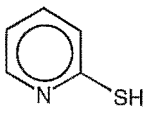
Fig. 2.4

A second group of substituted pyridyl compounds has received selective, but far less comprehensive attention in the literature. Heterocyclic thiolate complexes have found interesting applications in a variety of different areas.[67] While the pyridine-2-thiolate anion (2.5a) has been widely used as a monodentate, chelating or bridging coordination ligand,[68-72] complexes of neutral 2-thiopyridine compounds have been far less investigated. Of these, the coordination of pyridine-2-thiol (2.5b) comprises the majority of this literature.[73-76] Examination of the coordination chemistry of 2-pyridylsulfides (2.5c) has received little attention.

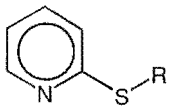
Complexes of methyl 2-pyridyl sulfide (2.5c, R=Me) with gold, silver and palladium were recently synthesised and characterised on the basis of microanalysis and



2.5a



2.5b

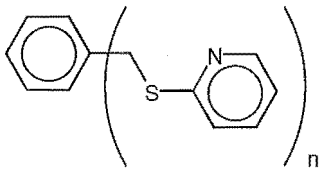


2.5c

Fig. 2.5

spectroscopic techniques, and the coordinative tendencies of the metal and donors involved.[67] While [2+2] silver and gold complexes, and monodentate structures for palladium complexes, were proposed, no X-ray structure determinations were carried out to support these conclusions. A rhodium complex containing this ligand has also been reported, but was not isolated.[77]

The second part of this chapter reports the synthesis of a number of different poly(2-pyridylsulfanylmethyl)benzenes (fig. 2.6). The coordination chemistry of some of these compounds will be discussed including five X-ray structure determinations: four silver complexes and a copper complex, one of which is dimetallomacrocyclic while the others are metallopolymeric, although within the four metallopolymers, monodentate, chelating and [2+2] coordination modes are observed for the pyridyl sulfide moieties.

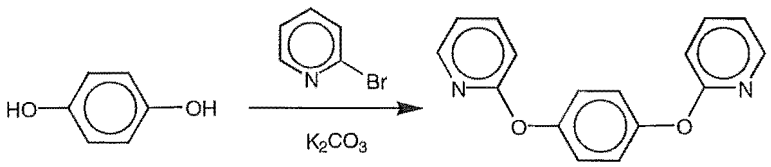


n = 2, 4

Fig. 2.6

2.2 Macrocycle Targeted Compounds.

The molecular design desired at the outset of this section of work involves a central benzene ring linked through 1,4-substituent atoms to the 2-position of pyridine rings. To maintain analogy to the model 4-substituted pyridine compounds, the linking atoms should ideally be poor donors. The best compromise between this and ease of synthesis was based on a reported synthesis of 2-phenoxypyridine synthesised in a one step melt reaction of phenol with 2-bromopyridine.[78] The use of poly(hydroxy)benzenes as starting materials should therefore allow for multiple 2-pyridoxy substituents to be attached to a central benzene ring. In accordance with this, reaction of 1,4-dihydroxybenzene with two equivalents of 2-bromopyridine in the presence of



200

Fig. 2.7

potassium carbonate at 210°C, gave 1,4-bis(2-pyridoxy)benzene, 200, in modest yield (fig. 2.7).

Palladium, silver and copper complexes, 201, 202 and 203 respectively, of this ligand were prepared. Each of these complexes analyse as [200.M.xH_2O], where M = $PdCl_2$, $AgNO_3$ or $CuCl_2$ and x = 0, 1 or ½ for 201, 202 and 203, respectively. The poor solubility of 201 and 203, possibly as a result of the formation of polymeric complexes, prevented any further characterisation of these two complexes. However, slow evaporation of an acetonitrile solution of 202 furnished crystals suitable for single-crystal X-ray structure determination.

Crystal Structure of 202.

The complex crystallises in the monoclinic space group $P2_1/n$ and is a centrosymmetric [2+2] dimetalloparacyclophane (fig 2.8). The macrocyclic structure has an intramolecular Ag···Ag separation of 10.384(1)Å. Each silver atom is coordinated

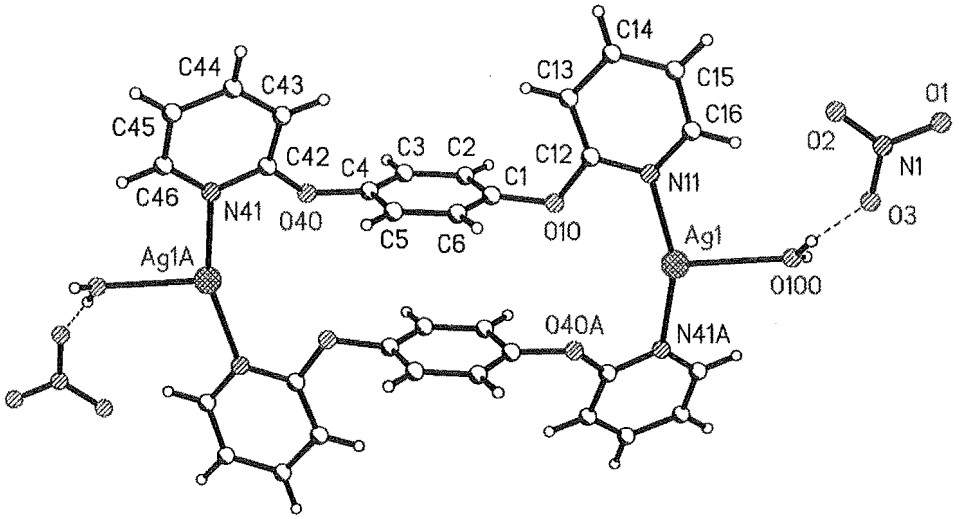


Fig. 2.8 Perspective view and atom labelling of 202. Selected interatomic distances (Å) and angles (°): Ag1-N11 2.212(2), Ag1-N41A 2.211(2), Ag1-O100 2.528(2), Ag1-O10 2.973(2), Ag1-O40A 2.942(2); N11-Ag1-N41A 157.11(7), N11-Ag1-O100 101.23(8), N41A-Ag1-O100 101.18(8).

to two pyridine nitrogens and, less strongly, to a water oxygen atom with all three silver-donor bond distances within the range expected for such coordination.[79-84] It is not uncommon for water to coordinate in the terminal positions of a dimer cage such as 202, however these typically extend into tetrameric or polymeric structures.[79] This is not the case in 202, as the water acts as a hydrogen bonding bridge to the non-coordinating nitrate counterion in the asymmetric unit (O100···O3 2.829(3)Å), and through the second hydrogen atom to an adjacent nitrate anion related by a crystallographic glide plane (O100···O2 2.928(3)Å). As has been observed in other [2+2] silver structures,[85-88] the geometry at the silver atom is distorted T-shaped. The main distortion from this geometry is the N11-Ag1-N41A angle (157.11(7)°), although the silver atom is also slightly (0.075(1)Å) out of the plane defined by the three coordinated atoms.

The single benzene and two pyridine rings are each planar (maximum out of plane distortion 0.013(4)Å for C45), but the oxygen linking atoms, O10 and O40, are both significantly out of the plane of the benzene ring (0.121(3) and 0.132(3)Å respectively). This distortion pulls the oxygen atoms towards the silver atoms suggesting a weak coordinative interaction between the silver and these ether oxygens (Ag1···O10 2.973(2)Å, Ag1···O40A 2.942(2)Å). The meanplanes of the pyridine rings are inclined at angles of 89.4° and 109.2° to the meanplane of the linking benzene ring, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 35.9°. As a result, any potential D_{2h} symmetry in the macrocycle is destroyed. The silver atom itself lies out of the extended planes of the coordinated pyridine rings by 0.192(1) and 0.455(1)Å.

A remarkable feature of the structure of 202 is the π–π stacking of the two coplanar benzene rings. The separation between the two is only 3.33(1)Å, a value similar to the layer separation in graphite (3.35Å). Other structures containing stacked benzene ring arrangements have been reported in the literature. A series of complexes of tetra(2-imidazolinyl)benzene ligands contain such an arrangement, although the separation of the benzene rings is significantly greater (3.9-4.4Å) in these structures.[89-91] More recently, the structure of a 1,4-bis(phosphino)benzene-containing molybdenum complex was reported,[92] which incorporated stacked benzenes with a separation of 3.6Å. The closer inter-benzene distance in 202 than in these previous reports indicates that the π–π interaction is clearly much stronger in this case. There has been considerable discussion in the recent literature about the nature of π–π interactions between arene rings, with much of this work focussed on determining the most favourable relative orientation of

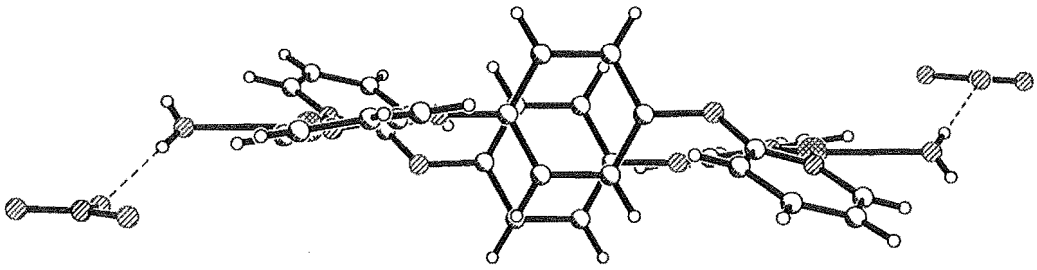


Fig. 2.9 Top view of 202 showing the relationship of the π–π stacked benzene rings.

the two rings.[31-33,93] In the related complexes discussed above the benzenes stack directly on top of one another, either in an eclipsed or staggered conformation. The benzene rings in 202 are displaced from one another in such a way that the centroid of a ring lies above an atom of the other ring (fig. 2.9), an arrangement recently reported to be the most stable for two π–π stacked benzene rings.[94,95]

The [2+2] structure of 202 containing π–π and weak coordinative interactions, raises questions regarding which of these interactions are necessary for the self-assembly of such a structure. The two issues to be addressed are i) to what extent the π–π aromatic interaction is responsible for [2+2] self-assembly; and ii) whether or not the ether oxygens are necessary for the formation of such a macrocycle. Investigations of each of these factors will now be described.

i) Aromatic Interaction.

The approach chosen to examine the contribution of this interaction was to synthesise bis(2-pyridoxy)aromatic ligands where the symmetry of 1,4-bis(2-pyridoxy)benzene is reduced. For such ligands, formation of [2+2] macrocycles

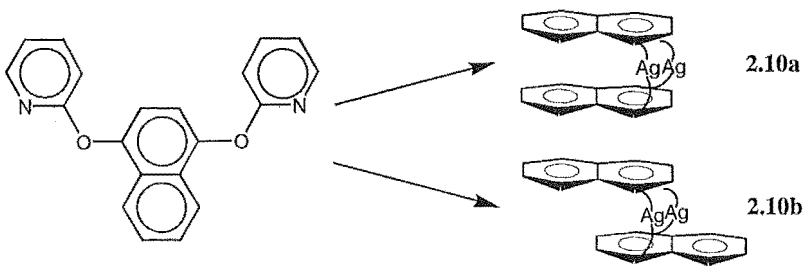
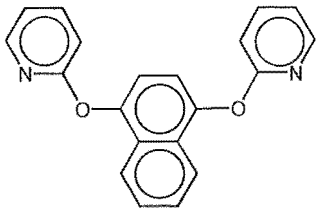
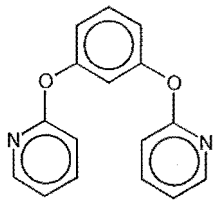


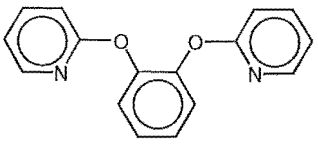
Fig. 2.10



204



205



206

analogous to 202 could produce two distinct orientations of the aromatic rings, as shown for naphthalene (fig.2.10). Both cisoid (2.10a) and transoid (2.10b) aromatic arrangements are possible, the former implying a greater influence of the π–π interaction in the self-assembly process than the latter.

The bis(2-pyridoxy)aromatic compounds 204, 205 and 206 were synthesised for the purposes of this investigation. The syntheses of 1,3-bis(2-pyridoxy)benzene, 205, and 1,2-bis(2-pyridoxy)benzene, 206, were carried out under the same reaction conditions as that of 200, using 1,3- and 1,2-dihydroxybenzene, respectively. Yields were comparable to that of the earlier 1,4- substituted compound. The synthesis of 1,4-bis(2-pyridoxy)-naphthalene, 204, required adjustment of the reaction conditions, as the melting point of 1,4-dihydroxynaphthalene (m.p. 206°C (dec.)) made a melt reaction impractical. As a result, dimethylformamide was used as a solvent and longer reaction times were employed, giving a yield of 204 similar to those of the related benzene compounds (fig. 2.11).

Investigations of the coordination chemistry of these compounds were then undertaken. Unfortunately, the poor solubility of 204 in suitable solvents did not allow for the synthesis of any complexes of this compound. However palladium, silver and copper complexes (207-209) of the 1,3-substituted ligand, 205, and complexes (210-212) of the same three metals with the 1,2-substituted ligand, 206, were able to be isolated, typically in high yields (>80%).

The copper complex, 209, isolated directly from the reaction mixture analyses as [205.$CuCl_2$], and like the analogous 1,4- complex is insoluble in any suitable solvent for further investigation. The palladium complex, 207, is soluble in DMSO but attempts to

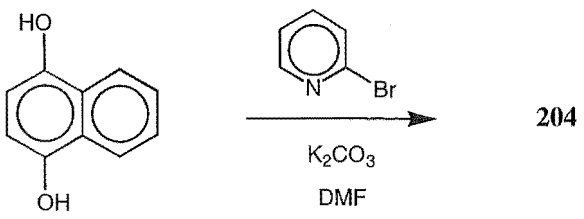


Fig. 2.11

obtain X-ray quality crystals from such solutions proved unsuccessful. The complex isolated from one such attempt - vapour diffusion of methanol into a DMSO solution of 207 - analyses as [205.$PdCl_2$.H_2O.¼DMSO]. The ^1H N.M.R. spectrum of this complex shows there to exist an equilibrium between noncoordinated ligand, 205, and a complex, 207, the dimeric/oligomeric nature of which is undetermined. Reaction of 205 with silver nitrate afforded, directly from the reaction mixture, crystals suitable for single-crystal X-ray structure determination. This complex, 208, analyses as [205.$AgNO_3$.H_2O], a composition equivalent to that of the [2+2] macrocycle previously characterised. Given this similarity in composition, the crystal structure of 208 was determined.

Crystal Structure of 208.

The complex crystallises in the monoclinic space group C2/c with one ligand in the asymmetric unit. Like 202, it is a [2+2] dimeric macrocycle (fig 2.12), but in this case has C_2 symmetry rather than a centre of inversion. To each silver atom is coordinated two pyridine nitrogens and a water oxygen atom in the axial site of the dimer. The silver-donor bond distances are similar to those of 202, although the Ag-O100 distance (2.486(2)Å) is slightly shorter in 208 than the analogous bond in 202 (2.528(2)Å). The intramolecular Ag···Ag separation (9.405(1)Å) indicates that the longest dimension of the macrocyclic cavity has been reduced by around 1Å on incorporation of 1,3- rather

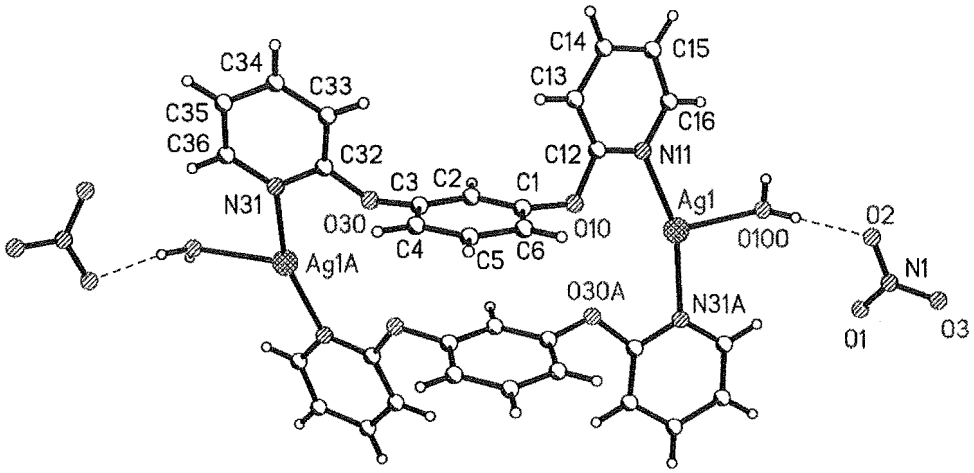


Fig. 2.12 Perspective view and atom labelling of 208. Selected interatomic distances (Å) and angles (°): Ag1-N11 2.196(2), Ag1-N31A 2.218(2), Ag1-O100 2.486(2), Ag1-O10 3.063(2), Ag1-O30A 2.899(2); N11-Ag1-N31A 158.06(6), N11-Ag1-O100 109.17(6), N31A-Ag1-O100 92.75(6).

than 1,4-bis(2-pyridoxy)benzene in the dimer. Such [2+2] cavity size variation, through changing the benzene substituent arrangement, has not previously been reported.

Again, rare terminal water coordination for a discrete silver(I) dimer is observed, with hydrogen-bonding to two different, but crystallographically related, nitrate ions (O100···O 2.878(3) and 3.034(3)Å). The geometry at the silver atom is distorted T-shaped with a similar N-Ag-N angle (158.08(6)°) to 202. However, while the water oxygen of 202 makes experimentally indistinguishable O-Ag-N angles (101.18(8) and 101.23(8)°), the oxygen of 208 has two distinct O-Ag-N angles (O100-Ag1-N11 109.17(6)°, O100-Ag1-N31A 92.75(6)°). In contrast, the coordination plane of the silver atom is planar in 208 (maximum out of plane distortion 0.002(1)Å for Ag1).

The single benzene and two pyridine rings are each planar (maximum out of plane distortion 0.010(6)Å for C12) but as for 202, the oxygen linking atoms, O10 and O30, are both significantly out of the plane of the benzene ring (0.088(4) and 0.163(4)Å respectively). Again, this distortion is towards the proximate silver atom, which in combination with the O···Ag distances (2.899(2) and 3.063(2)Å) implies a weak ether oxygen-silver interaction. The change in topology of the ligand from 1,4- to 1,3-benzene substitution also changes the relative inclinations of the the arene rings. The meanplanes of the pyridine rings are now inclined at angles of 83.6(1)° and 103.9(1)° to the meanplane of the linking benzene ring, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 17.5(1)°. Again the silver atom is significantly out of the extended meanplanes of the coordinated pyridine rings to the extent of 0.164(2) and 0.121(2)Å.

An important feature of this structure is the preservation of π–π stacking of the benzene rings in the cisoid manner described above, rather than the non-π-interacting transoid structure that may have been observed. Unlike 202, the benzene rings are not coplanar with the meanplanes inclined at an angle of 9.1°. Despite the splaying of the benzene rings away from each other, they are still displaced from one another in the

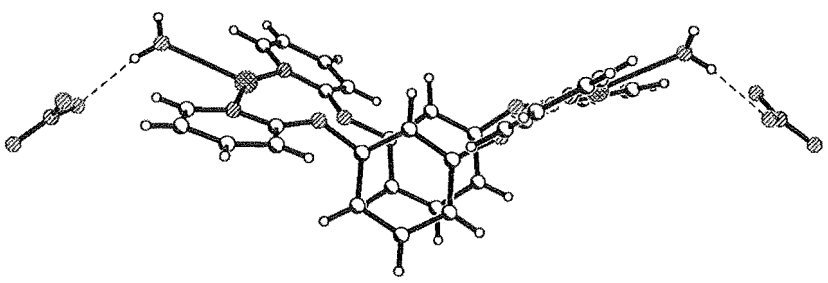
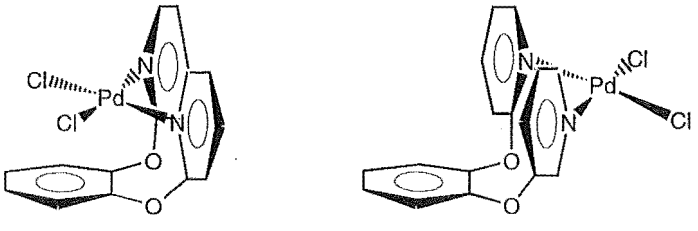


Fig. 2.13 Top view of 208 showing the relationship of the π–π stacked benzene rings.

same manner as in 202, with the centroid of one ring lying above an atom of the other ring (fig. 2.13). The interaction in 208 is not as strong however as indicated by the greater separation of the two rings (separation in 208 3.60(1)Å, in 202 3.33(1)Å).

The copper complex, 212, of 1,2-bis(2-pyridoxy)benzene was isolated directly from the reaction mixture and analyses as [206.$CuCl_2$.¼H_2O]. Recrystallisation of this complex furnished only microcrystalline solids not suitable for crystallographic characterisation. A silver complex, 211, of this same ligand was precipitated by vapour diffusion of diethyl ether into the methanolic reaction mixture and analyses as [$(206)_4(AgNO_3)_5$]. Despite this intriguing stoichiometry this complex was not able to be further characterised. Reaction of 206 with palladium chloride afforded, directly from the reaction mixture, crystals suitable for single-crystal X-ray structure determination.

This complex, 210, analyses as [206.$PdCl_2$] and is soluble in dichloromethane which suggests a monomeric structure. Assuming cis-coordination by the two pyridine nitrogens, this would result in a nine-membered chelate ring. Furthermore two distinct structures are possible, depending upon whether the benzene ring is proximate (endo) or distal (exo) to the palladium atom (fig. 2.14). The ^{1}H N.M.R. spectrum in CD_2Cl_2 shows only six signals which indicates the complex has two-fold symmetry. Significant coordination induced changes in chemical shift are observed in comparing the spectra of 210 and 206 in CD_2Cl_2. In particular, the two pairs of benzene hydrogens have the same chemical shift (7.27ppm) in the free ligand, while different chemical shifts downfield of this are observed in the complex (7.32ppm, 7.59ppm). Such changes in chemical shift can result from a number of factors such as a change in the conformation of the ligand upon coordination and through-space ring-current anisotropy effects. Significantly, no n.O.e. enhancement of any pyridine hydrogen signal was observed upon irradiation of



endo- **exo-**

Fig. 2.14

either benzene hydrogen signal. Inspection of molecular models shows that this would be so only for the more sterically congested endo isomer, which in turn raises the intriguing possibility that there may also be an interaction between the palladium and the benzene ring. Thus an X-ray structure determination was carried out.

Crystal Structure of 210.

The complex crystallises in the monoclinic space group $P2_1/c$ with one [206.$PdCl_2$] moiety in the asymmetric unit. The ligand, 206, is indeed cis-chelated to the palladium to give a nine-membered chelate ring, with the other two coordination sites occupied by cis-chloride ions to give a neutral complex (fig. 2.15). This is only the third example of an X-ray structure of palladium in a nine-membered chelate ring.[96,97] The Pd-N and Pd-Cl distances are within the range of values for related literature structures.[38,98-100] The three aromatic rings are close to planar with the largest distortions from this being for the oxygen linked carbons (largest out of plane distances C1 0.014(5)Å, C2 0.010(5)Å, C22 0.011(5)Å). The meanplanes of the two pyridine rings are inclined at angles of 90.6(1)° and 119.8(1)° to the benzene ring, and at 79.7(1)° to each other. The former angles destroy any potential two-fold crystallographic symmetry in the molecule. However, some conformational freedom will exist in solution which explains the symmetry observed in the ^{1}H N.M.R. spectrum of the complex. The palladium atom lies out of the extended meanplanes of the two pyridine rings by 0.155(1) and 0.103(1)Å;

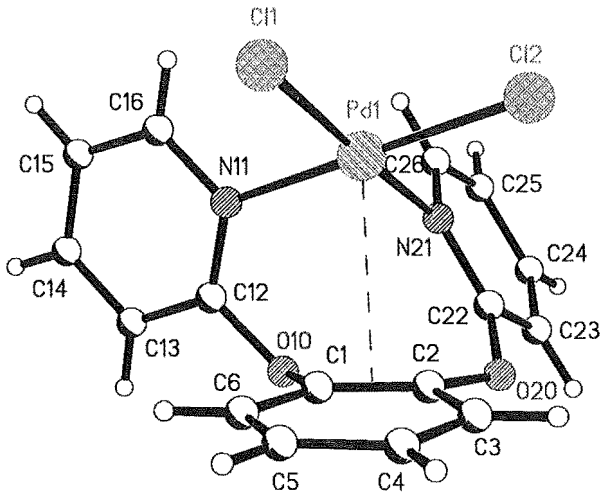


Fig. 2.15 Perspective view and atom labelling of 210. Selected interatomic distances (Å) and angles (°): Pd1-N11 2.059(2), Pd1-N21 2.040(2), Pd1-Cl1 2.2831(7), Pd1-Cl2 2.2871(7); N11-Pd1-N21 88.33(8), N11-Pd1-Cl1 90.77(6), N21-Pd1-Cl2 89.07(6), Cl1-Pd1-Cl2 91.67(3), N11-Pd1-Cl2 176.63, N21-Pd1-Cl1 175.78(6).

however the reasons for this slight distortion are not clear.

As suggested by the N.M.R. experiments, the complex exists as the endo-isomer with a semicoordinative interaction between the palladium and the benzene ring, as indicated by certain features of the structure. While the distance from the palladium to the centre of the benzene ring is 3.421(3)Å, a far more realistic distance for weak coordination, 2.879(3)Å, separates the palladium from the centre of the C1-C2 bond. This coordination is strong enough to slightly pyramidalise the square planar palladium by pulling it out of the coordination plane and towards the benzene. This is observed in the slight displacement of the palladium from the meanplane defined by N11, N12, Cl1 and Cl2 (deviation of Pd1 from plane of 0.060(1)Å). Another distortion which allows for a smaller Pd-benzene separation is the displacement of the ether oxygens below the plane of the benzene ring (out of benzene meanplane distortions: O10 0.134(4)Å; O20 0.142(4)Å). This moves the whole [Pd(pyridine)$_2$Cl$_2$] moiety closer to the benzene ring. This therefore represents an attractive intramolecular interaction between the benzene π-orbitals and the palladium d_{z2} orbital; related interactions have recently been proposed to account for the intermolecular packing of palladium complexes containing aromatic ligands.[101]

ii) Effect of the Ether Oxygens.

The approach taken to examining the significance of the ether oxygen was to synthesise ligands (and their complexes) in which the position of the ether oxygen was varied with respect to the benzene and pyridine rings. The two ligands included in this investigation are shown (fig. 2.16). Characterisation of the silver complexes of these compounds will determine whether an oxygen adjacent to the pyridine or adjacent to the benzene ring (or both), is necessary for the formation of a [2+2] macrocycle. Aside from examining the contribution of an Ag-O interaction in forming a [2+2] system, it may also elucidate the influence of the electronic effects of oxygen substituents on the benzene. There is speculation in the literature as to what benzene substituents make π–π

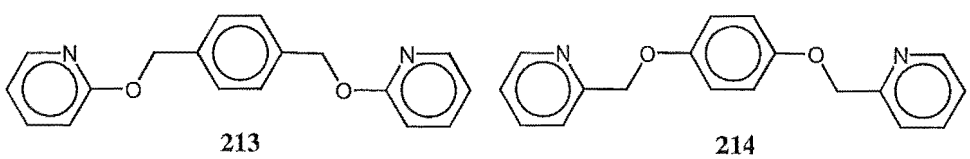


Fig. 2.16

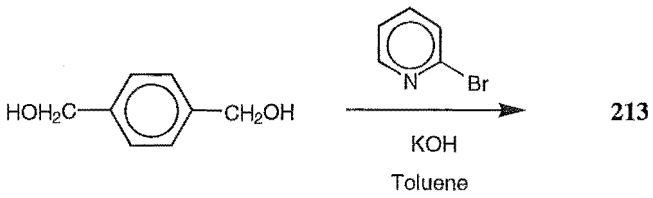


Fig. 2.17

stacked interactions most favourable.[32,33] The structural variation in 213 and 214 may allow for the investigation of this effect.

The synthesis of 1,4-bis(2-pyridoxymethyl)benzene, 213, involves an adaption of a reported synthesis of phenyl 2-pyridyl ether,[102] the monosubstituted benzene analogue, where 2-bromopyridine and benzyl alcohol were used as starting materials. The disubstituted compound was therefore synthesised by reaction of 1,4-benzenedimethanol with 2-bromopyridine in the presence of potassium hydroxide in refluxing toluene (fig. 2.17). The palladium and copper complexes, 215 and 217, of this ligand were synthesised and analyse as [213.M.xH_2O] where M = $PdCl_2$ or $CuCl_2$ and x = 1 or ½ for 215 and 217 respectively. The low solubility of these complexes did not allow for further characterisation. In the reaction of 213 with silver nitrate, crystals of the resulting complex, 216, suitable for single-crystal X-ray structure determination were obtained directly from the reaction mixture. Thus, the crystal structure of this compound, which analyses as [213.$AgNO_3$], was determined.

Crystal Structure of 216.

The complex crystallises in the monoclinic space group C2/c, and is a metallopolymer. The asymmetric unit contains half of a 213 ligand, positioned about a centre of inversion and coordinated to a silver atom which lies on a two-fold rotation axis; the nitrate ion also lies with two atoms on this axis. The asymmetric unit is labelled and shown together with its adjacent units (fig. 2.18).

The silver atom is coordinated to two pyridine nitrogens with non-linear geometry (N11-Ag1-N11B 139.6(2)°) and to a chelated nitrate ion, disordered over two sites, (Ag1-O1/O1B 2.545(3), Ag1-O1A/O1AA 2.503(4)Å). The silver-donor bond distances are in agreeement with distances in related literature compounds,[79-84] as well as the structures described previously in this work. As for other silver complexes described in this work, the silver atom is displaced from the planes of the coordinated pyridine rings (displacement from plane 0.115(5)Å).

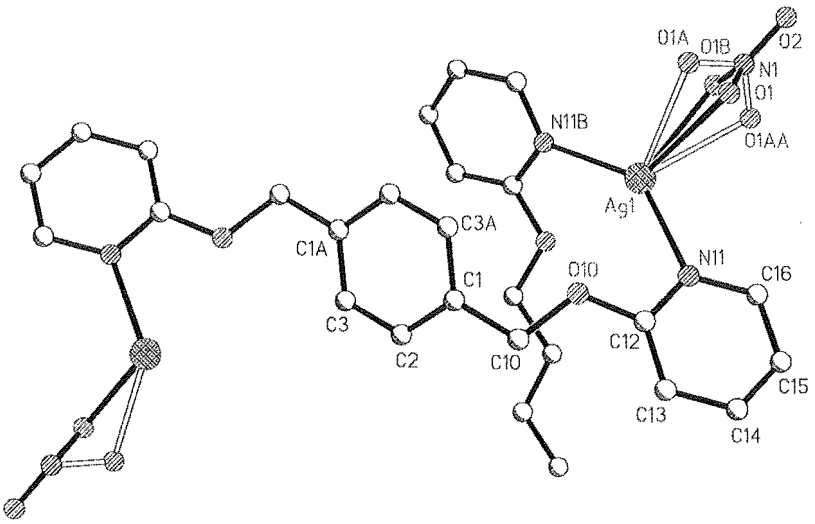


Fig. 2.18 Perspective view and atom labelling of 216 with hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (°): Ag1-N11 2.216(5), Ag1-O1 2.545(3), Ag1-O1A 2.503(4), Ag1-O10 2.874(4); N11-Ag1-N11A 139.6(2), N11-Ag1-O1 97.0(2), N11-Ag1-O1A 120.0(2), N11-Ag1-O10 49.5(5), N41A-Ag1-O2B 117(1).

The benzene and pyridine rings are planar (maximum displacement from plane 0.01(1)Å). The meanplane of the pyridine ring is inclined to that of the benzene at an angle of 46.5(6)°, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 62.8(6)°.

An important point to note in the structure of 216 is the presence of a Ag-O_{ether} interaction (Ag1-O10 2.874(4)Å). This distance is shorter than those observed for 202 and 208 as the oxygen, O10, is pulled towards Ag1 as seen in the distortion from ideal geometry around C12 (O10-C12-N11 111.4(7)°, O10-C12-C13 125.1(8)°). Despite this Ag-O interaction, 216 is metallopolymeric rather than a [2+2] macrocycle. Therefore, such an interaction alone does not lead to the formation of the π–π stacked macrocyclic structures observed in 202 and 208. In fact, in the case of 216, the packing of the metallopolymeric structure still appears to be controlled in part by π–π interactions but between pyridine and benzene rings of adjacent units, rather than the benzene-benzene stacks of 202 and 208. Three stacked rings, two pyridine and one benzene, are arranged so that interatomic bonds in the rings are eclipsed with separations of 3.41(1)Å and pyridine meanplanes inclined at an angle of 17.9(8)° to the central benzene ring (fig. 2.19).

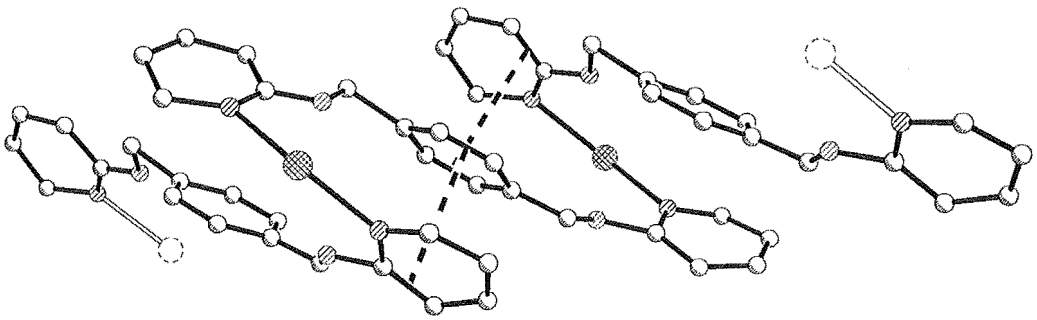


Fig. 2.19 Perspective view of 216 with hydrogens omitted showing the inter-ligand π–π stacking of aromatic rings.

The coordination chemistry of 214 was then investigated to examine whether the benzene-benzene stack was more favoured by oxygen substituents, thus leading to a [2+2] macrocycle. The ligand, 1,4-bis(2-pyridylmethoxy)benzene, was isolated in satisfactory yield from a phase transfer catalysed reaction of 1,4-dihydroxybenzene and 2-picolylchloride (fig. 2.20). Palladium, silver and copper complexes (218-220) of this ligand were then synthesised.

The copper complex, 220, analyses as [214.$CuCl_2$.¼H_2O] but was not able to be further characterised. The palladium complex, 218, was soluble and stable in DMSO, which allowed for characterisation by ^{1}H N.M.R. spectroscopy. The spectrum, with coordination induced shifts ranging between 0.10 and 0.57ppm downfield from those of the noncoordinated ligand, also showed that in solution the two pyridine rings are equivalent. Given this was the first of the 1,4-substituted benzenes for which the palladium complex was soluble, further characterisation of this complex was carried out. To this end, vapour diffusion of acetone into a DMSO solution of the complex furnished crystals suitable for single-crystal X-ray structure determination, that analyse

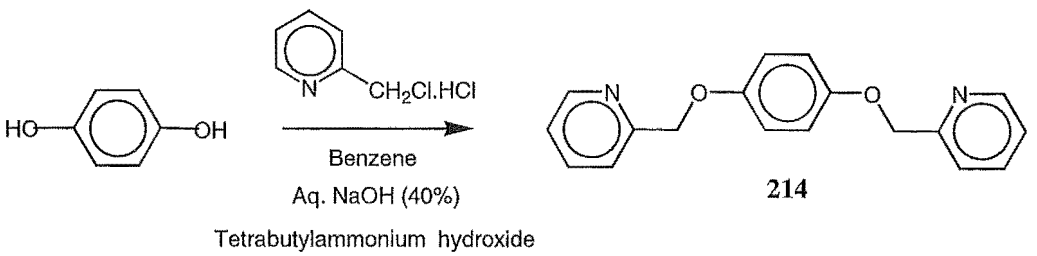


Fig. 2.20

as [214.$PdCl_2$.½CH_3COCH_3]. The silver complex, 219, precipitated from the reaction mixture as thin needles that analyse as [214.$AgNO_3$]. Slow evaporation of an acetonitrile solution of this complex yielded crystals suitable for single crystal X-ray structure determination. Discussion of the two crystal structures of 218 and 219 follows, with the structure of the silver complex described first because of its relevance to those discussed previously.

Crystal Structures of 219 and 218.

The silver complex, 219, crystallises in the monoclinic space group $P2_1/c$ and is a one dimensional metallopolymer, the asymmetric unit of which, [214.$AgNO_3$], is shown together with ½ units on each side of it (fig. 2.21). The silver atom is coordinated to two pyridine nitrogens (Ag1-N11 2.203(3), Ag1-N41A 2.195(3)Å) and in ½ of the units, to an oxygen of one of the two equal occupancy nitrates (Ag1-O2A 2.557(5)Å). The silver-donor bond distances are in agreement with the distances of related literature compounds,[79-84] as well as the structures described previously in this work. The N-Ag-N vector propagates along the metallopolymeric direction, while the ligand vector is approximately orthogonal to it to give a 'zig-zag' shaped structure.

The pyridine-silver-pyridine coordination geometry is non-linear (N11-Ag1-N41A

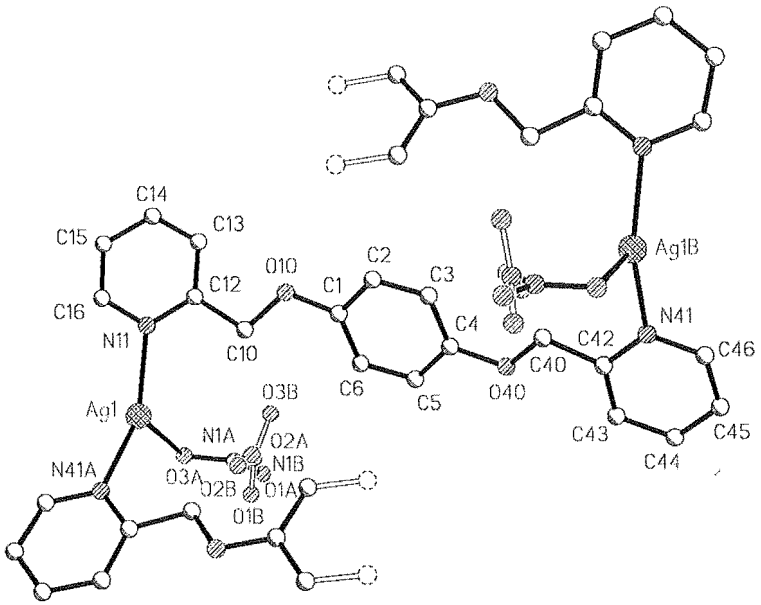


Fig. 2.21 Perspective view and atom labelling of 219 with hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (°):Ag1-N11 2.203(3), Ag1-N41A 2.195(3), Ag1-O3A 2.557(5); N11-Ag1-N41A 150.3(1), N11-Ag1-O3A 104.9(1), N41A-Ag1-O3A 104.2(1).

150.3(1)°) with the ½ occupancy coordinated oxygen bisecting the larger N-Ag-N angle (N11-Ag1-O3A 104.8(1)°, N41A-Ag1-O3A 104.2(1)°). There is a small distortion from planarity of the AgN_2O moiety with the silver atom slightly (0.089(3)Å) out of the plane defined by the three coordinated atoms. This is due to a small steric repulsion between the coordinated nitrate ion and proximate methylene hydrogens in the ligand ($O2A\cdots H_{methylene}$ distances 2.55(4), 2.59(4)Å).

The single benzene and two pyridine rings are each planar (maximum out of plane distortion 0.012(6)Å for C45) and the substituents linking the three rings together are only slightly out of the plane of their respective attached ring (out of ring plane distortion range 0.01(5)-0.05(6)Å). The meanplanes of the pyridine rings are inclined at angles of 48.4(3)° and 2.4(3)° to the meanplane of the linking benzene ring, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 48.6(3)°. As for the other silver complexes described, the silver atom is significantly out of the extended meanplanes of the coordinated pyridine rings by 0.230(3) and 0.097(3)Å.

The zig-zag structure of the polymeric strand as well as the inter-strand packing is influenced by π–π stacked interactions (fig. 2.22). Two ligands that coordinate to the same silver atom at one end are also weakly tethered by a pyridine-pyridine π interaction

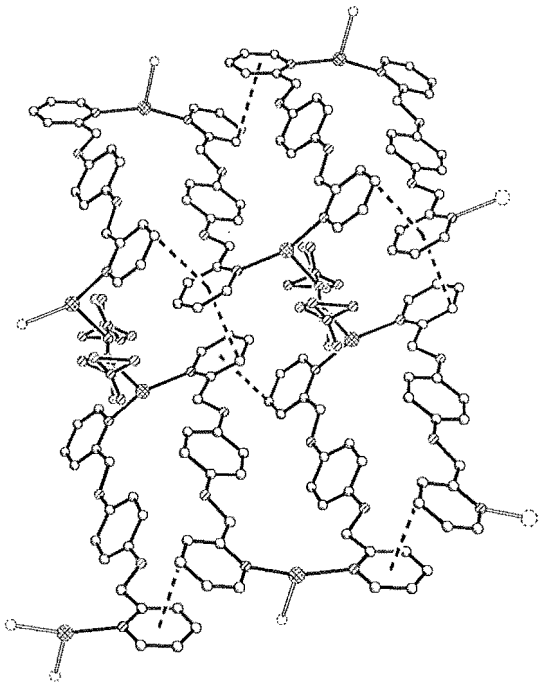


Fig. 2.22 Perspective view of 219 with hydrogens omitted showing the intra- and inter-polymer π–π stacking of aromatic rings.

at the other end. The orthogonal vector of a bond in one of the pyridines sits over the other pyridine (bond-centre of pyridine distance 3.716(4)Å) which leads to the anti-parallel arrangement of the ligands. Even stronger interactions exist between different strands of the polymer. A pyridine of one strand is coplanar to a crystallographically equivalent pyridine of another strand, and the two are separated by 3.33(1)Å with an atom of one lying over the centroid of the other, a relationship similar to that existing in 202. Hence, π–π interactions appear to contibute to the assembly of the complex, and certainly to its crystal packing.

The palladium complex, 218, crystallises in the monoclinic space group $P2_1/c$ with one [214.$PdCl_2$] moiety and half an acetone solvate in the asymmetric unit in accordance with the microanalysis of the crystals (fig. 2.23). The complex is a dimetalloparacyclophane incorporating a 26 membered macrocycle. The intramolecular Pd···Pd separation in the [2+2] structure is 11.269(2)Å. This dimension of the macrocycle is larger than those of the silver structures described earlier, as a result of the additional methylene groups incorporated in the ligand. The two non-stacked benzene rings are inclined at an angle of 44(1)° to each other with their centroids separated by 6.45(3)Å, which indicates that this dimension of the macrocycle is also enlarged from

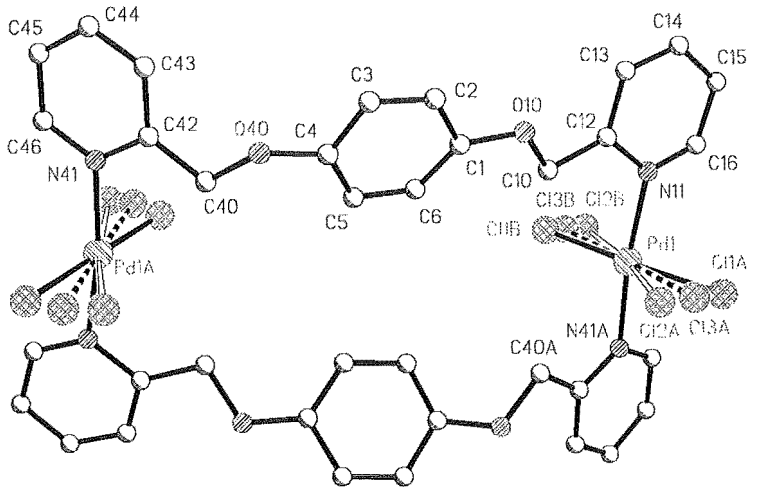


Fig. 2.23 Perspective view and atom labelling of 218 with hydrogens and the acetone solvate omitted for clarity Selected interatomic distances (Å) and angles (°): Pd1-N11 2.03(1), Pd1-N41A 2.06(1), Pd1-Cl range 2.267(6)-2.383(6); N11-Pd1-N41A 172.1(8), N11-Pd1-Cl range 86.9(4)-92.5(4), N41A-Pd1-Cl range 87.1(6)-92.1(4), Cl1A-Pd1-Cl1B 178.4(3), Cl2A-Pd1-Cl2B 171.8(7), Cl3A-Pd1-Cl3B 178.6(5).

the earlier [2+2] structures.

Each palladium atom is approximately square planar and is trans-coordinated to two pyridine nitrogens and two disordered chlorine atoms. The Pd-N and Pd-Cl distances are within the range of reported values for related structures;[103-109] the Pd-Cl distances in this structure vary somewhat, as a result of difficulties in modelling the disorder of the chlorine atoms. The conformational freedom provided by the $-CH_2-O-$ groups along with the lack of intramolecular π–π interactions also leads to disorder in the ligand. This disorder appears to be over several slightly different conformations and proved difficult to model. Given this, the structure was refined with the ligand in its averaged conformation. As a consequence, structural features, such as the planarity of arene rings, are less accurately known.

Within a ligand, the meanplanes of the pyridine rings are inclined at angles of 25(1)° and 47(1)° to the meanplane of the benzene ring, while two pyridines coordinated to the same palladium atom are inclined at an angle of 15(1)°. The overall shape of the macrocycle is curved (fig. 2.24). This is as a result of hydrogen bonding interactions between a coordinated chlorine and the acetone present in the lattice (closest Cl···H distance 2.59(2)Å). This has the effect of wrapping the macrocycle around the solvate to give the concave curvature. However the complex will have significant conformational freedom in solution, which explains the symmetry observed in its ^{1}H N.M.R. spectrum.

Although there is a lack of intramacrocyclic π–π stacking, the intermolecular packing of the macrocycles is strongly influenced by such interactions. As shown in two different views of the crystal packing (fig. 2.25), the top ligand in one macrocycle interacts with the bottom ligand of an adjacent macrocycle, which goes on to interact

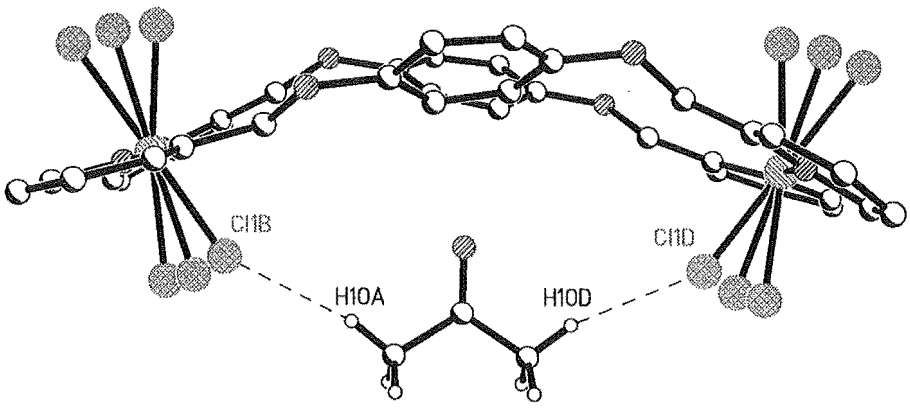


Fig. 2.24 Top view of 218 showing the macrocycle wrapping around the hydrogen-bonded acetone. All hydrogens except those of the acetone omitted for clarity.

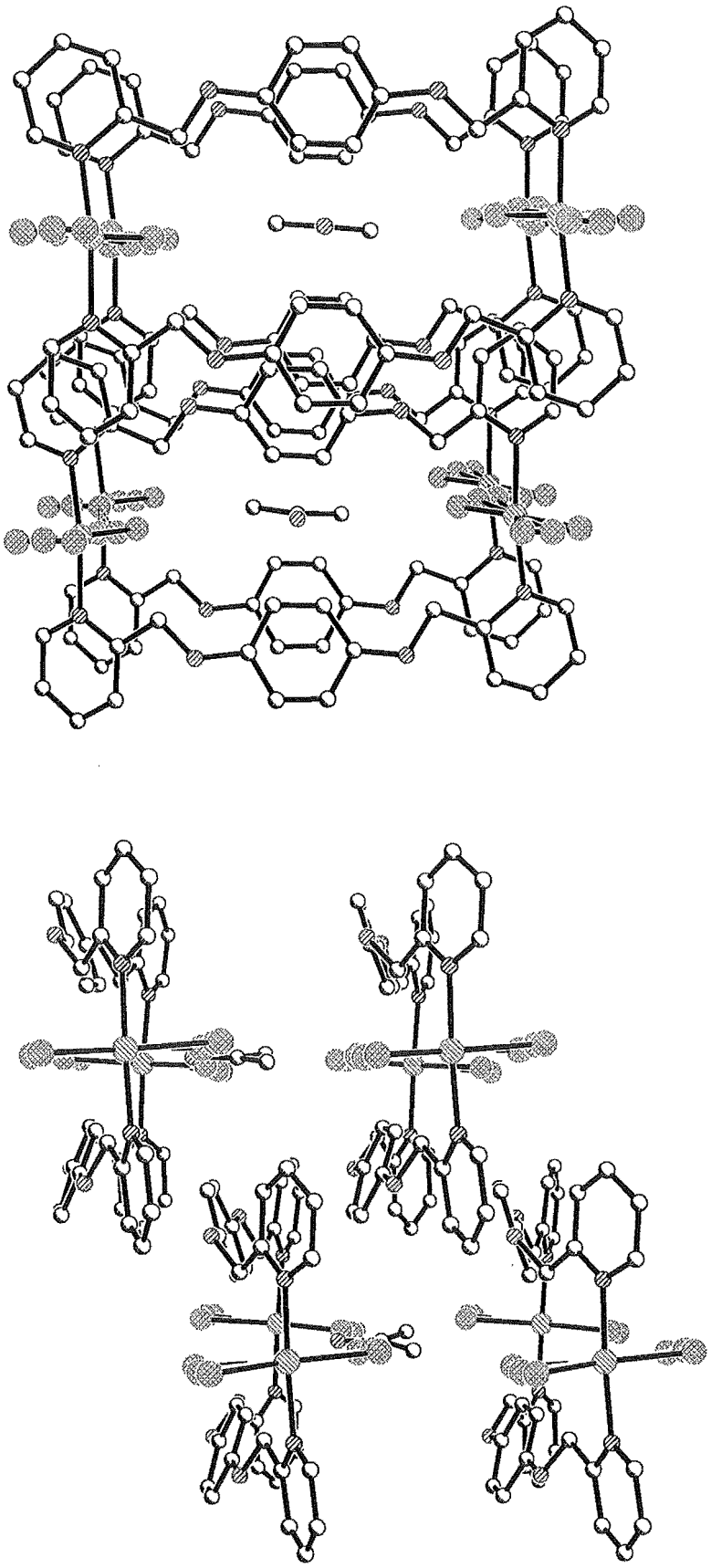
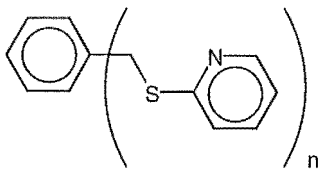


Fig. 2.25 Front and side views of 218 showing the π–π aromatic stacks resulting from the alternating packing arrangement of the macrocycles.

with the top ligand of the next and so on. The result is an alternating array of macrocycles through the lattice of the crystal, although the curvature discussed previously is always in the same direction. The strength of the π–π interaction is significant (typical interpyridine atom···centroid distance 3.8Å), although not as strong as those in other structures discussed previously.

2.3 Poly(pyridyl sulfide) Complexes.

In the complexes discussed above speculation arose as to the effect of semi-coordinated oxygen, particularly with respect to the formation of [2+2] macrocyclic silver complexes. This was investigated by varying the position of the oxygen in the ligand, then comparing the structures of the respective complexes. By changing the ligand to include a more strongly coordinating atom in the place of oxygen, the formation of [2+2] structures might be made more favourable. On this basis, ligands incorporating sulfur atoms in the benzene-pyridine linkage (fig. 2.26) were synthesised and their coordination chemistry investigated.



n = 2, 4

Fig. 2.26

The bis(2-pyridylsulfanylmethyl)benzene compounds, 221-223, were obtained by reaction of 2-mercaptopyridine with the appropriate bis(bromomethyl)benzene in the presence of triethylamine (fig 2.27).[110] The yield of 1,4-bis(2-pyridylsulfanylmethyl)benzene, 221, was satisfactory (55%), while the yields of the other two isomers were excellent (>80%). While the assignments of the ^{1}H N.M.R. spectra of 221 and 222 were trivial, there is significant overlap of pyridine and benzene hydrogen signals in the spectrum of 1,2-bis(2-pyridylsulfanylmethyl)benzene, 223. To resolve this, a 1D-TOCSY experiment was carried out, wherein irradiation of the H6' signal (8.41ppm) allowed for assignment of signals for the four pyridine hydrogens. To assign the two signals for the benzene hydrogens an nOe experiment was performed, wherein irradiation of the methylene signal (4.62ppm) gave an enhancement for only one of the signals (7.43ppm), which could therefore be assigned to H3/6.

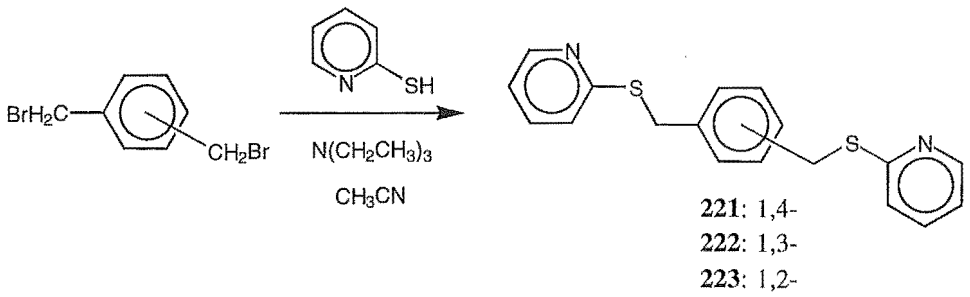


Fig. 2.27

Palladium, silver and copper complexes, 224, 225 and 226 respectively, of 1,4-bis(2-pyridylsulfanylmethyl)benzene were prepared in good yield (>80%). Each of these complexes analyse as [221.M.xH_2O] where M = $PdCl_2$, $AgNO_3$ or $CuCl_2$ and x = 2, 0 or 0 for 224, 225 and 226 respectively. The poor solubility of 226, possibly as a result of the formation of a polymeric complex, prevented any further characterisation of this compound. The palladium complex, 224, is soluble in DMSO but attempts to obtain X-ray quality crystals from such solutions proved unsuccessful. The ^{1}H N.M.R. spectrum of this complex indicated an equilibrium between noncoordinated ligand, 221, and a complex, 224, the dimeric/oligomeric nature of which is undetermined. It is likely however, that the ligand is coordinated to palladium through the nitrogens rather than the sulfurs on the basis of established trends for palladium.[67]

Recrystallisation of the silver complex, 225, yielded crystals suitable for single crystal X-ray structure determination. 1,4-bis(2-pyridylsulfanylmethyl)benzene differs from 1,4-bis(2-pyridoxymethyl)benzene only in that sulfur takes the place of oxygen in the pyridine-benzene linkage. The silver complex, 216, of 1,4-bis(2-pyridoxymethyl)benzene is metallopolymeric, but the different coordination affinities of silver to oxygen and sulfur may lead to a different mode of coordination in 225. To investigate this possibility, the structure of 225 was determined.

Crystal Structure of 225.

The complex crystallises in the triclinic space group P-1 and is a centrosymmetric [2+2] dimetalloparacyclophane (fig. 2.28). The macrocyclic structure has an intramolecular Ag···Ag separation of 12.196(2)Å. Each silver atom is coordinated to two pyridine nitrogens and an oxygen atom of the nitrate anion, with all three silver-donor bond distances within the range expected for such coordination.[79-84] There is also a weak coordinative interaction between the silver and the sulfur atoms of the ligand (Ag1···S10 3.160(1)Å, Ag1···S40A 3.164(1)Å). The coordination geometry of the silver

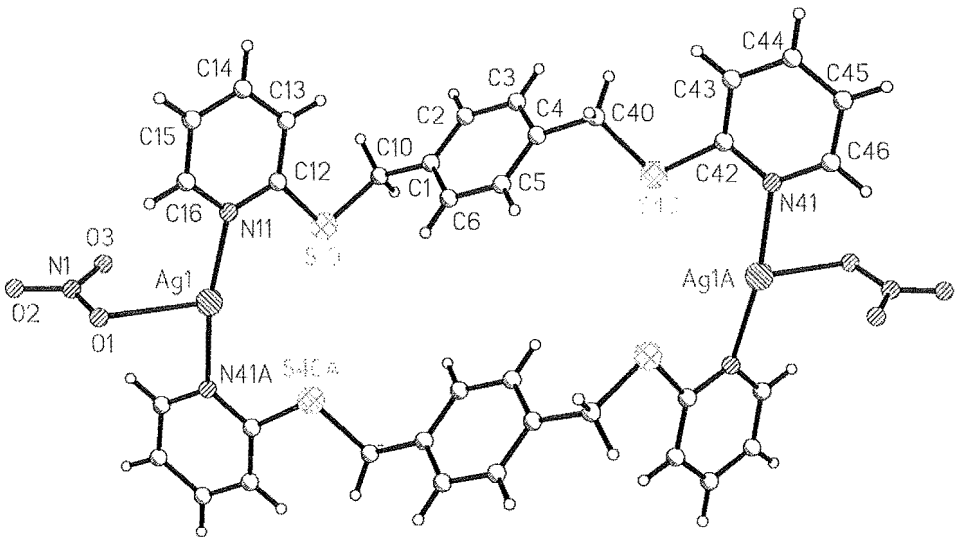


Fig. 2.28 Perspective view and atom labelling of 225. Selected interatomic distances (Å) and angles (°): Ag1-N11 2.166(2), Ag1-N41A 2.165(2), Ag1-O1 2.592(2), Ag1-S10 3.160(1), Ag1-S40A 3.164(1); N11-Ag1-N41A 169.70(8), N11-Ag1-O1 98.36(8), N41A-Ag1-O1 91.60(8).

is distorted T-shaped (N11-Ag1-N41A 169.70(8)°) with the coordinated oxygen slightly displaced towards one of the pyridines (N11-Ag1-O1 98.36(8)°, N41A-Ag1-O1 91.60(8)°). There is also a small distortion from planarity of the AgN_2O moiety with the silver atom slightly (0.047(1)Å) out of the plane defined by the three coordinated atoms.

The single benzene and two pyridine rings are each planar (maximum out of plane distortion 0.009(5)Å for C14). The meanplanes of the pyridine rings are inclined at angles of 91.9(2)° and 125.2(2)° to the meanplane of the linking benzene ring, while the two pyridine ring meanplanes at each silver atom are inclined to one another at an angle of 57.0(2)°. The silver atom itself lies out of the extended planes of the coordinated pyridine rings by 0.292(2) and 0.034(2)Å.

An important feature of this macrocycle is the absence of an intramolecular π–π interaction, as the two coplanar benzene rings are significantly displaced from one another (fig. 2.29). Therefore, this structure provides some elucidation as to whether π–π interactions, or semicoordinate Ag-Y (Y = O, S) interactions are necessary for the self-assembly of such [2+2] macrocycles. The three silver dimetalloparacyclophanes characterised, 202, 208 and 225, all have weakly coordinating atoms attached to the pyridine groups, while only two contain π–π stacked benzene rings. Intramolecular

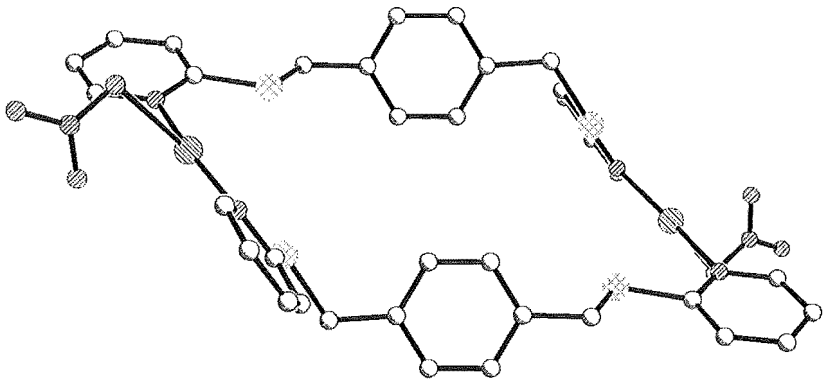


Fig. 2.29 Top view of 225 showing the displaced relationship benzene rings.

π–π benzene interactions can, therefore, contribute to the self-assembly of silver [2+2] systems, but are they not a necessity for the formation of such complexes.

While there is an absence of intramolecular aromatic stacking, the packing of the macrocycles is controlled, in part, by such interactions (fig. 2.30). Again, the aromatic rings arrange with an atom of one ring lying approximately over the centroid of the other. The intermolecular aromatic···aromatic interactions are similar in strength to those of the palladium-containing macrocycle, 218, as indicated by their similar ring separations (both with average distances of 3.80Å). Note, however, that in 218 each macrocycle interacts with two others, while in 225 each [2+2] unit interacts with four other macrocycles.

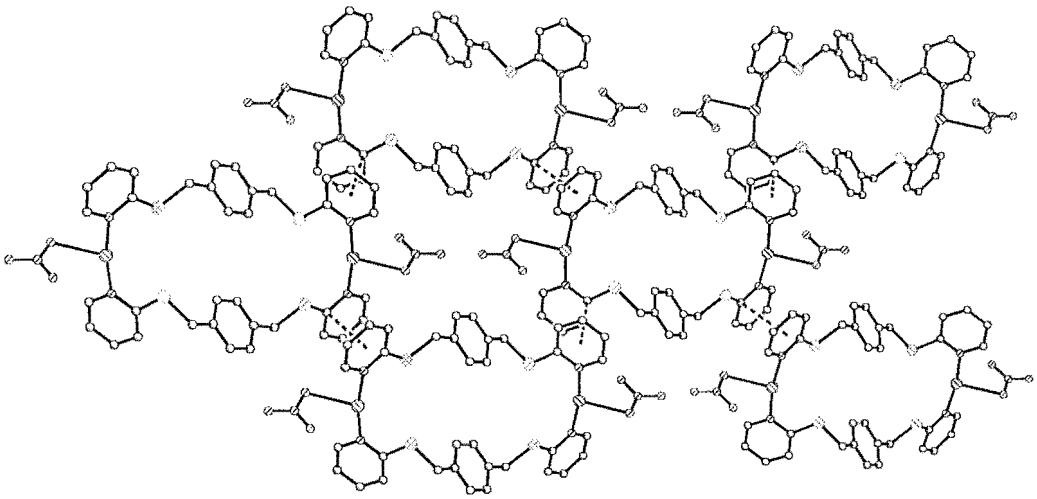


Fig. 2.30 View of 225 showing the π–π aromatic interactions between the macrocycles.

The palladium and copper complexes, 227 and 229 respectively, of 1,3-bis(2-pyridylsulfanylmethyl)benzene are similar in nature to those of the 1,4- ligand described above. The copper complex again analyses as [222.$CuCl_2$] and is insoluble, suggesting that a polymeric complex may have formed. The palladium complex analyses as [222.$PdCl_2.2H_2O$], the ^1H N.M.R. spectrum of which again shows a ligand/complex equilibrium to exist in solution. Reaction of 222 with one equivalent of silver nitrate gave a colourless complex, 228, crystals of which, suitable for single-crystal X-ray structure determination, were obtained by slow evaporation of an acetonitrile solution of the complex.

Crystal Structure of 228.

The complex crystallises in the triclinic space group P-1 and is a one dimensional metallopolymer, the asymmetric unit of which, [222.$AgNO_3$], is shown (fig. 2.31). A picture and a schematic representation of the extended polymeric structure of the complex is also shown (fig. 2.32a and b). The silver atom is coordinated to two pyridine nitrogens and a sulfur, each from different ligands, as well as an oxygen from the nitrate counterion. The geometry of these four donors around the silver is highly distorted tetrahedral (donor-Ag-donor angles between 88.8(3) and 119.9(3)°). The distortion from tetrahedral geometry is possibly due to a semicoordinated sulfur attached to one of the coordinated pyridines (Ag1···S10 3.128(3)Å), as shown by the dashed line in fig. 2.32a.

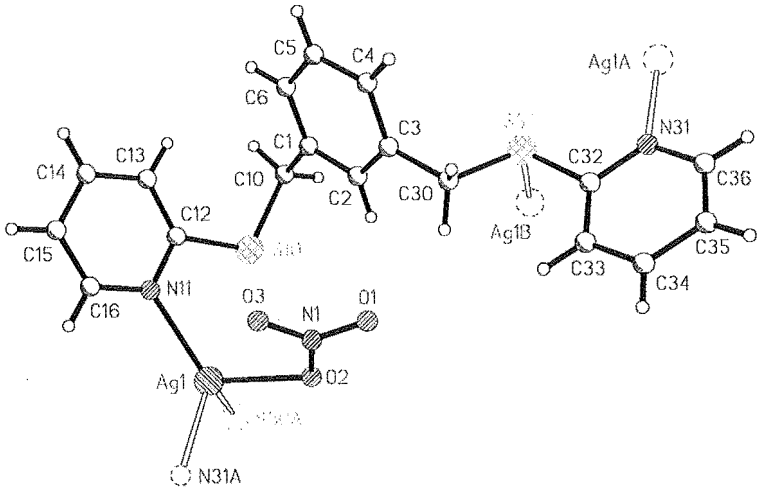


Fig. 2.31 Perspective view and atom labelling of 228. Selected interatomic distances (Å) and angles (°):Ag1-N11 2.285(7), Ag1-N31A 2.327(6), Ag1-S30A 2.658(3), Ag1-O2 2.418(7); N11-Ag1-N31A 119.9(3), N11-Ag1-S30A 118.5(2), N11-Ag1-O2 112.5(3), N31A-Ag1-S30A 106.6(2), N31A-Ag1-O2 88.8(3), S30A-Ag1-O2 105.9(2).

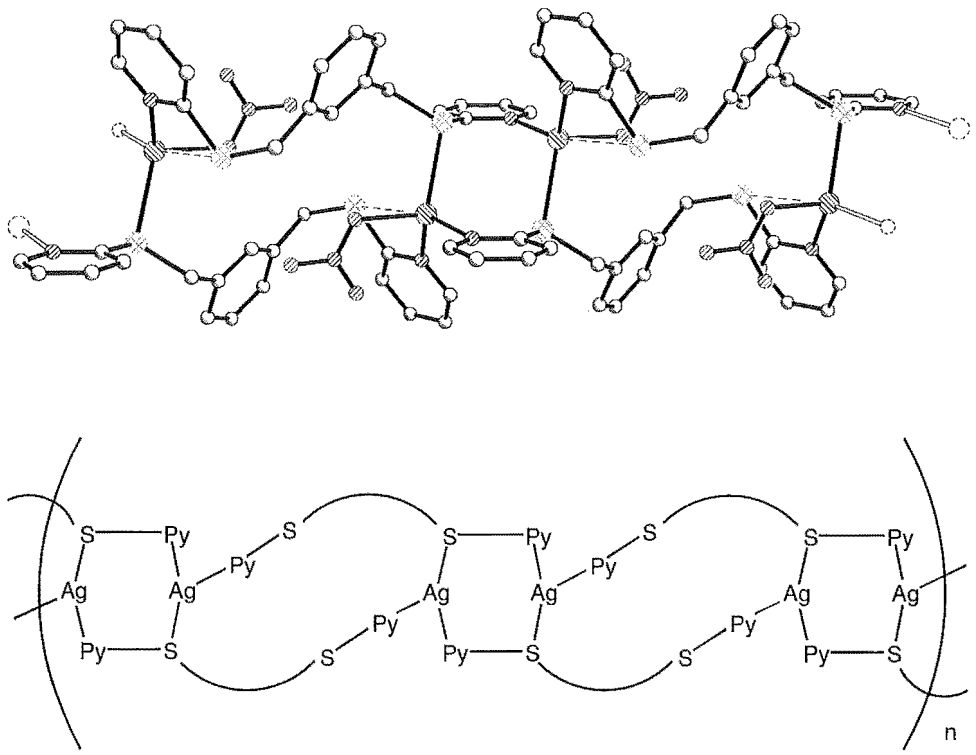


Fig. 2.32a and b Perspective view (**a**, top) with hydrogens omitted, and schematic representation (**b**, bottom) of the polymeric structure of 228.

The single benzene and two pyridine rings in the asymmetric unit are each planar (maximum out of plane distortion 0.02(2)Å for C2) with the largest out of plane distortions being unsystematic and not assignable to any steric or semicoordinating factors. The meanplanes of the pyridine rings are inclined at angles of 84.2(9)° and 63.3(9)° to the meanplane of the linking benzene ring, destroying any crystallographic symmetry within the ligand, while the two pyridine ring meanplanes are inclined to one another at an angle of 62.1(9)°. The silver atom lies out of the extended planes of the coordinated pyridine rings by 0.15(1) and 0.25(1)Å as a consequence of coordination to the sulfur from the third attached ligand.

The polymer itself is an alternating array of two different sizes of macrocycle fused by a common bond. The smaller of the two is a centrosymmetric eight-membered macrocycle containing two silver atoms (Ag···Ag 4.340(2)Å) bridged by a pair of pyridyl sulfide moieties, with the two pyridine rings coordinated to different silver atoms. This manner of dinuclear silver coordination of two alkylthiopyridine units has previously been proposed,[67] but not crystallographically confirmed. This eight membered ring adopts a chair conformation (fig. 2.33) with the two pyridine rings transoid with respect to the Ag_2S_2 plane, as necessitated by the crystallographic centre of inversion.

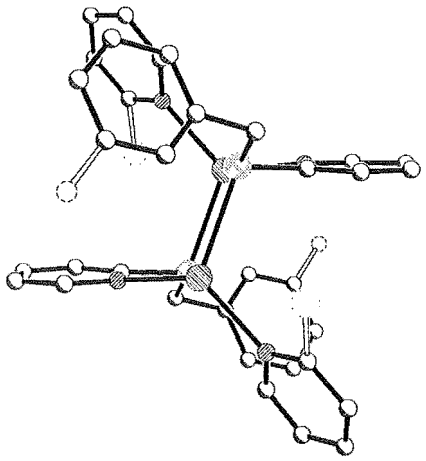


Fig. 2.33 Side view of the chair conformation of the eight-membered macrocycle of 228.

Fused to this macrocycle is a twenty-membered centrosymmetric dinuclear ring. Again the ring is formed by coordination of a pyridine nitrogen and a sulfur atom to each of two silver atoms. However in this case, instead of the coordinating sulfur bonding directly to the coordinating pyridine, they are separated by the arene spacer of the ligand. As a result, the macrocycle is enlarged to 20 members with an Ag···Ag interatomic distance of 7.920(2)Å.

While there appears to be no π–π stacking interactions contributing to the formation of this polymer chain, the same can not be said for the crystal packing of the chains. A continuous series of interchain pyridine stacking can be seen in the structure of the complex (fig. 2.34). The pyridines involved are those of the eight-membered macrocycle and are ideally disposed to interact with the pyridines of an adjacent chain.

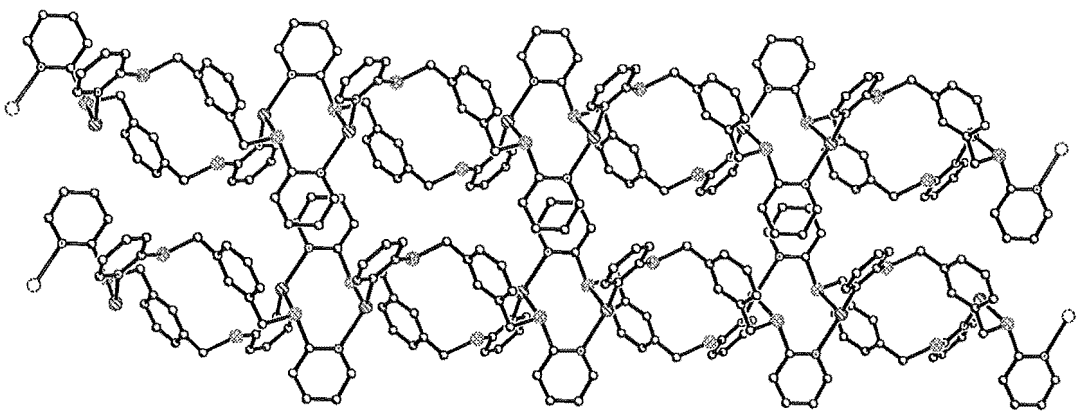


Fig. 2.34 Perspective view of 228 with hydrogens omitted showing the inter-polymer π–π stacking of aromatic rings.

The crystallographically related pyridines are coplanar and stack in a now familiar arrangement with one atom of a ring lying over the centroid of the other. The rings are separated by only 3.18(1)Å indicating a very strong π–π interaction.

The palladium complex, 230, of 1,2-bis(2-pyridylsulfanylmethyl)benzene analyses as [223.$PdCl_2$.1½H_2O], and like the palladium complexes above, the ^1H N.M.R. spectrum again shows a ligand/complex equilibrium to exist in solution. Reaction of 223 with one equivalent of silver nitrate gave a colourless complex, 231, and like the silver complex of the 1,3-substituted ligand, crystals suitable for single-crystal X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the complex. This complex analyses as [223.$AgNO_3$], an elemental composition the same as that of 225 and 228. Reaction of 223 with one equivalent of copper chloride dihydrate afforded 232 as green crystals, suitable for single-crystal X-ray structure determination. Microanalysis of this compound revealed a [223.$CuCl_2$.CH_3OH] composition. The structures of both 231 and 232 were determined in order to fully characterise the topologies of these complexes.

Crystal Structures of 231 and 232.

The silver complex, 231, crystallises in the monoclinic space group $P2_1/n$ and is a one dimensional metallopolymer the asymmetric unit of which, [223.$AgNO_3$], is shown (fig. 2.35). A picture and a schematic representation of the extended polymeric structure of the complex is also shown (fig. 2.36a and b). The silver atom is coordinated to two pyridine nitrogens and a sulfur, each from different ligands, as well as an oxygen from the nitrate counteranion. However, in this complex the silver is bonded to a crystallographically related silver atom (Ag-Ag1A bond length 2.9874(5)Å). Such metal-metal bonds have previously been observed in complexes of other 2-donor-substituted heterocycles, with the bond distance observed here being within the range of distances previously observed.[111-114] The other silver-donor distances are unremarkable.

The geometry of the five atoms around the silver is distorted from trigonal bipyramidal, with the central silver, sulfur and two nitrogens approximately coplanar (maximum out of plane distortion 0.014(7)Å for Ag1) with the second silver and nitrate oxygen occupying the axial sites. Some bond angles are significantly different from the ideal trigonal bipyramidal angles (Ag1A-Ag1-O2 155.46(6)° (should be 180°), N11A-

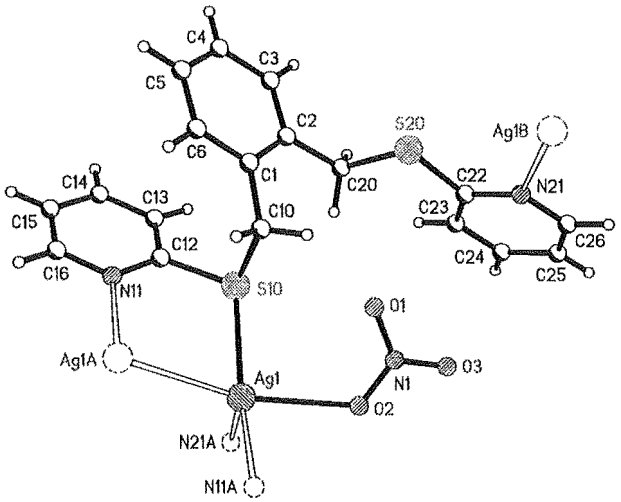


Fig. 2.35 Perspective view and atom labelling of 231. Selected interatomic distances (Å) and angles (°):Ag1-Ag1A 2.9874(5), Ag1-N11A 2.288(2), Ag1-N21A 2.377(2), Ag1-S10 2.4984(8), Ag1-O2 2.571(2); Ag1A-Ag1-N11A 90.79(6), Ag1A-Ag1-N21A 117.51(6), Ag1A-Ag1-S10 78.35(2), Ag1A-Ag1-O2 155.46(6), N11A-Ag1-N21A 103.82(8), N11A-Ag1-S10 154.44(6), N11A-Ag1-O2 85.09(8), N21A-Ag1-S10 101.71(6), N21A-Ag1-O2 86.91(8), S10-Ag1-O2 95.21(5).

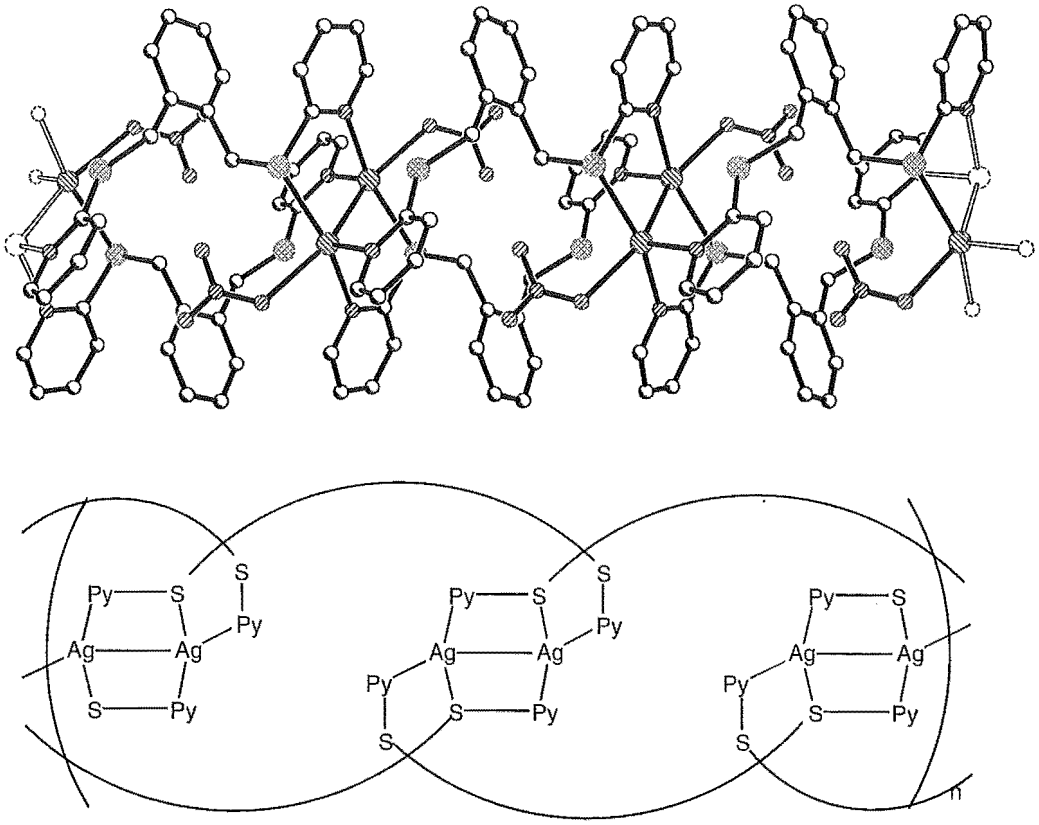
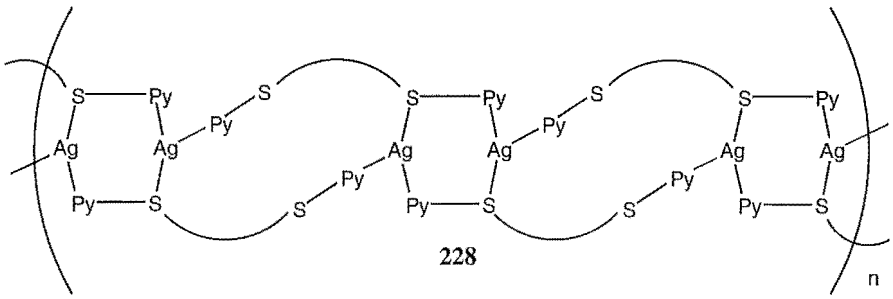


Fig. 2.36a and b Perspective view (**a**, top) with hydrogens omitted, and schematic representation (**b**, bottom) of the polymeric structure of 231.

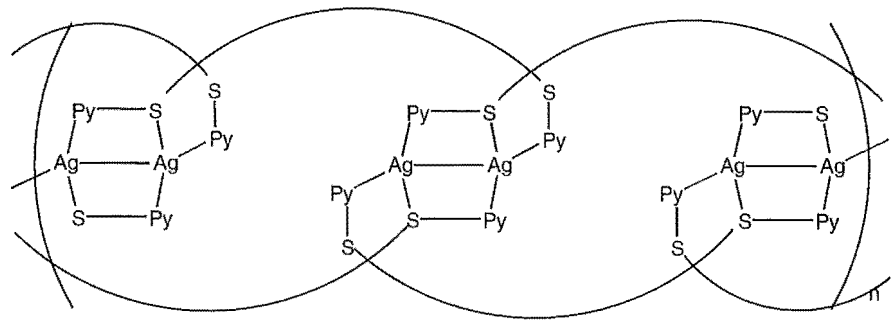
Ag1-S10 154.44(6)° (120°)); however, this is still the closest approximation to the coordination geometry.

The single benzene and two pyridine rings in the asymmetric unit are each planar (maximum out of plane distortion 0.011(4)Å for C15). The meanplanes of the pyridine rings are inclined at angles of 27.9(2)° and 77.9(2)° to the meanplane of the linking benzene ring, destroying any crystallographic symmetry within the ligand, while the two pyridine ring meanplanes are inclined to one another at an angle of 62.7(2)°. The silver atom lies out of the extended planes of the coordinated pyridine rings by 0.214(3) and 0.226(3)Å.

There are noticable similarities between this complex and the silver complex of the 1,3-substituted ligand described previously. Aside from the presence of a silver-silver bond in 231, as opposed to the 4.340(2)Å silver-silver separation of 228, the topologies of 228 and 231 are similar, as shown by the schematic representations of the two polymers (fig. 2.37). In both structures the dinuclear bis(pyridylsulfide) moiety is present, and the pyridyl sulfide unit at the opposite end of each of these ligands coordinates through the pyridine nitrogen to a silver atom of the next dinuclear unit. There is a slight change in this pyridine coordination between the two, as to which silver of the dinuclear pair is bonded to the "bridging" pyridine. In 228 the "bridging" pyridine coordinates to the closer silver of the next dinuclear pair, while in 231 it coordinates to



228



231

Fig. 2.37 Schematic representations of **228** and **231**

the more distant silver of the next pair. As a result, the macrocycle linking two dinuclear units is 20 membered but incorporates four silver atoms (smallest Ag···Ag interatomic distance of 8.138(1)Å) as opposed to the dinuclear 20 membered macrocycle of 228.

Like 228 there appears to be no π–π stacking interactions contributing to the formation of this polymer, but again pyridine-pyridine stacking assists with the crystal packing of the polymers (fig 2.38). These interactions, shown as dashed bonds for clarity, are not as strong as those of other structures (ring separation 3.55(1)Å); however the atom/centroid relationship of the two coplanar rings is again observed.

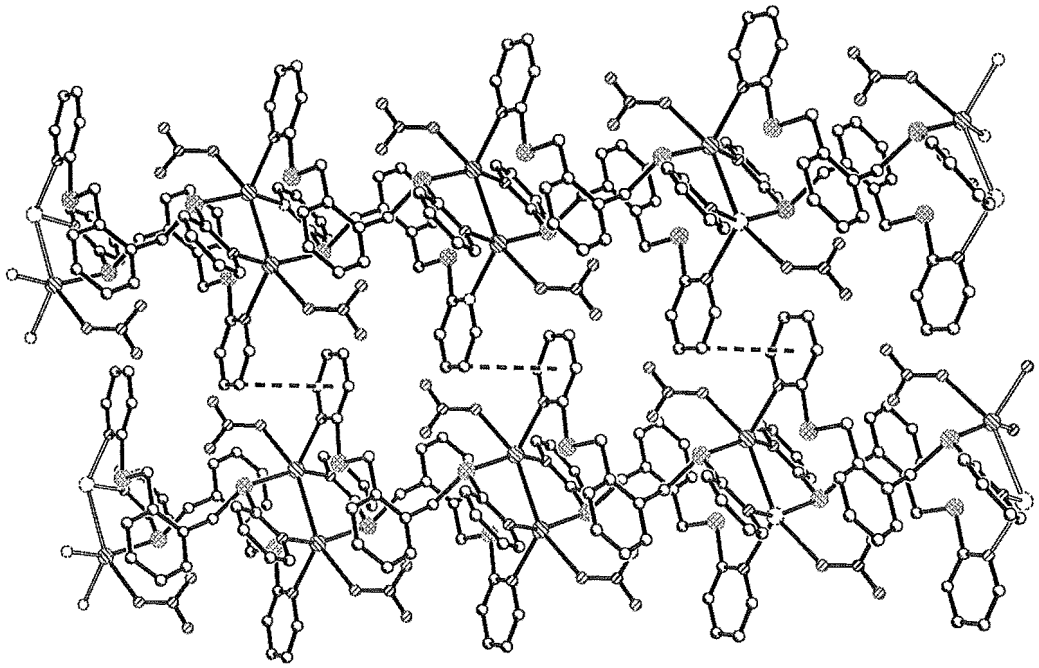


Fig. 2.38 Perspective view of 228 with hydrogens omitted showing the inter-polymer π–π stacking of aromatic rings.

The copper complex, 232, crystallises in the triclinic space group P-1 and is a one dimensional metallopolymer the asymmetric unit of which, [222.$CuCl_2$.CH_3OH], is shown (fig. 2.39). The two half-occupancy copper atoms each lie on special positions (Coordinates: Cu1 (0.5, 0, 0.5), Cu2 (0.5, 0.5, 0)). The N_2Cl_2 coordination at each copper is square planar (only distortion 91.0(2)°), although the sulfur atoms are semicoordinating (Cu1···S10 3.116(3)Å, Cu2···S20 3.019(3)Å), to give a tetragonally distorted octahedral geometry around the copper atoms.

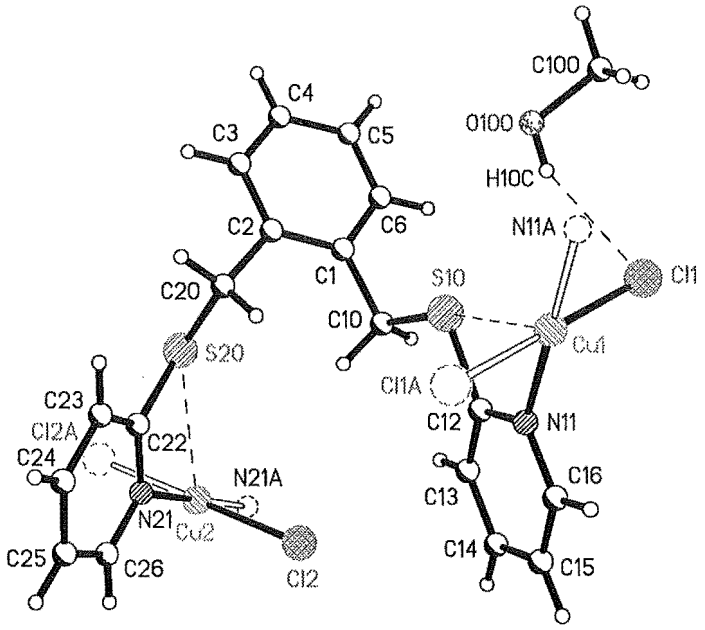


Fig. 2.39 Perspective view and atom labelling of 232. Selected interatomic distances (Å) and angles (°): Cu1-N11 1.993(6), Cu1-Cl1 2.220(2), Cu1-S10 3.116(2), Cu2-N21 1.987(6), Cu2-Cl2 2.243(2), Cu2-S20 3.019(2); N11-Cu1-Cl1 91.0(2), N21-Cu2-Cl2 90.5(2).

The single benzene and two pyridine rings in the asymmetric unit are each approximately planar, with the largest out of plane distortions being for C1 and C2 (-0.02(1) and 0.02(1)Å). This is most likely a result of steric relief of the proximate methylene substituents. The meanplanes of the pyridine rings are inclined at angles of 87.2(8)° and 53.7(8)° to the meanplane of the linking benzene ring, destroying any crystallographic symmetry within the ligand, while the two pyridine ring meanplanes are inclined to one another at an angle of 56.1(8)°. Cu2 lies slightly (0.106(8)Å) out of the extended plane of the coordinated pyridine ring, while Cu1 is in the plane of its coordinated pyridine (0.006(8)Å).

The presence of the hydrogen-bonded methanol to Cl1 (H10C-Cl1 2.54(1)Å) leads to distinct differences in the Cu1 and Cu2 sections of the polymer chain. For Cu2, with no nearby methanol, the inclination of the coordinated pyridines allows for a relatively compact conformation. The presence of methanol in the Cu1 section decompresses the polymer, thus spacing the benzene rings on either side out. This is difference is shown (fig. 2.40) by viewing the two sections of the polymer chain in the plane of both the benzene, and pyridine rings wherein the difference in inclination of the pyridine rings to the benzene rings is observed.

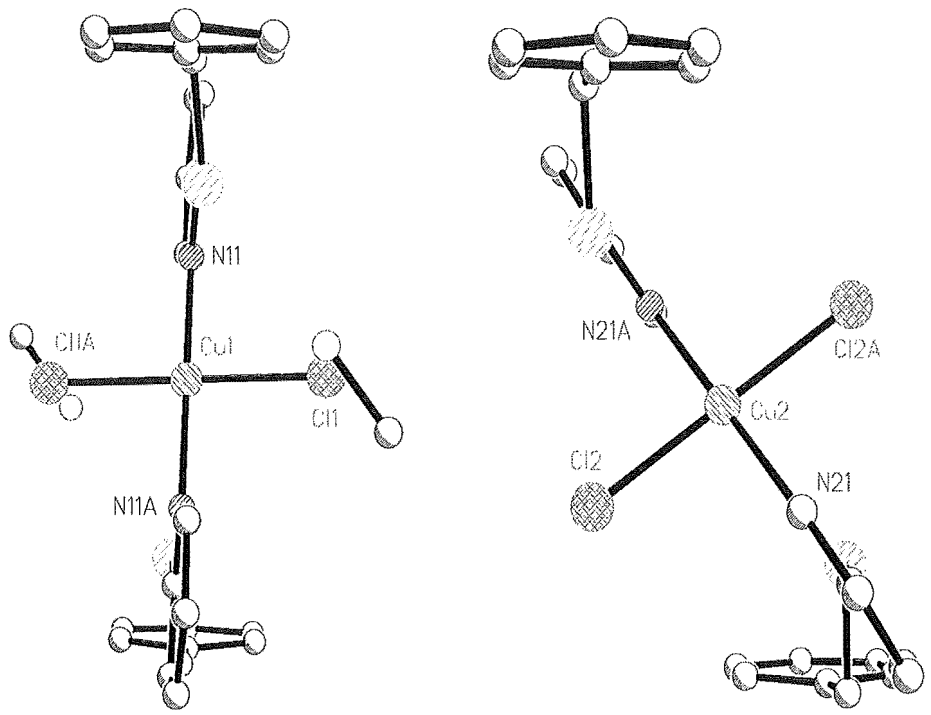
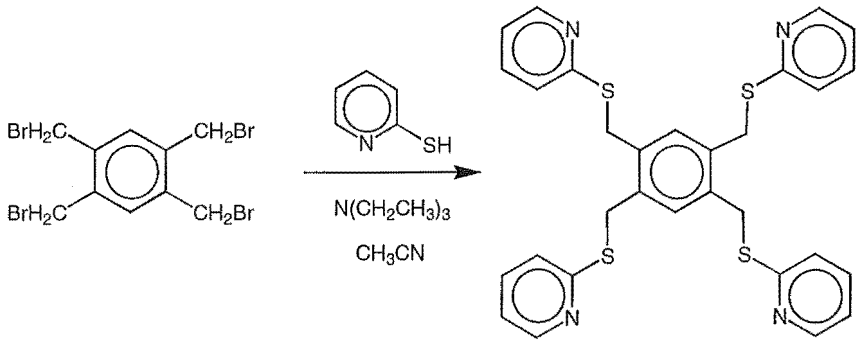


Fig. 2.37 Perspective view of the two different sections of polymer in 232 showing the structural difference with and without hydrogen-bonded methanol.

For the three bis(pyridylsulfide) ligands discussed above, a discrete [2+2] macrocycle, as well as three polymeric structures were characterised. As discussed earlier, the use of a central benzene core allows for as many as six coordinating substituents. If either of the above modes of coordination are observed upon increasing the number of substituents, then complexes with interesting topologies and properties may occur. In the case of macrocycle formation, novel cage structures may result, while polymer formation might also lead to interesting complexes. Investigation of self-assembled two- and three-dimensional metallopolymers is rapidly increasing as a result of their possible application as functional materials.[16] The polymeric structures above are one-dimensional polymers rather than the more desirable multidimensional compounds. However given that bis-substituted compounds lead to one-dimensional polymers, an analogous tetrasubstituted benzene might be expected to give a multidimensional polymer.

To this end 1,2,4,5-tetra(2-pyridylsulfanylmethyl)benzene, 233, was synthesised in good yield from 2-mercaptopyridine and 1,2,4,5-tetrakis(bromomethyl)benzene (fig. 2.41). Palladium, silver and copper complexes, 234, 235 and 236 respectively, of this

ligand were prepared in good yields (>80%). Each of these complexes analyse as [233.M_2.xH_2O] where M = $PdCl_2$, $AgNO_3$ or $CuCl_2$ and x = 2, 2 or 0 for 234, 235 and 236 respectively. Not unexpectedly, the copper complex, 236, was very insoluble and further characterisation was not possible. As for the previous palladium complexes, the ^{1}H N.M.R. spectrum of 234 shows a ligand/complex equilibrium to exist in solution. Crystals of the silver complex, 235, suitable for single-crystal X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the complex. The structure of this complex was determined to investigate whether a multidimensional metallopolymeric structure had assembled.



233

Fig. 2.41

Crystal Structure of 235.

The complex crystallises in the triclinic space group P-1 with the asymmetric unit containing half a [233.2$AgNO_3$.2H_2O] unit, although the complete ligand is shown with the asymmetric unit labelled (fig. 2.42). The nitrate ion and water molecule are disordered approximately evenly over two sites, wherein one site is occupied by water while the other is occupied by nitrate and vice versa. The extended polymeric structure of the complex is also shown (fig. 2.43), where the one dimensional nature of the polymer can be seen. To each silver atom is coordinated a chelated pyridyl sulfide moiety and a pyridine nitrogen from a different ligand, with all bond lengths consistent with related structures. For half of the silver atoms, a water oxygen is also coordinated (Ag1-O100 2.360(8)Å), and for the other half two nitrate oxygens are weakly coordinated to the silver (Ag1-O1A 2.639(9)Å, Ag1-O2A 2.793(9)Å).

The single benzene and two pyridine rings in the asymmetric unit are each approximately planar with the largest out of plane distortions being for N11 and C12

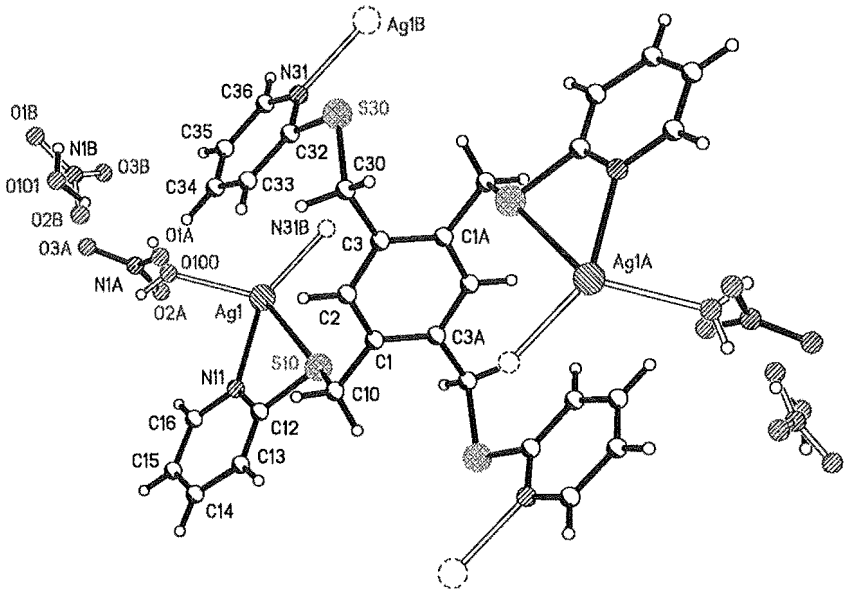


Fig. 2.42 Perspective view and atom labelling of 235. Selected interatomic distances (Å) and angles (°):Ag1-N11 2.271(3), Ag1-N31B 2.227(3), Ag1-S10 2.956(1), Ag1-O100 2.360(8), Ag1-O1A 2.639(8), Ag1-O2A 2.793(8); N11-Ag1-N31B 145.5(1), N11-Ag1-S10 57.03(8), N11-Ag1-O100 91.0(2), N31B-Ag1-S10 88.80(8), N31B-Ag1-O100 119.5(2), S10-Ag1-O100 133.4(2).

(-0.016(7) and 0.014(7)Å). This is a result of strain in the four membered S10-C12-N11-Ag1 chelate ring. The meanplanes of the pyridine rings are inclined at angles of 87.1(8)° and 94.7(8)° to the meanplane of the linking benzene ring, and at 7.9(8)° to each other. The silver atom lies out of the extended planes of the coordinated pyridine rings by 0.461(2) and 0.006(2)Å.

The polymeric structure is a chain of twenty-membered macrocycles joined through incorporation of a common benzene ring into adjacent macrocycles. The Ag-Ag separation across the macrocycles (7.447(1)Å) is shorter than those of the previously described twenty-membered dinuclear rings, possibly as a result of a π–π interaction between pyridines coordinated to each silver in the ring. (fig. 2.43). This interaction is relatively strong (separation of meanplanes 3.34(1)Å) and again places an atom of one ring over the centroid of the other.

Examination of the crystal packing of 235 (fig. 2.44) shows that a weaker π–π interpolymeric interaction may exist (ring separation 3.56(1)Å) although this interaction has overlaying ring centroids rather than the more favoured atom-centroid overlay (thick dashed lines of fig. 2.44). The reason for this less favoured situation may be the

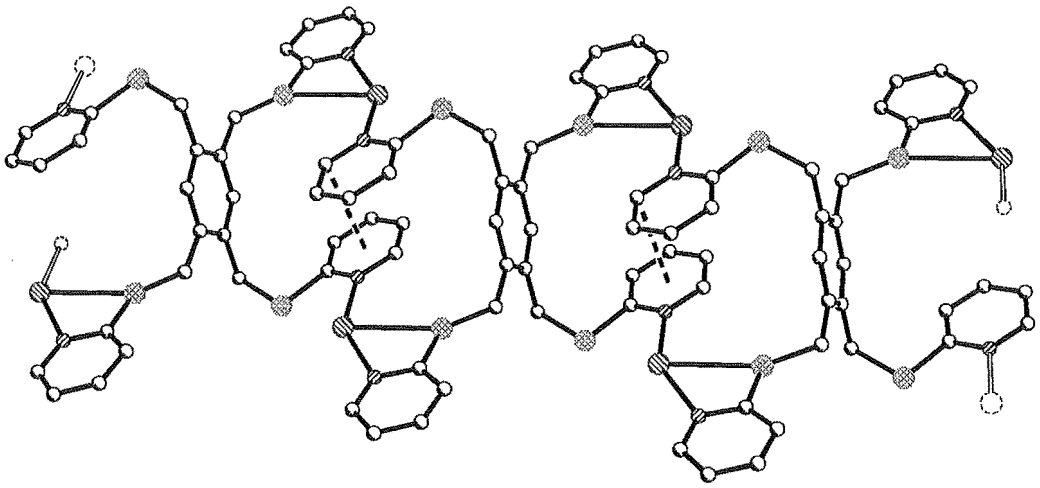


Fig. 2.43 Perspective view of the polymeric structure of 235 with hydrogens omitted, but the intra-polymer π–π stacking of aromatic rings shown.

semicoordination of sulfur atoms from one polymer to silver atoms of the adjacent polymer (AgS 3.531(1)Å) as well as a weak interpolymer sulfur-sulfur interaction (3.412(2)Å), both shown as thin dashed lines (fig. 2.44). So while the polymer is formally one dimensional, it also has a weak two dimensional character.

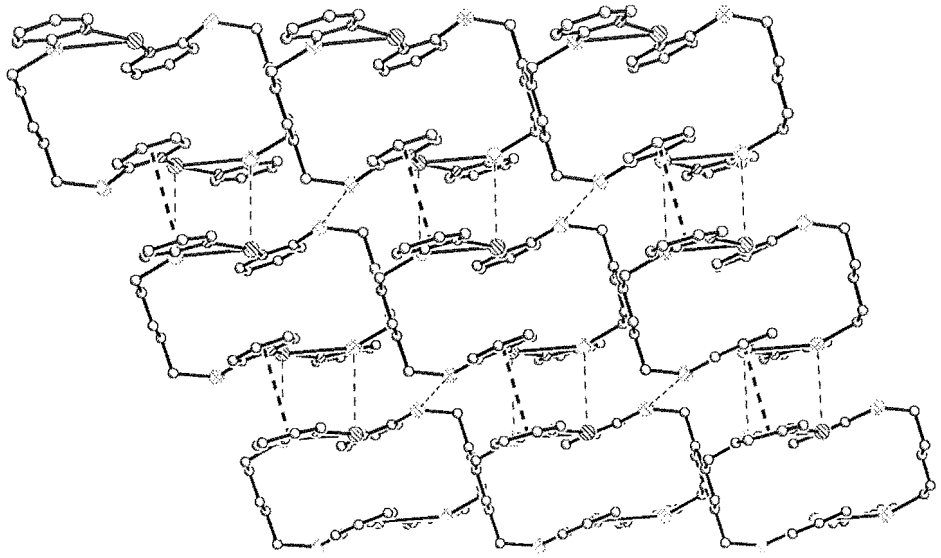


Fig. 2.44 Perspective view of 235 with hydrogens omitted showing the inter-polymer Ag-S and S-S interactions (thin dashed lines) and π–π stacking of aromatic rings (thick dashed lines).

Chapter 3

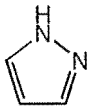
Complexes of Bis- and Tetrakis-pyrazolyl Ligands

Complexes of Bis- and Tetrakis-pyrazolyl Ligands

3.1 Introduction.

The coordination chemistry of pyrazole-derived ligands has received much attention in the past 25 years, and comprehensive reviews of this area exist.[9] Over this period, pyrazole subunits have been incorporated into an extensive number of ligands, or indeed, have been used as ligands in their own right without any structural modification. The study of pyrazole-containing ligands continues to develop as a result of several interesting features this class of compound offers.

The presence of two nitrogens in the pyrazole ring, 3.1a, as opposed to the one of pyridine, increases the coordinative versatility of the heterocycle - while pyridine is limited to nitrogen coordination to one metal, pyrazole, or more specifically, the pyrazolate anion, 3.1b, can coordinate through each nitrogen to bridge two metals.[2,9] This mode of coordination of pyrazolate groups has been extensively used, and many complexes have been reported in which two metal centres are bridged by one, two or three pyrazolate groups. In particular, the systems containing two pyrazolate bridges are of interest, as the proximity of the two metals imparts a potential use of such complexes as catalytic reagents.

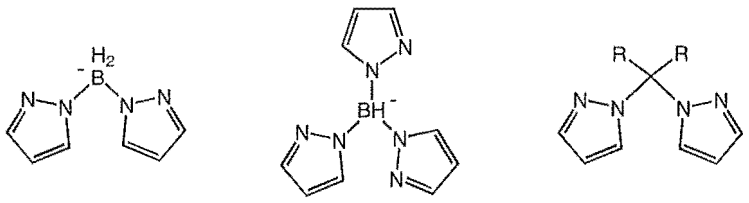


3.1a

3.1b

Fig. 3.1

Ruthenium complexes of pyrazole-containing ligands are also a subject of some interest. Investigation of these complexes developed out of the extensive study of $[Ru(bpy)_3]^{2+}$ and its redox and photophysical properties.[115] These properties can be tuned by variation of the ligands coordinated to the ruthenium. While tuning can be achieved using substituents in the pyridine rings, far greater changes of the properties of the complex occur by replacing pyridine with other nitrogen-containing heterocycles. In particular, incorporation of pyrazole (or another azole five membered heterocycle) results in dramatic changes in the properties of the ruthenium complex. This results from the π-excessive pyrazole group being a poorer π-acceptor than the π-deficient pyridine group. Numerous biheterocyclic pyrazole-containing bpy analogues have been



3.2a 3.2b 3.2c

Fig. 3.2

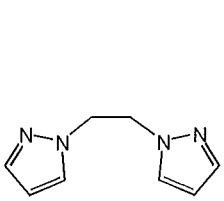
reported for the purposes of this research.[4,116]

While the pyrazole-containing chelating ligands synthesised for $[Ru(bpy)_3]^{2+}$ modification consist of two directly linked heterocycles, polypyrazolyl ligands with the pyrazole groups linked by one atom, have also been extensively investigated. Of these, the poly(pyrazol-1-yl)borates are the most studied, with the anionic bis(pyrazol-1-yl)borates, 3.2a, and tris(pyrazol-1-yl)borates, 3.2b, comprising the majority of these;[9] the coordination chemistry of the latter will be discussed in chapter four. In complexes containing bis(pyrazol-1-yl)borates, this ligand is typically chelated to the metal.[9,117] The coordination chemistry of neutral analogues of 3.2a, the bis(pyrazol-1-yl)methanes, 3.2c, has also been investigated and, like the anionic borates, chelation of the ligand to a single metal is typically observed.[9,117-124]

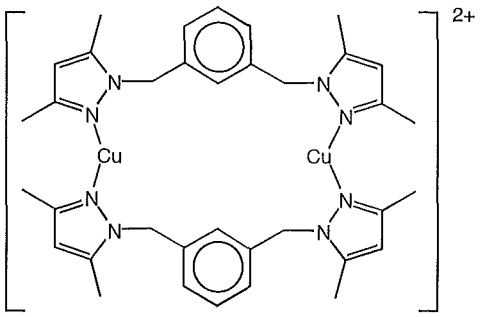
The coordination of ligands where the link between the two pyrazole groups is extended has also been investigated. In complexes of bis(pyrazol-1-yl)ethane, 3.3a, with a number of different metals, including a $[Rh(3.3a)(cyclooctadiene)]^+$ complex, the ligand chelates to the metal.[125] A range of other bis(pyrazolyl) ligands has also been investigated,[126-134] with particular emphasis on their copper complexes as models for copper-containing proteins.[130,134] Included in these are a [2+2] Cu(I) macrocycle, 3.3b, of 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene,[133] as well as Cu(II) complexes of 1,2-bis(pyrazol-1-ylmethyl)benzene, where the ligand chelates to the copper.[134] Cyclometallated complexes of 1,3-bis(pyrazol-1-ylmethyl)benzene have also been reported [135] (see chapter 5).

Numerous bis(pyrazolyl) compounds have been reported where other heterocycles are also incorporated in the ligand.[136-140] For example, complexes of many bis-bidentate ligands have been designed, again as models for dicopper proteins, but also in the study of electrochemical and antiferromagnetic coupling in binuclear complexes.[2]

A variety of tetrakis(pyrazol-1-yl) ligands have also been reported. The coordination of tetrapyrazolylborates, 3.4a, has been investigated, wherein the ligand acts as a tridentate ligand to a metal or as a bis-bidentate bridging ligand, but not in a



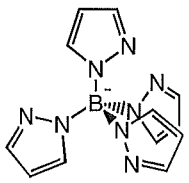
3.3a



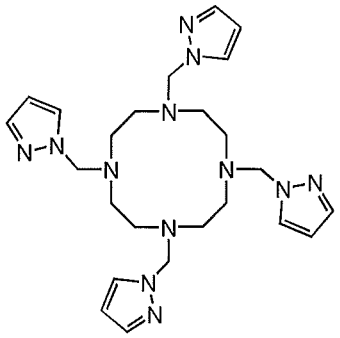
3.3b

Fig 3.3

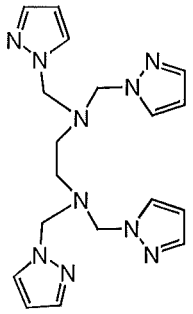
tetradentate fashion, as a result of the tetrahedral disposition of the pyrazole groups around the boron centre.[9] Other tetrakis(pyrazol-1-yl) ligands, 3.4b-d, have been reported which do allow for tetradentate coordination of the four pyrazole groups to a single metal.[141-143] The macrocyclic ligand, 3.4b, acts as an eight coordinate ligand with additional coordination of the four nitrogen atoms in the macrocyclic ring.[142] Likewise, in complexes of 3.4c, the two aliphatic amine nitrogen atoms coordinate to the same metal as the four pyrazoles making this ligand hexadentate.[143] An exception to this is a silver complex of 3.4c, in which the ligand is bis-bidentate through the four pyrazoles with only weak silver - amine nitrogen interactions.[144] Copper complexes of amine linked tetrakis(pyrazol-1-yl) compounds, for example 3.4e, in which one amine and two pyrazole nitrogens are coordinated to each copper centre, have also been used to model dicopper proteins.[145] As for 3.3b, a meta-xylyl bridge is used to link the two tridentate moieties.



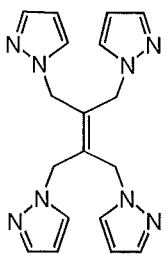
3.4a



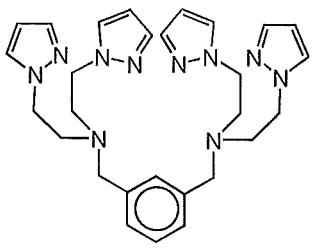
3.4b



3.4c

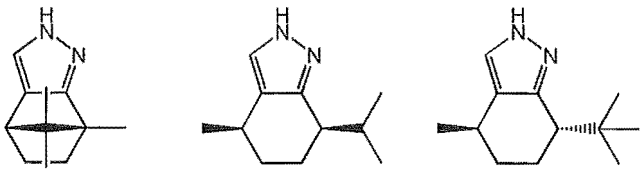


3.4d



3.4e

Fig. 3.4



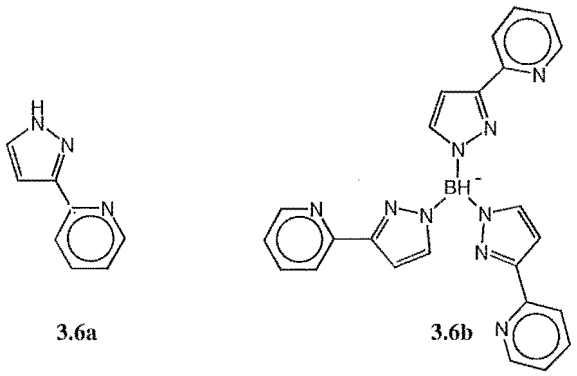
3.5a 3.5b 3.5c

Fig 3.5

The incorporation of pyrazole groups into ligands offers the important advantage that variously substituted pyrazoles are relatively easy to synthesise.[146] The use of these different pyrazoles allows for control of both the electronic and steric properties of metal complexes.[116] While ligands incorporating a variety of different substituted pyrazoles have been reported, one class of these - chiral pyrazoles - has recently received much attention.

The chemistry of complexes containing chiral ligands has been an area of intense research in recent years, with respect to development of new methods of asymmetric catalysis. In these catalytic processes, a single enantiomer of a chiral molecule is produced from a prochiral substrate by means of interaction with a chiral metal complex.[147,148] Several chiral pyrazoles, such as 3.5a-c, have been incorporated into ligands, complexes of which have been used in a variety of different asymmetric reactions.[149-158] Of these, a ligand containing (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazole (camphorpyrazole), 3.5a, has recently been used in enantioselective epoxidation of styrenes.[158]

The coordination of polybidentate ligands has also been an area of intense interest. The complexes of such ligands self-assemble into helix, knot or cage structures, among others, the formation of which has seen rapid development in the theme of supramolecular chemistry.[24,25,28-30] While ligands containing linked bpy units have been extensively studied in this context, those of analogous pyrazole-containing ligands have lagged behind. The recent synthesis of 2-(3'-pyrazolyl)pyridine (3.6a)[159] provides a means for such an investigation to be undertaken. The remarkable coordination chemistry of tris(3.6a)hydroborates (3.6b) has recently been reported, including encapsulation of one metal centre (U or Sm)[160] or a trinuclear silver cluster by two ligands,[161] and formation of a tetrameric $[Mn_4(3.6b)_4]$ unit.[162] Despite this realisation of the potential for forming complexes with interesting structures and properties, coordination chemistry of other poly(2-(3'-pyrazolyl)pyridine) ligands has not been reported.



3.6a 3.6b

Fig. 3.6

In this chapter, the coordination chemistry of bis- and tetrakis(pyrazolyl) ligands will be discussed. In keeping with the structural motif outlined previously, these ligands have the general structures shown (fig. 3.7) with pyrazole units linked, through methylene groups, to a central benzene ring. Four different pyrazole groups will be used in this investigation, including camphorpyrazole and 2-(3'-pyrazolyl)pyridine.

The syntheses of all the bis- and tetrakis(pyrazolyl)methylbenzenes employ the same general approach. The poly(bromomethyl)benzene is first prepared by bromination of the appropriate polymethylbenzene using N-bromosuccinimide. In this manner, 1,2-, 1,3- and 1,4-bis(bromomethyl)benzene,[163] as well as 1,2,4,5-tetrakis(bromomethyl)benzene[164] were prepared according to literature procedures. These poly(bromomethyl)benzene compounds were then used in phase-transfer-catalysed alkylations[165] of a selection of pyrazole-based heterocycles, whereby, the bromomethyl compound and a slight excess of the pyrazole are refluxed in benzene and 40% aqueous sodium hydroxide, in the presence of tetrabutylammonium hydroxide catalyst. The discussion of the coordination chemistry of the bis- and tetrakis(pyrazolylmethyl)benzenes includes eleven X-ray structure determinations in which a variety of modes of coordination are observed.

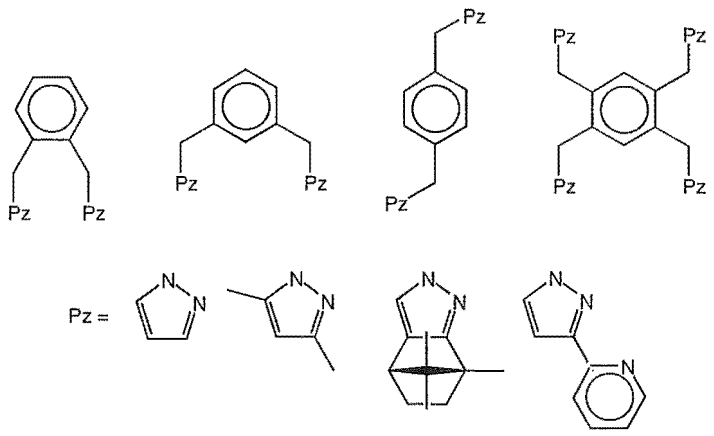
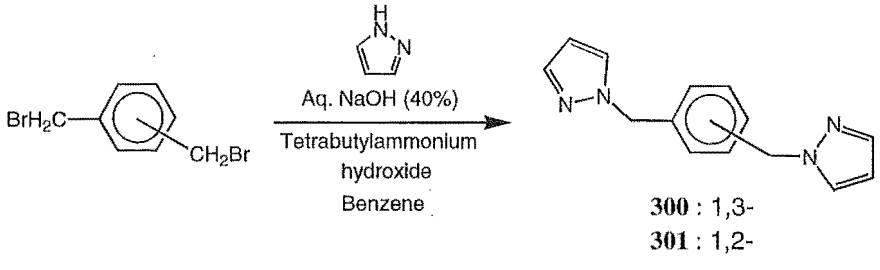


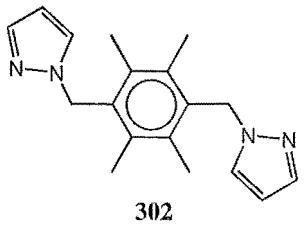
Fig 3.7

3.2 Synthesis and Complexes of Bis(pyrazol-1-ylmethyl)benzene Ligands.

The bis(pyrazol-1-ylmethyl)benzenes, 300 and 301, were synthesised by alkylation of pyrazole with 1,3- and 1,2-bis(bromomethyl)benzene, respectively (fig. 3.8). The 1,2-substituted ligand, 301, isolated in satisfactory yield (57%), has recently been synthesised in similar yield by other workers using solid sodium carbonate instead of aqueous sodium hydroxide, and no catalyst.[134] This report, however, contained errors in the assignment of ^{1}H N.M.R. signals, wherein the signals for H5' and H4,5 were assigned incorrectly. The 1,3-substituted ligand, 300, isolated in excellent yield (88%), has also been synthesised by other workers by reaction of potassium pyrazolate with 1,3-bis(bromomethyl)benzene,[135] although ^{13}C N.M.R. data were not reported. The synthesis and coordination chemistry of 1,4-bis(pyrazol-1-ylmethyl)benzene has been investigated in previous work,[166] although no X-ray crystal structure determinations were carried out. Following on from the coordination chemistry of poly(pyridyl)benzenes discussed in the previous chapter, the coordination chemistry, in particular the silver complexes, of 1,4-(pyrazol-1-ylmethyl)benzenes were of renewed interest. To this end, 1,4-bis(pyrazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene, 302, was prepared, according to a procedure from work undertaken prior to this thesis.[166]

While the coordination chemistry of 1,4-bis(pyrazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene has been investigated previously,[166] silver complexes of this ligand had not been prepared. Reaction of 302 with silver nitrate gave a white precipitate, 303, which analysed as [302.$AgNO_3$]. Slow evaporation of an acetonitrile solution of 303 furnished crystals suitable for single-crystal X-ray structure determination.





302

Fig 3.8

Crystal Structure of 303.

The complex crystallises in the monoclinic space group C2/c, and is a metallopolymer. The asymmetric unit contains half of a 302 ligand, positioned about a centre of inversion and coordinated to a silver atom which lies on a two-fold rotation axis; the nitrate ion also lies with two atoms on this axis. The asymmetric unit is labelled and shown together with its adjacent units (fig. 3.9).

The silver atom is coordinated to two pyrazole nitrogens with non-linear geometry (N12-Ag1-N42A 169.4(1)°). There are also semicoordinate chelating nitrate oxygens, O1 and its symmetry equivalent generated by the rotation axis, O1B (Ag1-O 2.662(2)Å). The silver-donor bond distances are in agreement with the distances of related literature compounds,[83,144,167] as well as the structures described in this work. The silver atom is significantly out of the planes of the two coordinated pyrazole rings (displacement from planes 0.373(2)Å), a magnitude of distortion comparable to those observed in other silver complexes.

The benzene and pyrazole rings are planar (maximum displacement from plane 0.005(3)Å). The meanplanes of the pyrazole group is inclined to that of the benzene at an angle of 85.6(2)°.

The packing both within, and between polymer chains is controlled by steric factors. No π–π interactions either within or between chains, and no polymer-bridging nitrate interactions exist in the structure.

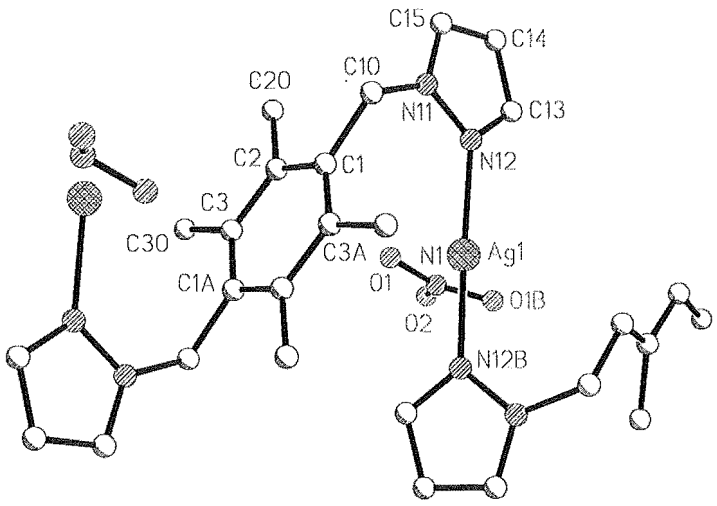


Fig. 3.9 Perspective view and atom labelling of 303 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N12 2.141(2); N12-Ag1-N12B 169.4(1).

Palladium, silver and copper complexes, 304, 305 and 306, of 1,3-bis(pyrazol-1-ylmethyl)benzene were prepared. Each of these complexes analyse as [300.M.xH_2O], where M = $PdCl_2$, $AgNO_3$ or $CuCl_2$ and x = ¼, 0 or 0 for 304, 305 and 306 respectively. The palladium complex, 304, is soluble in DMSO and although attempts to obtain X-ray quality crystals from such solutions proved unsuccessful, vapour diffusion of methanol into a DMSO solution of 304 isolated the complex. The ^{1}H NMR spectrum of this complex shows that there exists an equilibrium between noncoordinated ligand, 301, and a complex, 304, the dimeric/oligomeric nature of which is undetermined. The copper complex, 306, was recrystallised from 1:1 acetonitrile/ethanol, suggesting that this complex is of monomeric or dimeric nature, rather than a polymeric complex which would be insoluble in such solvents. Although a dimeric structure would be consistent with the previously characterised copper(I) complex of 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene,[133] no further characterisation of 306 was made. Reaction of 301 with silver nitrate afforded a white precipitate of 305. Slow evaporation of an acetonitrile solution of this precipitate furnished crystals suitable for single-crystal X-ray structure determination.

Crystal Structure of 305.

The complex crystallises in the orthorhombic space group $Pna2_1$, and is a metallopolymer, the asymmetric unit of which contains a [300-Ag(NO_3)-300-Ag(NO_3)] unit (fig. 3.10). The silver atom, Ag1, is coordinated to two pyrazole nitrogens and to an oxygen of a nitrate ion (Ag1-O6 2.599(7)Å). The second silver atom, Ag2, is also coordinated to two pyrazole nitrogens and is weakly coordinated to the same oxygen as Ag1 (Ag2-O6 2.739(6)Å). The silver-donor bond distances are in agreement with the distances of related literature compounds,[84,144,167] as well as the structures described in this work. The N-Ag-N angles are both non-linear (162.1(3) and 161.5(2)°) with the coordinated oxygen, O6, approximately bisecting the larger N-Ag-N angles (N-Ag1-O6 97.1(2) and 100.8(2)°, N-Ag2-O6 97.2(2) and 86.8(2)°) to give a distorted T-shaped geometry for both. Again, the silver atoms are significantly displaced from the planes of their coordinated pyrazoles (by between 0.133(8) and 0.413(8)Å).

The two benzene and four pyrazole rings are each planar (maximum displacement from plane 0.01(1)Å). However, there are significant differences in the geometry of the two ligands in the asymmetric unit. This can be observed in the inclinations of the two pairs of pyrazole groups to the meanplane of their methylene-linked benzenes (68.8(8) and 103.0(8)° for one ligand, 80.4(8) and 94.0(8)° for the other ligand). The two ligands

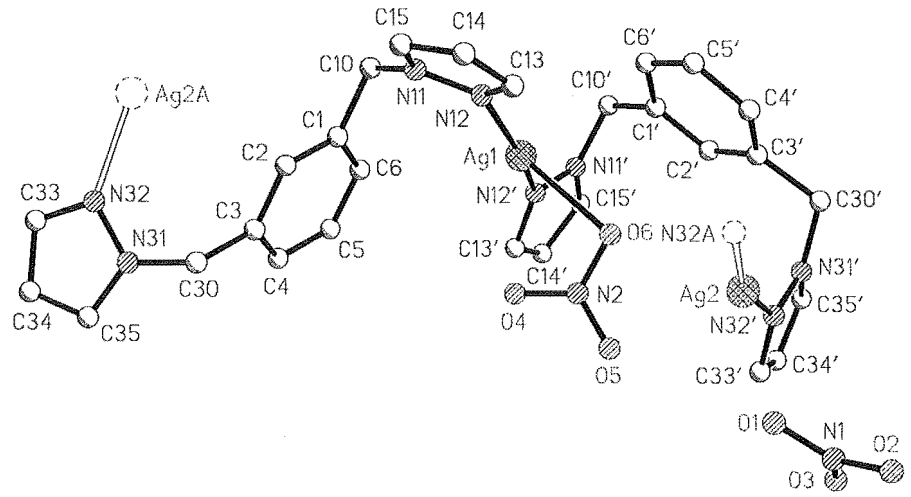


Fig. 3.10 Perspective view and atom labelling of 305 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N12 2.135(7), Ag1-N12' 2.167(7), Ag1-O6 2.599(7), Ag2-N32' 2.160(6), Ag2-N32A 2.186(6); N12-Ag1-N12' 162.1(3), N12-Ag1-O6 97.1(2), N12'-Ag1-O6 100.8(2), N32'-Ag2-N32A 161.5(2).

are also distinguishable by the different conformations of the pyrazole groups (fig. 3.11), where one of the ligands has the two pyrazole groups on opposite sides of the benzene meanplane, while the other has both on the same side of the benzene plane. The latter conformation arises from the mutual (semi-)coordination of both silver atoms to O6. As a result, the two pyrazoles of the bridging ligand are held on the same side of the benzene ring. Such a Ag-O-Ag interaction does not restrict the next ligand in the same manner. Hence, the pyrazoles are on opposite sides of the benzene ring which, due to steric factors, is likely to be the more favoured arrangement.

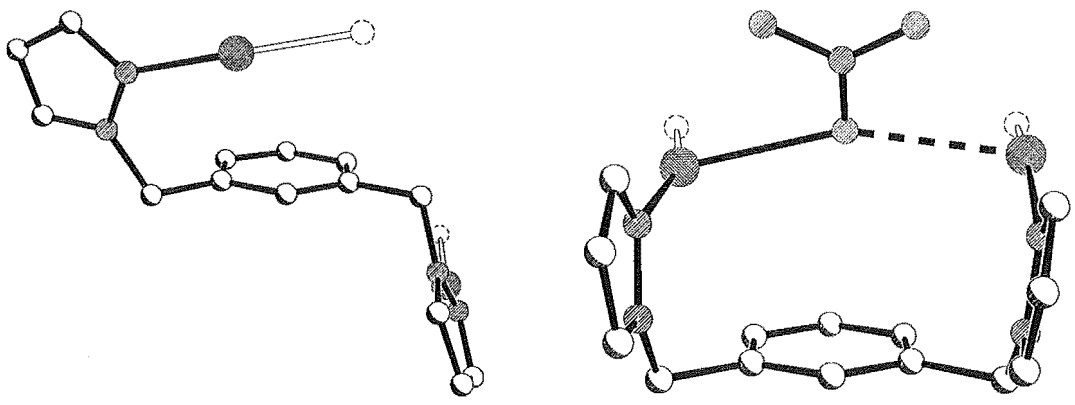


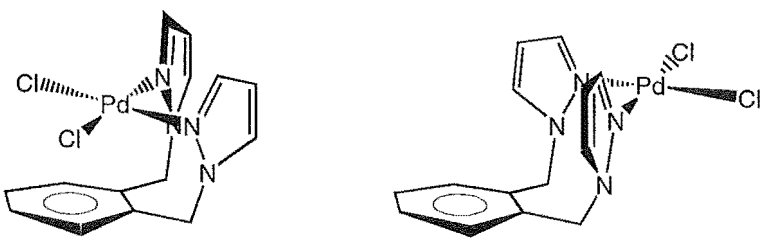
Fig. 3.11 Perspective view of the two different ligand conformations in 305.

As for 303, the packing both within, and between, polymer chains is again controlled by steric factors. No π–π interactions, either within or between chains, and no polymer-bridging nitrate interactions exist in 305.

Palladium and silver complexes, 307 and 308, of 1,2-bis(pyrazol-1-ylmethyl)benzene were prepared. X-ray crystal structures of copper complexes of this ligand have previously been determined by other workers.[134] Both of these complexes analyse as [301.M], where M = $PdCl_2$ or $AgNO_3$ for 307 and 308 respectively. The palladium complex, 304, is soluble in DMSO and although attempts to obtain X-ray quality crystals from such solutions proved unsuccessful, one such attempt - vapour diffusion of methanol into a DMSO solution of 304 - isolated the complex.

The ^1H NMR spectrum of this complex in DMSO shows that there exists an equilibrium between noncoordinated ligand, 301, and a complex, 307. Ignoring the signals of the free ligand, the spectrum shows seven signals, arising from three pyrazole, two benzene and two methylene hydrogen environments. While the pyrazole and benzene signals indicate the complex has two-fold symmetry, the two sharp, geminally coupled methylene signals, centred at 5.78 and 7.69ppm, shows the complex to be locked in a conformation which makes the two hydrogens in a CH_2 group different. A probable structure for 307, with 301 cis-chelated to palladium, is consistent both with these observations, and with the structure of 210.

As for 210, two distinct cis-chelated structures are possible depending upon whether the benzene ring is proximate (endo) or distal (exo) to the palladium atom (fig. 3.12). Although downfield coordination induced shifts of between 0.10 and 0.62ppm are observed for the benzene and pyrazole hydrogens, the most significant shifts for determining the structure of 307, are those of the two methylene signals discussed above (5.64ppm in the free ligand). The significant downfield shift of one pair of hydrogens



endo- **exo-**

Fig 3.12

compared to the other pair, is consistent with an agostic interaction for the lower field methylene hydrogens[168,169] that would exist only in the exo-isomer. While the endo-structure was observed for 210, there are no methylene hydrogens in that complex to stabilise the exo-structure. Hence, the endo- structure was observed due to benzene ring coordination in 210, while the exo- structure, with agostic Pd-H interactions, is the proposed structure of 307.

The structure of 307 was not confirmed by X-ray crystal structure analysis, and n.O.e. experiments were not possible due to the complication of the complex/free ligand equilibrium. An exo- structure for 307 is, however, consistent with that of the palladium complex, 322a, of 1,2-bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl)methyl]benzene, where an exo- structure was confirmed by n.O.e. experiments (see section 3.3).

Reaction of 301 with silver nitrate afforded small crystals of 308. These crystals were redissolved in acetonitrile, where, upon slow evaporation, this solution yielded crystals suitable for single-crystal X-ray structure determination.

Crystal Structure of 308.

The complex crystallises in the orthorhombic space group Pbca, and is a metallopolymer, the asymmetric unit of which, [301.$AgNO_3$], is labelled and shown together with the adjacent ½ units (fig. 3.13).

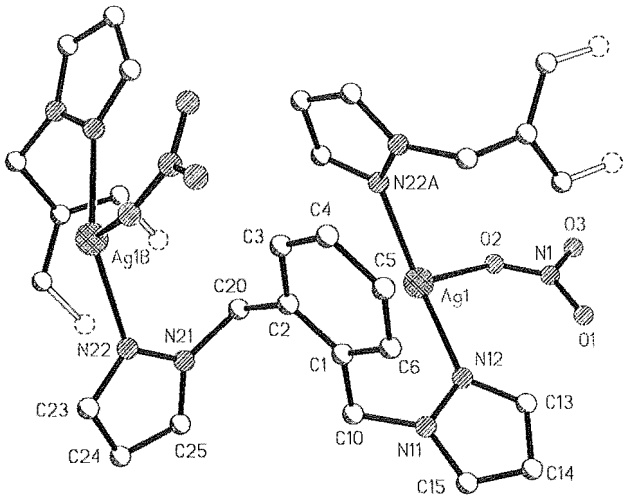


Fig. 3.13 Perspective view and atom labelling of 308 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N12 2.219(4), Ag1-N22A 2.224(4), Ag1-O2 2.511(3); N12-Ag1-N22A 141.2(1), N12-Ag1-O2 100.5(1), N22A-Ag1-O2 107.1(1).

The silver atom is coordinated to two pyrazole nitrogens and a nitrate oxygen, with the silver-donor bond distances in agreement with the distances of related compounds.[144,167,170-172] The coordination geometry of the silver atom is closer to trigonal than it is to being T-shaped (N-Ag1-N 141.2(1)°, N-Ag1-O2 100.5(1) and 107.1(1)°). As with other silver complexes, the silver atom is significantly displaced from the planes of its coordinated pyrazoles (by 0.015(4) and 0.571(4)Å).

The benzene ring and the two pyrazole rings are planar (maximum displacement from plane 0.007(6)Å). The meanplanes of the two pyrazole groups are inclined to that of the benzene at angles of 96.8(5) and 75.6(5)°, destroying any potential crystallographic symmetry in the ligand, and at an angle of 124.7(6)° to each other.

As for 303 and 305, there are no π–π interactions, either within or between polymer chains, contributing to the structure of the polymer. The crystal packing is controlled by steric factors and also by the nitrate ions bridging two silver atoms of different polymeric chains (Ag1-O2 2.511(3)Å, Ag1-O1A 2.615(3)Å).

While it is interesting that a metallopolymeric structure was observed for 308 when a chelated structure was expected, the metallopolymeric structure of 303, involving 1,4-bis(pyrazol-1-ylmethyl)benzene, has greater significance with respect to the structures of the silver complexes observed previously. The ligand, in this case, contains a carbon-only link between the benzene and the heterocycle. The polymeric structure of 303 therefore supports the concept of a requirement for a coordinating atom in the benzene/heterocycle linkage in order to assemble a [2+2] dimer, as proposed in the previous chapter. It is therefore interesting to speculate as to whether a ligand with one hetero-atom linkage and one carbon-only linkage would form a [2+2] or metallopolymeric silver complex. To examine this, 1-(2-pyridoxy)-4-(pyrazol-1-ylmethyl)benzene, 309, was synthesised, and its coordination chemistry investigated.

The ligand, 309, was synthesised in three steps from 4-methylphenol (fig. 3.14). 1-(2-Pyridoxy)-4-methylbenzene was first synthesised according to a reported procedure.[78] The methyl group was then brominated, using N-bromosuccinimide in the presence of strong light and benzoylperoxide catalyst, to give 1-(2-pyridoxy)-4-(bromomethyl)benzene. Without purification, this was then used in a phase-transfer-catalysed alkylation of pyrazole to give 309, which was subsequently isolated by column chromatography in modest yield.

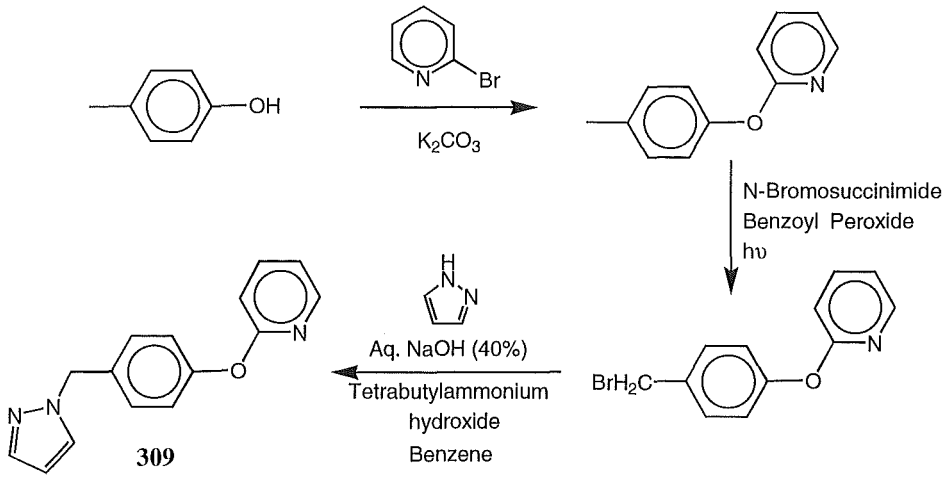


Fig 3.14

Palladium, silver and copper complexes, 310, 311 and 312, of this ligand were prepared. Each of these complexes analyse as [309.M.xH_2O], where M = $PdCl_2$, $AgNO_3$ or $CuCl_2$ and x = 1, 0 or ¼ for 310, 311 and 312 respectively. The poor solubility of 310 and 312, possibly as a result of the formation of polymeric complexes, prevented any further characterisation of these two complexes. However, slow evaporation of an acetonitrile solution of 311 furnished crystals suitable for single-crystal X-ray structure determination.

Crystal Structure of 311.

The complex crystallises in the monoclinic space group $P2_1/n$, and is a metallopolymer, the asymmetric unit of which contains two [309-Ag(NO_3)] units of different polymeric chains (fig. 3.15).

The silver atoms are both coordinated to a pyridine nitrogen, a pyrazole nitrogen and to an oxygen of a nitrate ion, with silver-donor bond distances consistent with those of related structures.[82-84,170] While the coordination geometry of Ag2 is distorted T-shaped (N11'-Ag2-N42' 156.8(5), N-Ag2-O5 111.9(4), 91.2(5)°), that of Ag1 is closer to trigonal (N11-Ag1-N42 138.5(4), N-Ag2-O3 112.9(4), 89.1(5)°). The silver atoms are again out of the planes of their coordinated heterocycles by varying distances (between 0.01(1) and 0.21(1)Å).

The two benzene and four heterocyclic rings are each planar (maximum displacement from plane 0.06(2)Å), with the largest distortions from planarity being nonsystematic and not attributable to any obvious reasons such as strain. Although the heterocycle meanplanes for each ligand are inclined at different angles to their

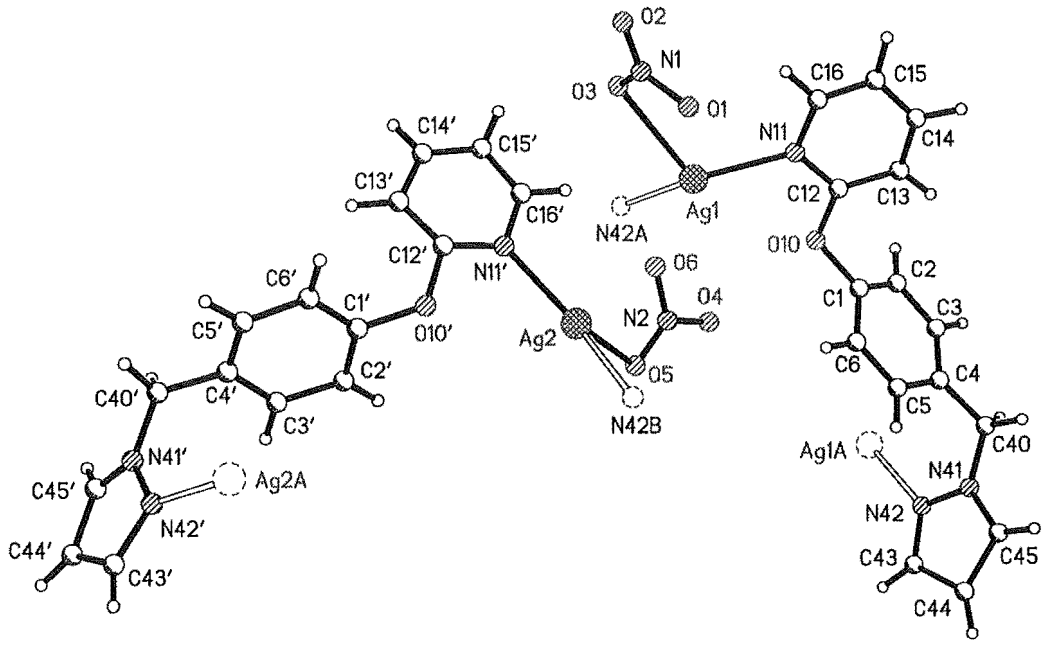


Fig. 3.15 Perspective view and atom labelling of 311. Selected bond lengths (Å) and angles (°): Ag1-N11 2.202(9), Ag1-N42A 2.25(1), Ag1-O3 2.620(9), Ag2-N11' 2.18(1), Ag2-N42'A 2.19(1), Ag2-O5 2.58(1); N11-Ag1-N42A 138.5(4), N11-Ag1-O3 112.9(4), N42A-Ag1-O3 89.1(4), N11-Ag2-N42'B 156.8(5), N11'-Ag2-O5 111.9(4), N42'B-Ag1-O5 91.2(4).

respective benzene rings (68(1) and 97(1)° for one ligand, 91(1) and 106(1)° for the other ligand), the overall geometry of the two polymeric chains is remarkably similar (fig. 3.16). This is as a result of the pyridine-benzene π–π interaction present in both, where an atom of one ring is only slightly displaced from the centroid of the other. This interaction is stronger in the Ag1 polymer (centroid-atom distance 3.80(1)Å) than for that of Ag2 (4.00(1)Å), a difference which is transmitted through the ligand to make the respective N-Ag-N angles different. As a consequence of the similarity of the Ag1 and Ag2 polymers, a low percentage of reflections were observed during data collection, due to the pseudosymmetry in the structure. For this reason, the atomic coordinates and derived interatomic distances/angles are not as precisely determined as those of related structures.

In both polymers, the pyridine is on one side of the benzene meanplane, which then coordinates to a silver on the other side of the benzene plane. Such an arrangement is also observed in the [2+2] silver macrocycles previously described, and allows for the weak coordination of the ether oxygen to the silver (Ag···O distances 3.02(1) and

3.12(1)Å). In contrast to this, the pyrazole and coordinated silver are on the same side of the benzene plane, as the methylene link will not coordinate to silver in this manner. Since only one end of the ligand is suitably arranged for [2+2] macrocycle assembly, the result is metallopolymer formation. The presence of a coordinating atom in the benzene-heterocycle linkage is, therefore, necessary for formation of the [2+2] silver complexes described previously. When present, the weak coordination of this atom favours the correct silver-ligand orientation for macrocycle assembly.

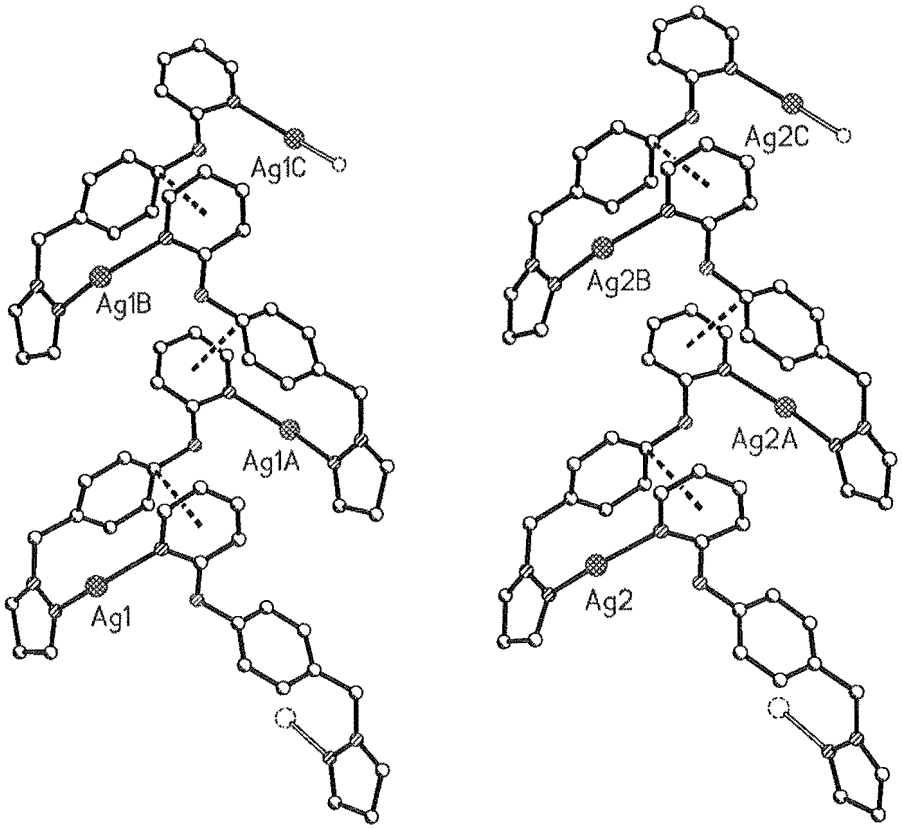


Fig. 3.16 Perspective view showing the similar geometry of the two polymeric chains of 311.

3.3 Synthesis and Complexes of Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene Ligands.

The bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzenes, 313-315, were synthesised by phase-transfer-catalysed alkylation of camphorpyrazole with 1,4-, 1,3-, and 1,2-bis(bromomethyl)benzene, respectively (fig. 3.17). For each of these reactions, two other isomers are formed in addition to those shown in fig. 3.17. These isomers arise as the two nitrogens of the indazole are non-

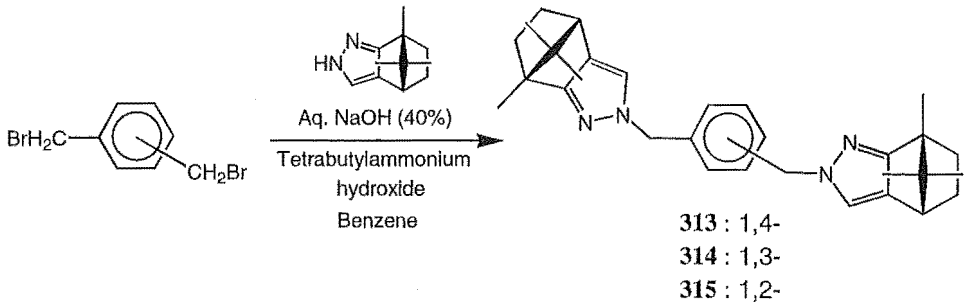


Fig. 3.17

equivalent, so reaction at each therefore leads to a different isomer. Given that two alkylations are required for formation of 313, two other isomers are also formed (fig. 3.18). The major isomer is 313 as alkylation of N2 is more rapid since this is less hindered than N1, an observation also made in previous phase-transfer-catalysed alkylations of (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazole.[173] The same situation applies in the reactions to form 314 and 315. The products of reaction of N1 and N2 are readily distinguishable by ^{1}H N.M.R., wherein characteristic shifts are observed for H3 and the methyl group protons, depending on which nitrogen has been alkylated.

In each case, the isomeric mixture from the reaction was subjected to column chromatography, whereby the major isomers, 313-315, were isolated in moderate yields (40-50%). ^{1}H N.M.R. showed that the unsymmetrical isomers, resulting from alkylation of one indazole at the N2, and the other at N1, were also isolated but these were not further characterised. The third isomer in the reaction mixtures, resulting from

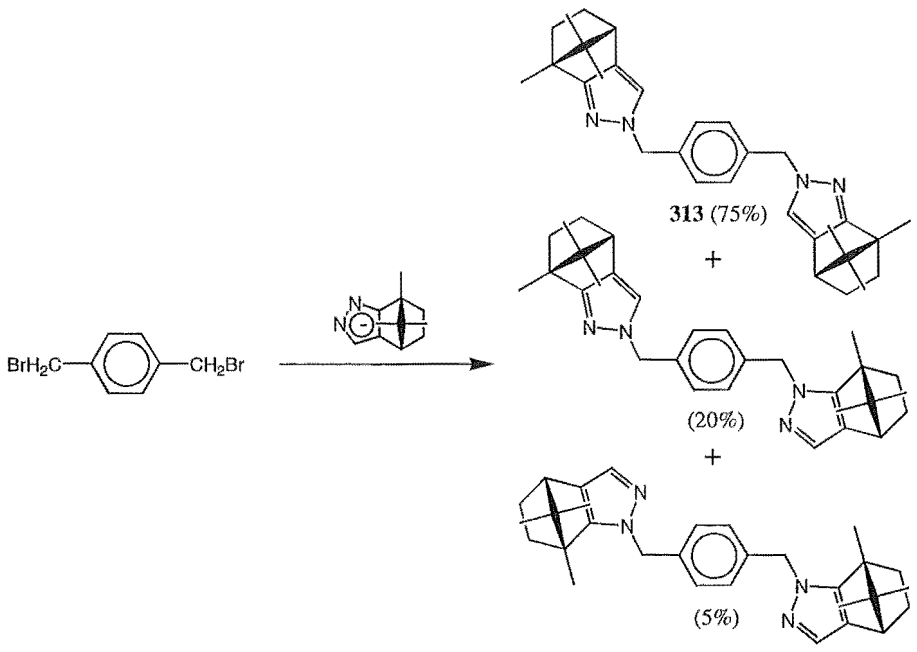


Fig. 3.18

alkylations of both indazoles at N1, was shown by ^{1}H N.M.R. to be less than 5% of the product in each case and was not isolated in any of these three reactions.

Palladium, silver and copper complexes, 316, 317 and 318, of 1,4-bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl)methyl]benzene were prepared. Mixing of methanolic solutions of copper(II) chloride and 313 gave a dark green solution. Diffusion of diethyl ether into this reaction mixture gave a green precipitate, 318, in good yield, which analyses as [313.$CuCl_2$.½H_2O]. Given the solubility of this complex in methanol it is unlikely to be polymeric. This being the case, a [2+2] macrocycle is a likely structure for 318.

Mixing of solutions of 313 and silver nitrate gave 317 as small crystals which analyse as [313.$AgNO_3$]. Given the structures discussed in section 3.2, it could be expected that 317 is also metallopolymeric. In a previous report,[174] a silver complex of a chirally resolved ligand is a metallopolymer with helical chirality, while the complex of the racemic mixture of the ligand is a [2+2] metallomacrocycle. Arising from this, 317 may have a structure where there is helical chirality in the polymer induced by the chirality of the ligand. To examine this possibility, crystals of 317 suitable for single crystal X-ray structure determination were obtained from slow evaporation of an acetonitrile solution of the complex, and the structure was determined.

The palladium complex, 316, precipitated from its reaction mixture upon removal of the methanol, and analyses as [313.$PdCl_2$]. The ^{1}H N.M.R. spectrum of 316 in DMSO shows that the ligand in this complex is symmetrical, although the signal for the methylene hydrogens is an AB quartet, indicating non-equivalence of the methylene hydrogens. The most significant coordination induced shifts are for these methylene hydrogens (geminally coupled doublets centred at 5.67 and 5.76ppm in the complex, cf 5.24ppm for the free ligand in DMSO), and for the hydrogens of the methyl group on the 7'-position of the indazole (2.03ppm in the complex, 1.25ppm in the free ligand). Such changes in chemical shift could result from a change in the conformation of the ligand upon coordination, through-space effects from the nearby coordinated $PdCl_2$ unit, or as a result of agostic Pd-H interactions. The solubility and stability of 316 in organic solvents suggests a discrete complex, such as a [2+2] macrocycle, rather than a polymeric structure for this complex. A macrocyclic structure for 316 would represent the first example of such a complex that incorporates chiral appended heterocycles.

Previously reported macrocyclic structures have been used as hosts in the molecular recognition of guest molecules. It has been noted, however, that the high degree of symmetry in these macrocycles may limit the range of substrates that can be

recognised.[175] Use of macrocycles that, due to the ligands used, are inherently chiral would be one way of tuning molecular recognition of the host. Given this, a more complete characterisation of 316 was desired. To this end, numerous attempts were made at recrystallising the complex, one of which - vapour diffusion of diethyl ether into an acetonitrile solution of 316 - gave crystals suitable for single crystal X-ray structure analysis.

Crystal Structures of 316 and 317.

The palladium complex, 316, crystallises in the orthorhombic space group $P2_12_12$ the asymmetric unit of which contains a [2+2] macrocyclic unit (fig. 3.19) The intramolecular Pd···Pd separation across the 22-membered ring is 9.136(3)Å, a shorter distance than those described in the previous chapter, due to the conformation of the indazole units with respect to their methylene linked benzene rings. Each palladium atom is square planar and is trans-coordinated to two pyrazole nitrogens and two chlorine atoms. The Pd-N and Pd-Cl distances are within the range of reported values for related structures.[176,177]

The two benzene and four pyrazole rings are each planar (maximum displacement from plane 0.02(2)Å). The geometry of the two ligands is very similar: the pyrazole ring meanplanes are inclined to that of the benzene at angles of 102(1) and 76(1)° in one ligand, and at 98(1) and 77(1)° in the other ligand; and the two pyrazoles are inclined to each other at an angle of 43(1)° in one ligand and 44(1)° in the other. The two benzene rings are coplanar (angle between meanplanes 1(1)°) as are the two PdN_2Cl_2 planes (angle between meanplanes 3.2(8)°). In fact, inversion symmetry through the centre of the complex is destroyed only by the chirality of the bornyl framework of the indazole groups.

Although, like the strongly π–π stacked complexes of the previous chapter, the two benzene rings are coplanar, in 316 the benzene rings are displaced from one another so no such interaction is contributing to the stability of the complex. Instead, significant agostic interactions between the palladiums and the methylene hydrogens (Pd1···H40B 2.66(2), Pd2···H20A 2.75(2)Å) are observed (fig. 3.20). There are also weak agostic interaction with the hydrogens of the C17M and C37M methyl groups (Pd1···H17B 3.22(2), Pd2···H37C 3.25(2)Å). These interactions are consistent with the significant coordination induced downfield shifts of these hydrogens in the ^{1}H N.M.R. spectrum of 316.[168,169] In this spectrum, the four methylene groups are equivalent due to the conformational freedom of the complex. Hence the downfield shifts are the average of

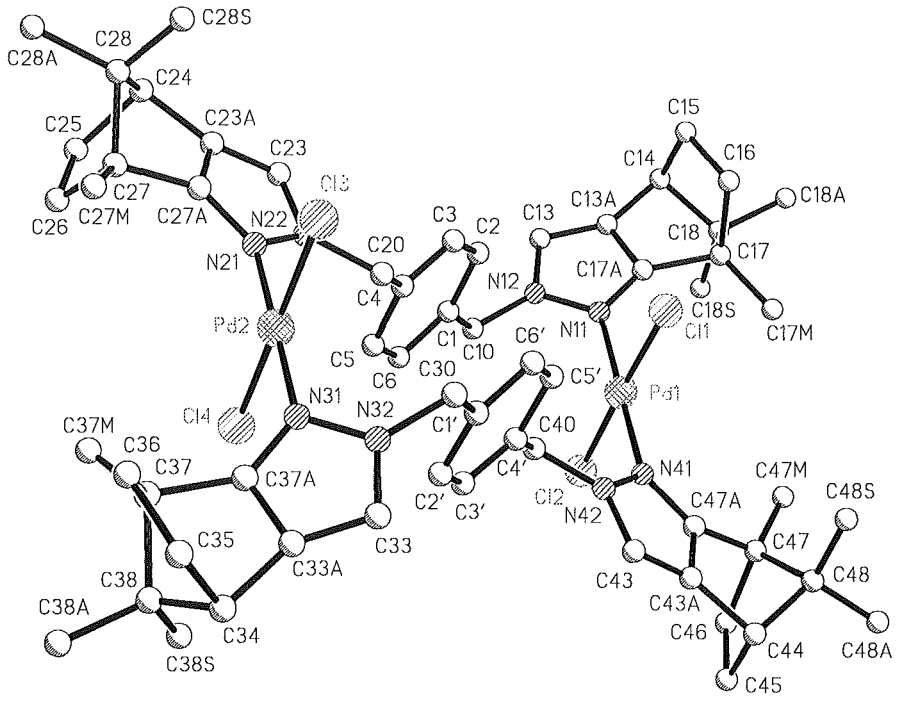


Fig. 3.19 Perspective view and atom labelling of 316 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-N11 2.01(1), Pd1-N41 1.97(1), Pd1-Cl1 2.285(5), Pd1-Cl2 2.299(5), Pd2-N21 2.01(1), Pd2-N31 2.01(1), Pd2-Cl3 2.287(5), Pd2-Cl4 2.307(5); N11-Pd1-N41 179.7(6), N11-Pd1-Cl1 90.0(4), N11-Pd1-Cl2 91.1(4), N41-Pd1-Cl1 89.7(4), N41-Pd1-Cl2 89.1(5), Cl1-Pd1-Cl2 178.3(2), N21-Pd2-N31 179.2(5), N21-Pd2-Cl3 89.5(4), N21-Pd2-Cl4 88.2(4), N31-Pd2-Cl3 90.8(4), N31-Pd2-Cl4 91.5(4), Cl3-Pd2-Cl4 177.4(2).

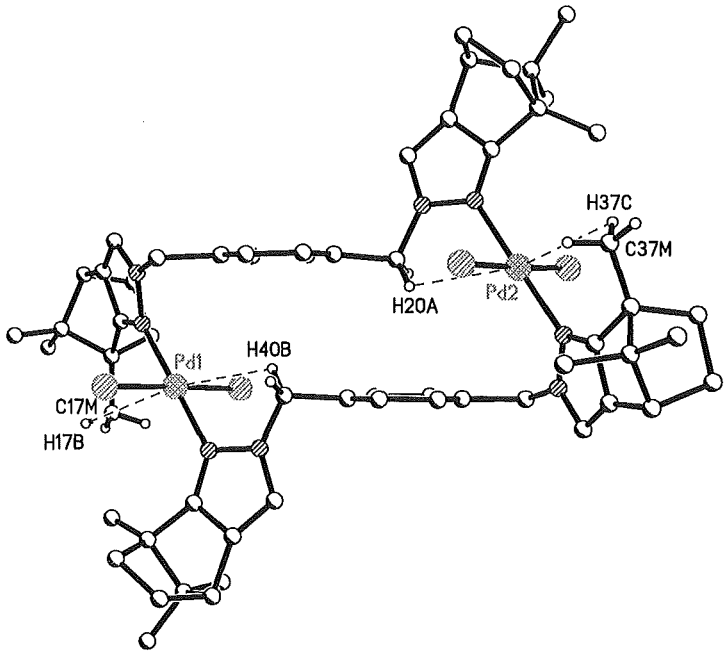


Fig. 3.20 Perspective view showing the agostic interactions in 316.

the agostically interacting and non-interacting orientations. The same applies for C17M, C27M, C37M and C47M, the methyl groups which interact with the palladium atoms.

The silver complex, 317, crystallises in the monoclinic space group $P2_1$, and is a metallopolymer, the asymmetric unit of which, [313.$AgNO_3$], is shown (fig. 3.21). The silver atom is coordinated to two pyrazole nitrogens and a nitrate oxygen, with the silver-donor bond distances in agreement with the distances for related compounds.[167,170,171] The silver coordination plane is close to approximately planar (maximum distortion from plane 0.025(4)Å), with the coordination geometry around the silver atom being closer to trigonal than to T-shaped (N-Ag1-N 143.1(2)°, N-Ag1-O1 123.3(2) and 93.6(1)°). As with other silver complexes, the silver atom is significantly more displaced from the plane of one coordinated pyrazole than from the other (out of plane distances 0.426(4) and 0.067(4)Å).

The benzene ring and the two pyrazole rings are planar (maximum displacement from plane 0.014(8)Å). The meanplanes of the two pyrazole groups are inclined to that of the benzene at angles of 71.9(5) and 113.2(5)°, and at an angle of 109.9(5)° to each other, destroying any potential two-fold crystallographic symmetry in the ligand.

Rather than the polymeric chains of 317 being helical, the [313.$AgNO_3$] units of a chain continuously overlay (fig 3.22). Although the benzene rings of the polymer are eclipsed, the separation between rings is large (>5Å) preventing any π–π interaction. No

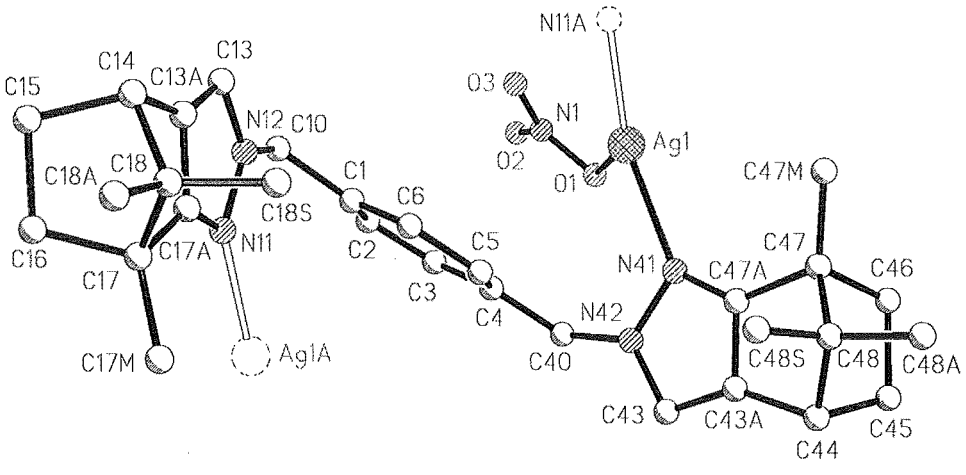


Fig. 3.21 Perspective view and atom labelling of 317 with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-N11A 2.193(4), Ag1-N41 2.216(4), Ag1-O1 2.465(4); N11A-Ag1-N41 143.1(2), N11A-Ag1-O1 123.3(2), N41-Ag1-O1 93.6(1).

π–π stacked interactions, or nitrate coordination to two different polymer chains contribute to the crystal packing in 317.

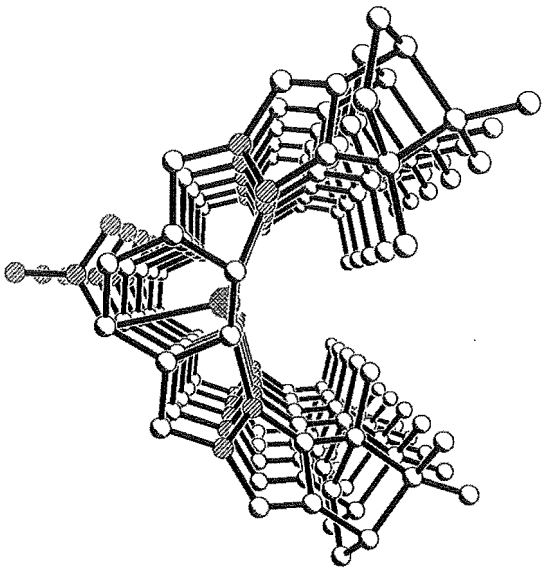


Fig. 3.22 Perspective view showing the overlaid arrangement of a polymeric chain in 317.

Palladium, silver and copper complexes, 319, 320 and 321, of 1,3-bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl)methyl]benzene, 314, were prepared.

In the reaction to form the palladium complex of 314, an orange precipitate was obtained. While a proportion of this is soluble in dichloromethane, the remaining solid, which analyses as [314.$PdCl_2$], was soluble only in DMSO. The ^{1}H N.M.R. spectrum of this less soluble complex, 319a, in DMSO was the same as that of the free ligand. The low solubility of this compound together with its instability in DMSO suggests this to be a metallopolymeric complex. The ^{1}H N.M.R. spectrum of the dichloromethane-soluble complex, 319b, is complicated with many signals being very broad. However, thin layer chromatography of this compound showed no indication of the presence of more than one complex. Fast atom bombardment mass spectrometry (FABMS) showed a set of highest mass ions centred around 1227 Daltons corresponding to $[(314)_2Pd_2Cl_3]^+$. This suggests a dimetallomacrocyclic structure for this complex.

Upon mixing of an aqueous solution of silver nitrate and a methanolic solution of 314, a colourless solution resulted. A silver complex of 314 was not able to be isolated

as the nitrate salt from this reaction mixture due to its high solubility. Addition of excess sodium perchlorate solution did however precipitate a silver complex, 320, as a perchlorate salt. Both microanalysis and FABMS of this complex were consistent with a chelated monomeric structure for 314.

Mixing of methanolic solutions of copper(II) chloride and 314 gave a green solution. Diffusion of diethyl ether into this reaction mixture gave a green/grey precipitate, 321, in good yield, which analyses as [314.$CuCl_2$]. Given the solubility of this complex in methanol it is likely to be a [314.$CuCl_2$] chelated complex, or a [2+2] macrocycle. Mass spectroscopy showed the former to be the case, although there is some uncertainty in this conclusion, as there is evidence of significant lability of the complex in the mass spectrometer.

Palladium, silver and copper complexes, 322, 323 and 324, of 1,2-[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl)methyl]benzene, 315, were also prepared.

An orange precipitate was obtained in the reaction to form the palladium complex of 315. Initial ^{1}H N.M.R. investigation showed the majority of this precipitate to be an unsymmetrical complex, 322a, with sharp signals, with the remainder being a complex, 322b, with very broad signals. These complexes were subsequently separated using column chromatography.

FABMS of 322b showed, like 319a, a set of highest mass ions centred around 1227 Daltons corresponding to $[(314)_2Pd_2Cl_3]^+$. The fragmentation patterns, and the relative abundances of different ions, in the spectra of 322b and 319a are also similar. Given this, and the very broad signals in the ^{1}H N.M.R. spectra of both, the structures are clearly similar. Dimetallomacrocyclic structures are proposed for both, with the N.M.R. broadness due to instability of these structures and/or significant conformational freedom in solution.

The ^{1}H N.M.R. spectrum of 322a (fig 3.23) shows four different methylene hydrogen environments, with the signal for each being a geminally coupled doublet. The four sets of signals are in two distinct groups; two upfield hydrogens at 5.18 and 5.19ppm, and two downfield hydrogens at 6.97 and 7.04. The sharpness of all the signals in the spectrum indicates that the hydrogens are locked in their respective environments. FABMS of this complex showed a set of highest mass ions centred around 597 Daltons, a mass corresponding to $[315.PdCl]^+$, suggesting 322a is [315.$PdCl_2$] with the ligand chelated to the palladium. A cis-chelated structure could be expected, in which case, as for 210 and 307, endo- and exo- isomers are possible.

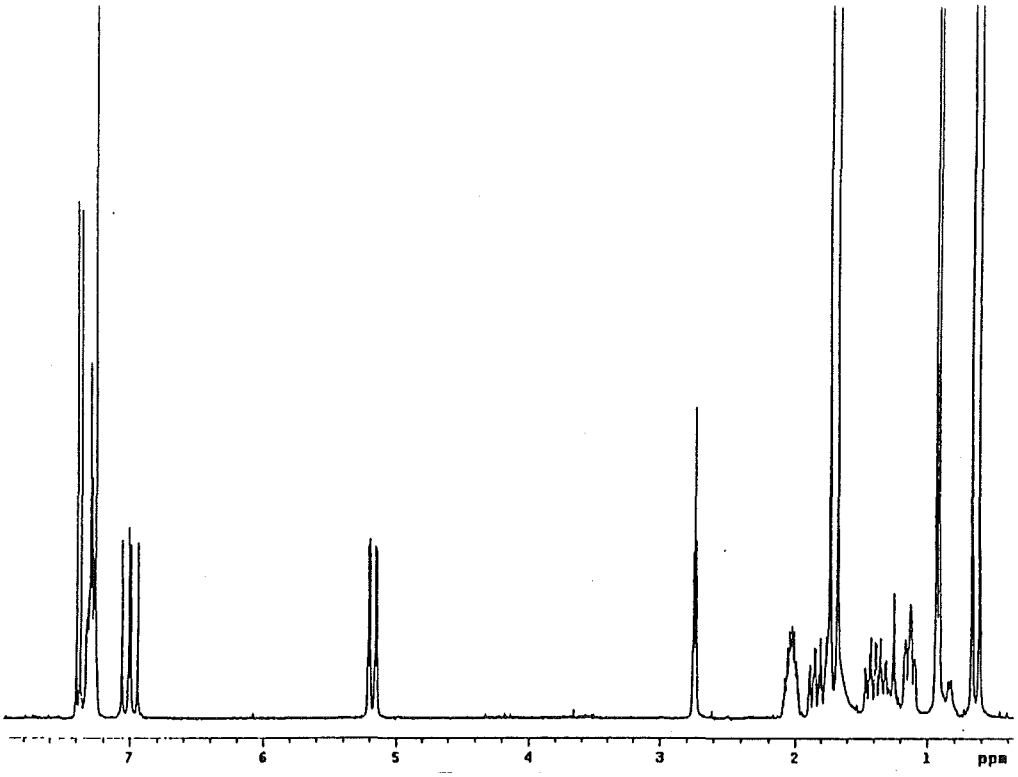


Fig. 3.23 ^{1}H N.M.R. spectrum of 322a

Unlike 307, the palladium complex of 1,2-bis(pyrazol-1-ylmethyl)benzene, 322a is soluble and, importantly, stable in an N.M.R. solvent. As such, n.O.e. experiments can be carried out on 322a to elucidate the structure of the complex. Based on inspection of molecular models, for the endo- structure, irradiation of each methylene hydrogen signal should lead to an enhancement of the signal for H3'. In contrast to this, for the exo- structure, irradiation of half the methylene signals should lead to enhancement of the H3' signal, while irradiation of the other methylene hydrogens will lead to no such enhancement (fig 3.24). It is important, therefore, to first unambiguously assign the H3'

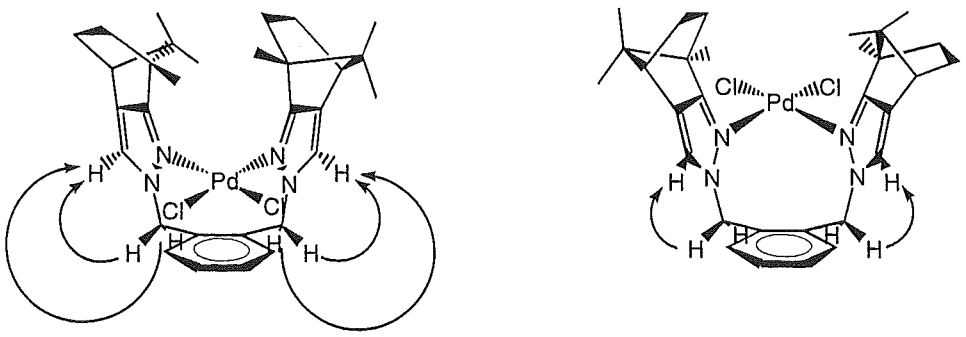


Fig 3.24 Different n.O.e enhancements for endo- and exo- structures of 322a.

signals, which may be any of those between 7.24 and 7.40ppm. This was achieved using an n.O.e experiment, wherein, irradiation of the H4' signals (2.74 and 2.76ppm) resulted in a 1.1% enhancement of the signals at 7.37 and 7.40ppm, which could therefore be assigned to H3' of the two indazole units.

The n.O.e. experiments, wherein the methylene hydrogen signals were irradiated, were then carried out, the resulting n.O.e. difference spectra of which are shown (fig. 3.25). Irradiation of the high field methylene signals (ca. 5.20ppm) lead to enhancements in the low field methylene signals (20.4%), the H3,6 aromatic hydrogens (4.3%) and in the signals for H3' (11.9%). Irradiation of the low field methylene signals (ca. 7ppm) leads only to an enhancement of the high field methylene signals (25.6%). Therefore the structure of 322a is the exo- isomer shown above. The locked nature of the complex leads to two sets of signals for the camphorpyrazole and methylene groups, as the chirality in the ligand destroys the mirror symmetry of the complex and creates two distinct environments for the benzene substituents.

The low field methylene signals can be assigned as those proximate to the palladium atom. These are at a chemical shift approximately 1.8ppm downfield of the

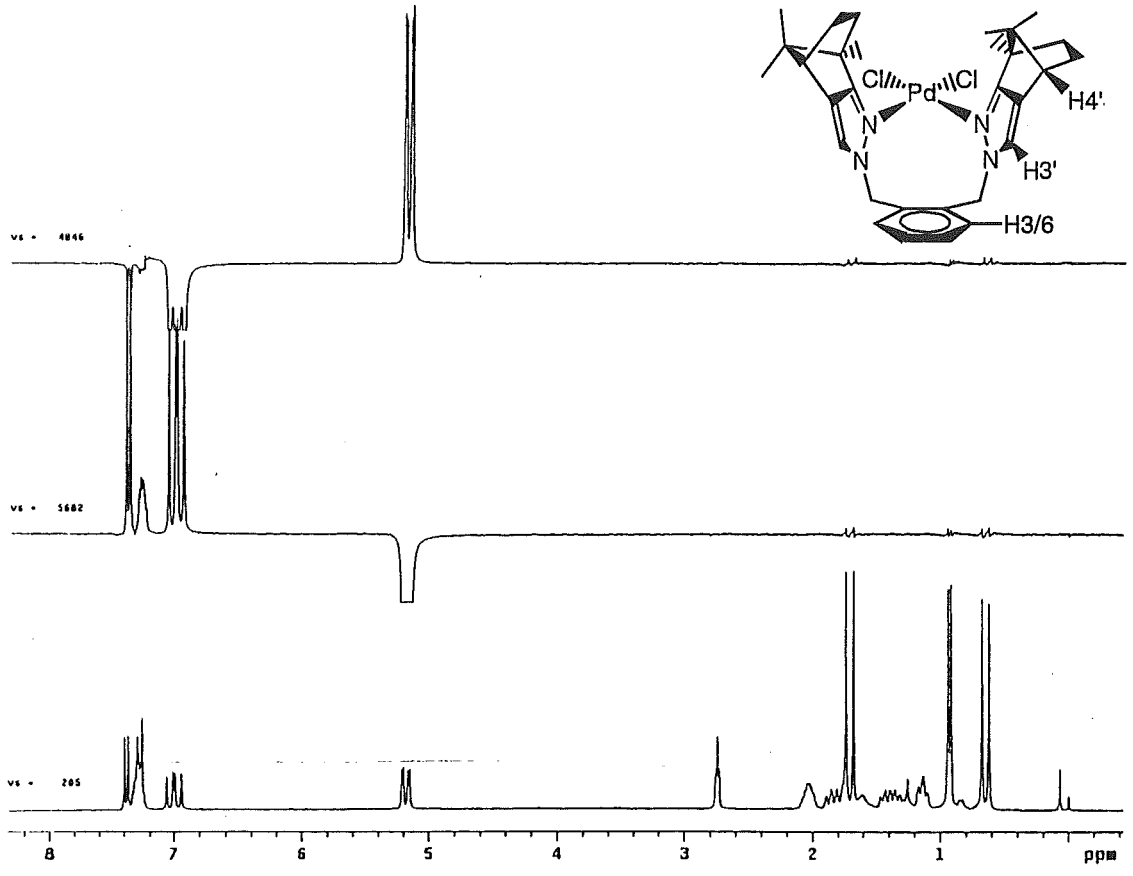


Fig. 3.25 Difference n.O.e spectra for 322a

signals for the other methylene hydrogens. By inspection of a model of this complex, this large downfield shift is probably due to a Pd-H agostic interaction in the complex. As discussed earlier, this result can also be extrapolated back to 307, the palladium complex of 1,2-bis(pyrazol-1-ylmethyl)benzene, where a locked complex with a large downfield shift of a pair of methylene hydrogens was also observed. The structure of 307, therefore, is also assigned to be the exo- isomer.

While the endo-structure was observed for 210, there are no methylene hydrogens in that complex to stabilise the exo-structure. Hence, the endo- structure was observed due to benzene ring coordination in 210, while the exo- structure, with agostic Pd-H interactions, is the structure of 322a and, by implication, of 307.

Upon mixing of an aqueous solution of silver nitrate and a methanolic solution of 315, a colourless solution resulted. A silver complex of 315 was not able to be isolated as the nitrate salt from this reaction mixture due to its high solubility. Addition of excess sodium perchlorate solution did however precipitate the silver complex, 323, as a perchlorate salt. Both microanalysis and FABMS of this complex were consistent with chelated monomeric structure for 323.

Mixing of methanolic solutions of copper(II) chloride and 315 gave a green solution. Diffusion of diethyl ether into this reaction mixture furnished crystals of 324, analysing as [315.$CuCl_2$], which were suitable for single crystal X-ray structure analysis. When using chiral ligands for asymmetric catalysis, chelating ligands are favoured over monodentate or bridging ligands.[178,179] In studying the coordination chemistry of chiral bidentate ligands, it is therefore important to first ascertain whether the ligand will chelate to any metal. Although strong evidence exists that the palladium complex, 322a, of this ligand is a chelated complex, no crystal structure determination was possible to confirm this. The single crystal X-ray structure of the copper complex was therefore determined.

Crystal Structure of 324.

The complex crystallises in the tetragonal space group $P4_3$, the asymmetric unit of which contains two [315.$CuCl_2$] chelate molecules; one of these molecules is shown with atoms labelled (fig. 3.26).

The copper atoms are each coordinated to two pyrazole nitrogens and to two chlorine atoms. The copper-donor bond distances are all consistent with those of related structures.[134,180,181] The coordination geometry around both copper atoms is strongly tetrahedrally distorted from square planar (average 'trans' coordination angle 151.8(3)°,

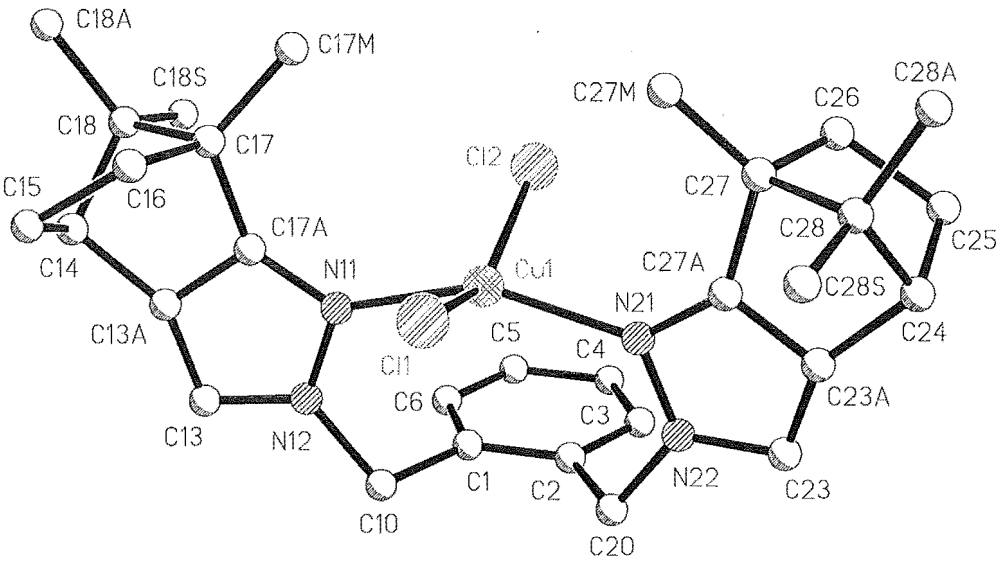


Fig. 3.26 Perspective view and atom labelling of one molecule in the asymmetric unit of 324. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for the Cu1 molecule: Cu1-N11 2.00(1), Cu1-N21 2.020(9), Cu1-Cl1 2.250(4), Cu1-Cl2 2.230(4); N11-Cu1-N21 152.5(4), N11-Cu1-Cl1 91.0(3), N11-Cu1-Cl2 97.5(3), N21-Cu1-Cl1 92.8(3), N21-Cu1-Cl2 94.2(3), Cl1-Cu1-Cl2 146.6(1).

average 'cis' coordination angle 93.4(3)°) The copper atoms are significantly displaced from the plane of their two coordinated pyrazoles (average out of plane distance 0.20(1)Å).

The two benzene and four pyrazole rings are each planar (maximum displacement from plane 0.02(2)Å). The geometry of the two ligands is very similar: the pyrazole ring meanplanes are inclined to that of the benzene at angles of 91(1) and 87(1)° in one ligand, and at 89(1) and 85(1)° in the other ligand; and the two pyrazoles are inclined to each other at an angle of 13(1)° in one ligand and 4(1)° in the other. Aside from this slight difference in pyrazole orientation, the only significant difference between the two chelate molecules is a torsional difference in the $CuCl_2$-ligand relationship (fig. 3.27). The $CuCl_2$ moiety in the Cu2 molecule is twisted from that of the Cu1 molecule, so that Cl4 lies 3.855(5)Å above the plane of the benzene, while Cl2 lies only 3.676(5)Å above the plane of its benzene. The Cl1-Cu1-Cl2 angle (146.6(1)°) is also slightly smaller than that of Cl3-Cu2-Cl4 (152.3(2)°).

It is interesting to compare the structure of 324 with that of the previously reported copper complex of 1,2-bis(pyrazol-1ylmethyl)benzene (fig 3.28).[134] While the

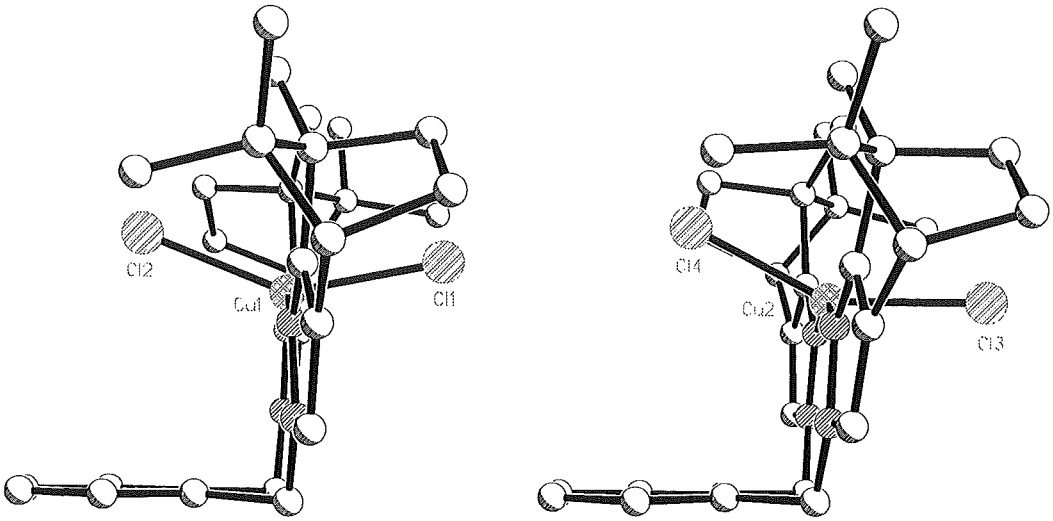


Fig. 3.27 Perspective view showing the different Cl-Cu-Cl orientations in the two molecules of 324.

inclination of the pyrazole rings in this complex was not reported, they are clearly inclined to each other at an angle significantly away from coplanarity. The arrangement of the $CuCl_2$ moiety is also different from 324, as the Cl-Cu-Cl vector is approximately orthogonal to the plane of the benzene, with neither chlorine atom directly over the benzene. The different geometry in 324 is due to the steric effect of the bornyl groups, whereby a conformation such as that in fig. 3.28 is not possible due to the close proximity that would result between the C17M and C27M methyl groups and Cl2.

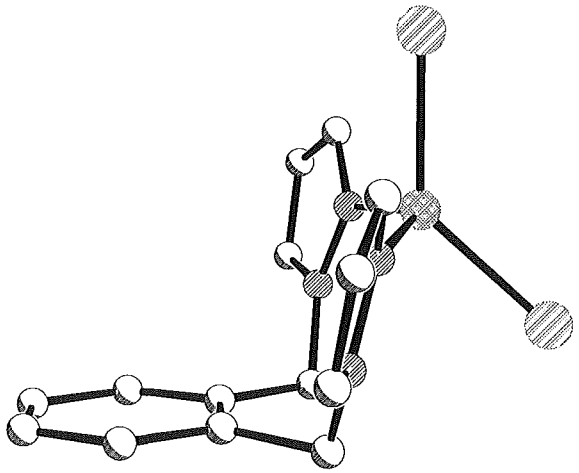


Fig 3.28

3.4 Synthesis and Complexes of Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene Ligands.

Like (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazole, phase-transfer-catalysed alkylation of 2-(3'-pyrazolyl)pyridine also results in the formation of different isomers, depending on which nitrogen of the pyrazole is alkylated. As such, the alkylations of 2-(3'-pyrazolyl)pyridine using 1,4-, 1,3- and 1,2-bis(bromomethyl)benzene result in the formation of 325-327 (fig 3.29), along with two other isomers in each case. The major isomers were identified as 325-327 by n.O.e. experiments, wherein irradiation of the methylene signal in each case lead to an enhancement of the H5' signal, but not H3". The opposite would be observed if alkylation had occurred at N2. However, while in the alkylations of camphorpyrazole the isomer ratios were independent of the bis(bromomethyl)benzene used, the isomer ratios in alkylating 2-(3'-pyrazolyl)pyridine vary depending on whether 1,4-, 1,3- or 1,2-bis(bromomethyl)benzene was used.

In the reaction of 1,4-bis(bromomethyl)benzene with 2-(3'-pyrazolyl)pyridine, 325 is formed in approximately a 2:1 ratio with the isomers resulting from alkylation of one, or both pyrazoles at N2. The major isomer, 325, was subsequently isolated using column chromatography in 49% yield. The product ratio observed suggests that the difference in steric hindrance between N1 and N2 is not as large as that of the two nitrogens of camphorpyrazole, as a greater proportion of alkylation occurs at the more hindered nitrogen of 2-(3'-pyrazolyl)pyridine than at that of camphorpyrazole. However, the reaction of 1,3-bis(bromomethyl)benzene with 2-(3'-pyrazolyl)pyridine results in a 3:1 product ratio, and, with the use of column chromatography, an isolated yield of 57% for 326. The reaction using 1,2-bis(bromomethyl)benzene involves still greater selectivity, in giving a 6:1 ratio of 327 to its isomers. This allowed for a 45% yield of

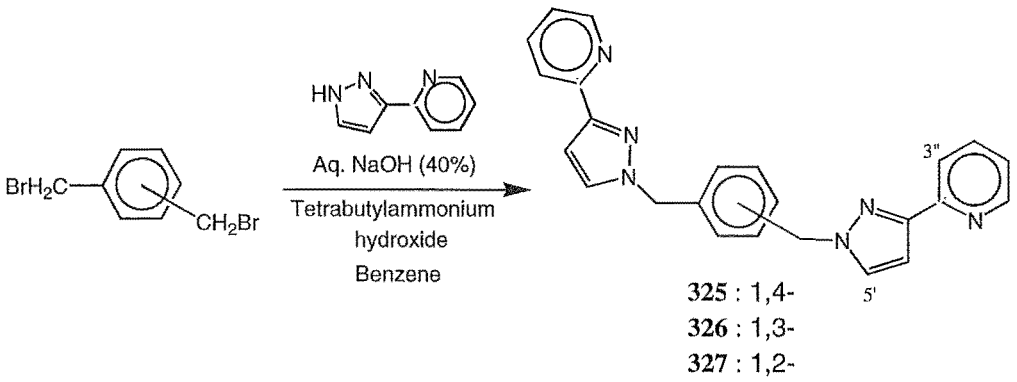
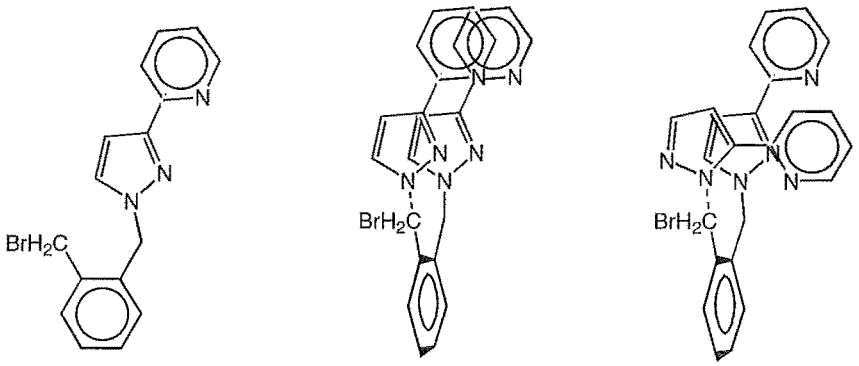


Fig 3.29

327 by recrystallisation, without any need for more time consuming chromatographic techniques.

The changing isomer ratios in these reactions can be explained by steric factors and the effect of π–π stacking. In the reactions to form 325-327, the first alkylation will be more favoured at the less hindered nitrogen, N1. For the 1,2- substituted isomer this bulky pyridylpyrazolyl group is close to the remaining bromomethyl group (fig. 3.30a). This close proximity may have two distinct effects. Firstly, it may hinder the pyridylpyrazole approach for alkylation at the more hindered nitrogen, N2, more than it does for alkylation at N1. Secondly, π–π interactions between the pyridylpyrazolyl group and the approaching pyridylpyrazole will be stronger for alkylation at N1 as greater overlap can occur than for alkylation at N2 (fig. 3.30b,c).



3.30a **3.30b** **3.30c**

Fig 3.30

The reaction for 1,4-bis(bromomethyl)benzene is unlikely to involve any such inter-pyridylpyrazole effects. The 2:1 product ratio obtained, therefore gives a clear indication that the difference in steric hindrance between N1 and N2 in 2-(3'-pyrazolyl)pyridine, is smaller than that of N1 and N2 in camphorpyrazole. The 3:1 product ratio for the reaction of 1,3-bis(bromomethyl)benzene favours N1 alkylation to a greater extent than the 1,4-substituted reaction. This indicates that even for 1,3 substituents, the first 3-(2'-pyridyl)pyrazol-1-ylmethyl group may have an influence on the second alkylation reaction.

Palladium, silver and copper complexes, 328-330, of 1,4-bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene were prepared. The palladium complex, 328, was isolated in excellent yield and analyses as $[325.(PdCl_2)_2]$. The most likely structure for this complex involves cis-coordination of the two pyridylpyrazole moieties to different palladium atoms (fig. 3.31). The ^1H N.M.R. spectrum of 328 in DMSO shows the

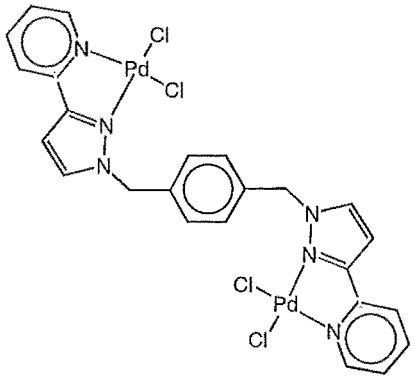


Fig. 3.31

complex to have two-fold symmetry in solution with only one signal (6.22ppm) for the methylene hydrogens. This supports the proposed structure in which the methylene hydrogens are all equivalent. The copper complex, 330, analyses as [325.$(CuCl_2)_2$. ½H_2O] and is assumed to have a similar structure to 328 with chelation of the ligand to two metal atoms. The silver complex, 329, isolated in good yield, analyses as [325.$AgNO_3$.¼H_2O] - a different stoichiometry to the palladium and copper complexes above. The insolubility of this complex in some organic solvents and its instability in others, prevented further characterisation of this complex. However, given these properties, a polymeric structure with pyridylpyrazole moieties from two different ligands coordinated to the same silver atom is proposed (fig 3.32).

The palladium, silver and copper complexes, 331-333, of 1,3-bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 326, have similar stoichiometries to those of the respective complexes of the 1,4-disubstituted ligand. The only difference in analyses between the two sets of complexes is that the copper complex for the 1,3-substituted ligand analyses with ½ a water solvate instead of a ¼. Like the palladium complex above, the ^{1}H N.M.R. spectrum of 331 in DMSO shows the complex to have two-fold

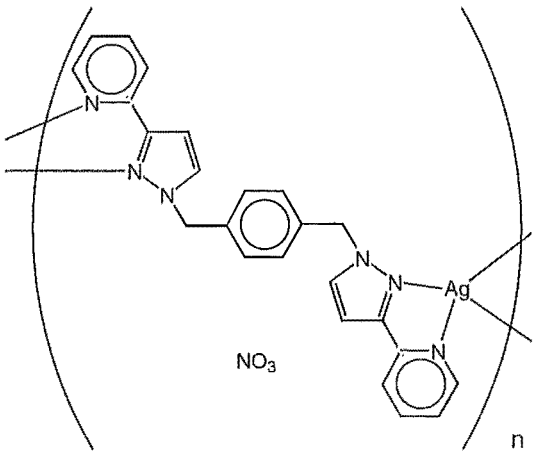


Fig. 3.32

symmetry in solution with only one signal (6.21ppm) for the methylene hydrogens. To assign the spectrum, n.O.e. and 1D-Tocsy N.M.R. experiments were performed. Irradiation of the methylene signal gave enhancements for the singlet at 7.29ppm (assigned to H2), a doublet at 7.38ppm (H4,6) and a doublet at 8.37ppm (H5'). The H6" signal was then irradiated in a 1D-Tocsy experiment which allowed for assignment of signals for H5" (7.69ppm), H4" (8.32ppm) and H3" (8.25ppm). Assignment of the remaining two signals at 7.45ppm (H4') and 7.49ppm (H5) was then possible. The spectra of 328 and 334, the 1,2- and 1,4- substituted palladium complexes were readily assigned by comparison with the spectrum of 331.

On the same basis as the 1,4- substituted complexes, bis-chelated structures are proposed for these 1,3- substituted palladium and copper complexes. As for 329, further characterisation of the silver complex, 332, was not possible. The structure of the latter complex is not as easy to predict, as the closer proximity of the two pyridylpyrazole units of the 1,3- substituted ligand make double chelation to the same metal centre a possibility.

Complexes of 1,2-bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 327, were also prepared. The same general observations are made for the palladium, 334, and copper, 336, complexes of this ligand as those of the 1,4- and 1,3- isomers. Both analyse as $[327.M_2]$ where M = $PdCl_2$ or $CuCl_2$; no water solvate is present in either complex. Again, bis-chelated structures are proposed for these complexes on the basis of these analyses and a symmetrical ^1H N.M.R. spectrum for the palladium complex.

The reaction of silver nitrate with 327 slowly furnished crystals of 335 suitable for single crystal X-ray structure determination. These analyse as $[(327)_2.(AgNO_3)_3]$, a different stoichiometry to that of the 1,3- and 1,4- substituted complexes with silver. A recently reported silver complex of tris[3-(2'-pyridyl)pyrazol-1-yl]borate also has 3:2 metal/ligand formulation and was found to be a trinuclear silver cluster encapsulated by the two ligands.[161] The structure of 335 was determined to examine what type of complex had formed with a bis(3-(2'-pyridyl)pyrazol-1-yl) ligand.

Crystal Structure of 335.

The complex crystallises in the triclinic space group P-1, the asymmetric unit of which, $[327(AgNO_3)_{1.5}]$, is shown, along with the complete $[(327)_2(AgNO_3)_3]$ structure of the complex (fig 3.33). The silver atom, Ag2, and the nitrogen, N2, each lie on crystallographic centres of inversion.

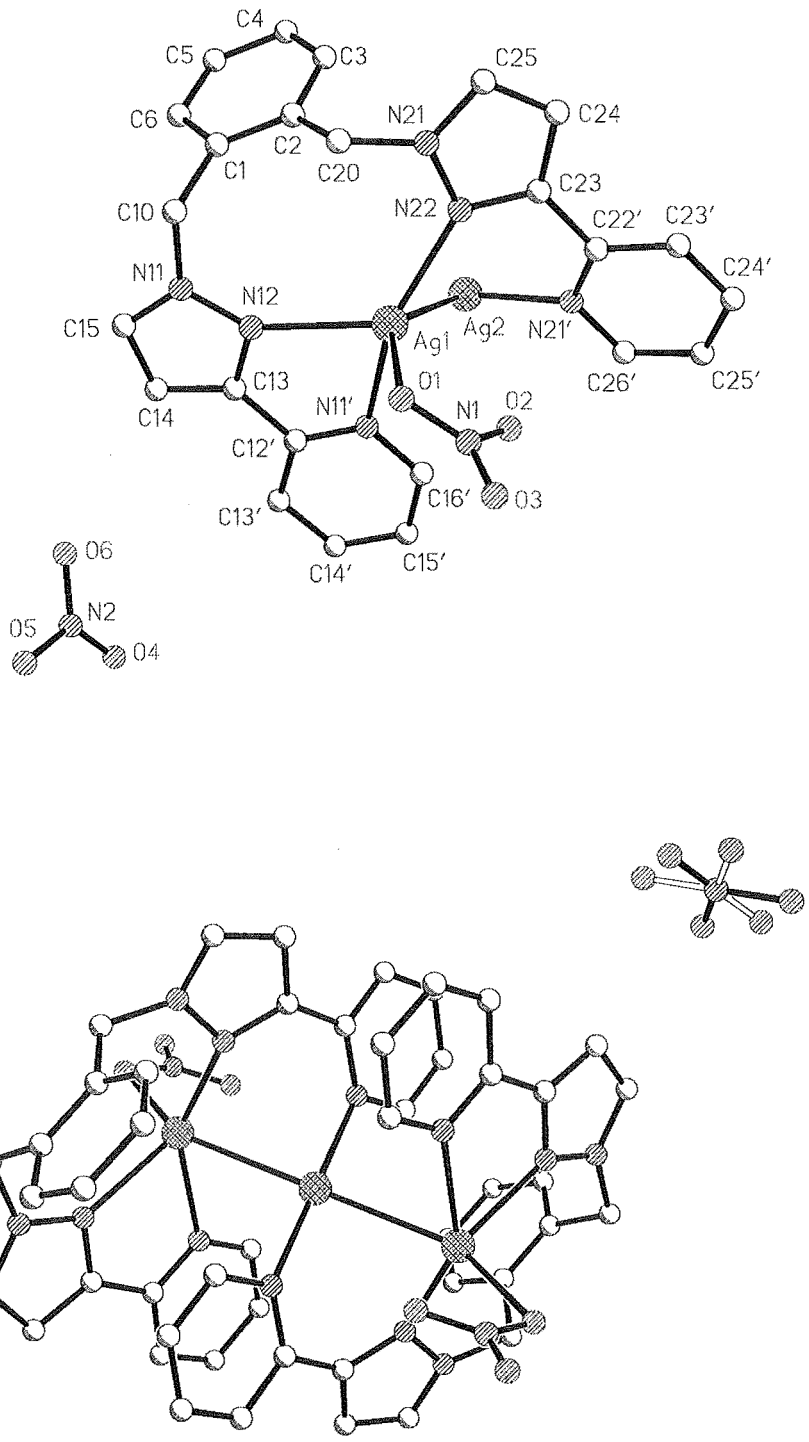


Fig. 3.33 Perspective view and atom labelling of the asymmetric unit of 335 (top) and perspective view of the discrete $[(327)_2(AgNO_3)_3]$ unit of 335 (bottom). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-Ag2 2.8992(8), Ag1-N12 2.415(5), Ag1-N11' 2.296(4), Ag1-N22 2.217(4), Ag1-O1 2.469(5), Ag2-N21' 2.159(4); Ag2-Ag1-N12 106.3(1), Ag2-Ag1-N11' 71.8(1), Ag2-Ag1-N22 74.5(1), Ag2-Ag1-O1 144.4(1), N12-Ag1-N11' 71.6(2), N12-Ag1-N22 124.2(2), N12-Ag1-O1 104.0(2), N11'-Ag1-N22 145.9(2), N11'-Ag1-O1 101.1(2), N22-Ag1-O1 103.0(2), Ag1-Ag2-N21' 83.9(1).

The silver atom, Ag1, is coordinated to two pyrazole nitrogens, a pyridine nitrogen and a nitrate oxygen. The silver-donor bond distances are within the range of previously observed values,[161,167,170] although the Ag1-N12 distance (2.415(5)Å) is at the long end of this range. Also bonded to Ag1 is another silver atom, Ag2. The silver-silver bond distance, 2.8992(8) is similar to the distance in metallic silver (2.89Å), which indicates that there is a significant bonding interaction between Ag1 and Ag2, although shorter Ag-Ag distances have been reported.[79,182-186] The bonding geometry around Ag1 is distorted trigonal bipyramidal (greatest distortion N11'-Ag1-N22 145.9(2)°).

The silver atom on the special position, Ag2, is coordinated to two pyridine nitrogens, one from each ligand, and is also bonded to Ag1 and its symmetry equivalent, Ag1A. The Ag1-N21' bond distance is consistent with other silver-nitrogen bond distances. The centre of inversion defines the Ag1-Ag2-Ag1A and N21'-Ag2-N21A angles to be 180°, making the only distortion from square planarity the N-Ag2-Ag angles (83.9(1)°).

The benzene ring and the four heterocyclic rings are planar (maximum displacement from plane 0.019(8)Å). The meanplanes of the two pyridylpyrazole groups are inclined to that of the benzene at angles of 102.5(5) and 98.8(5)°, and at an angle of 3.8(5)° to each other. The geometry of the two pyridylpyrazole groups is significantly different. In the unit which is chelated to Ag1, the two heterocycles are close to coplanar (angle between heterocycles 1.3(5)°). For the second pyridylpyrazole, in which the two heterocycles are coordinated to different silver atoms, the planes of the two rings are twisted (angle between heterocycles 30.8(5)°).

The most interesting feature of this structure is the linear Ag_3 moiety. Although there are many reported examples of structures containing silver-silver bonds, those which contain more than two silver atoms typically contain triangular, square or clustered arrangements of bonded silver atoms. The most closely related structure is a trinuclear Ag(I) complex of a phosphine based ligand with an Ag-Ag-Ag angle of 175.33(7)°. The Ag-Ag bond distances in this complex, 2.943(2) and 3.014(2)Å, indicate slightly weaker Ag-Ag bonds than in 335. This related Ag_3 structure, and other reported polynuclear silver complexes, have attracted recent interest with regard to the metal-metal interactions in such complexes.[187]

The structure of 335 is held together by π–π interactions between pyridylpyrazole units. A view from directly above this interaction (fig. 3.34) shows the familiar centroid-atom relationship of π–π stacks to exist between pyridine and pyrazole rings in this complex. The separation between interacting pyridylpyrazole (average separation

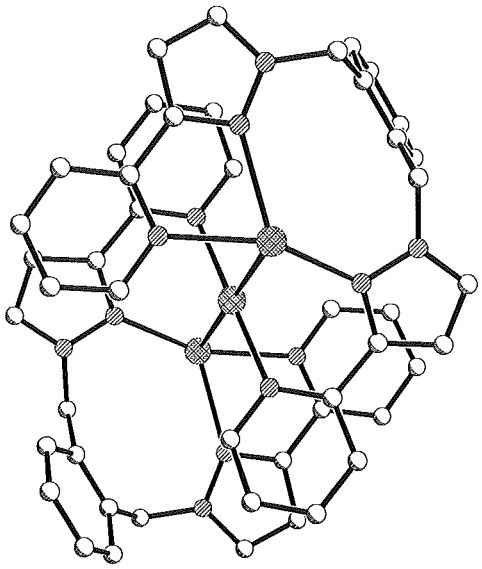


Fig. 3.34 Top view of the stacked pyridylpyrazole units of 335.

3.638(9)Å) indicates the π–π stacking is significant, although not as strong as interactions in complexes discussed in the previous chapter.

3.5 Synthesis and Complexes of Tetrakis(pyrazolylmethyl)benzene Ligands.

The tetrapodal ligand, 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene, 337, was synthesised in good yield, by a phase-transfer-catalysed reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with pyrazole (fig. 3.35). Although some 337 precipitated from the reaction mixture upon cooling, this was combined with the remaining product from the reaction mixture, and then recrystallised from benzene. Similarly, 1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338, also precipitated from the reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with 3,5-dimethylpyrazole upon cooling. Again, this was combined with the remaining product from the reaction mixture, and then recrystallised from benzene to give 338 in satisfactory yield. Given the alkylation site selectivity in the formation of 1,2-bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene and, to a lesser extent, the 1,3-substituted compound, a phase-transfer-catalysed reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with four equivalents of 2-(3'-pyrazolyl)pyridine might be expected to give 1,2,4,5-tetrakis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 339, in good yield. Such a reaction was carried out, from which, 339 precipitated upon cooling of the reaction mixture. The product remaining in the reaction mixture was a complicated mixture of different

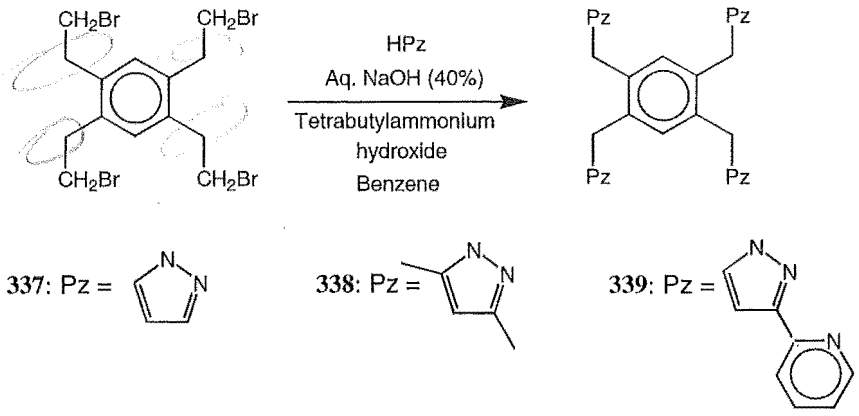


Fig. 3.35

isomers of which no separation was attempted. While the ^{1}H N.M.R. spectra of 337 and 339 are unremarkable, the two benzenoid protons in 338 are at the unusually high-field position of 5.72ppm. The presence of methyl substituents on the 3- and 5-positions of the pyrazoles presumably cause these pyrazoles to twist, such that the benzene ring protons are shielded by these pyrazoles. Note that twisting of these pyrazoles so that the shift of the aromatic protons is significantly affected, requires substituents in both the 3- and 5-positions as the benzene protons of 339 are at the more usual shift of 6.89ppm.

Palladium, silver and copper complexes, 340-342, of 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene, 337, were prepared. The palladium complex, 340, was isolated in good yield and analyses as [337.$(PdCl_2)_2$.$2H_2O$]. The ^{1}H NMR spectrum of this complex shows there to exist an equilibrium between noncoordinated ligand, 337, and a complex, 340, the nature of which is undetermined. This spectrum is not surprising given the N.M.R. spectra for palladium complexes of 1,2- and 1,3-bis(pyrazol-1-ylmethyl)benzene.

The silver complex, 341a, analyses as [337.$AgNO_3$]. Given the metallopolymeric structures of silver complexes of 1,2-, 1,3- and 1,4-substituted ligands, a polymeric structure was also expected for this complex, possibly of a multi-dimensional nature. A variety of recrystallisation procedures were employed in an attempt to grow crystals of this complex. Several attempts were made using slow evaporation of an acetonitrile solution of 341, each of which yielded needle-shaped crystals too small for single crystal analysis. However, one such solution, for which undistilled acetonitrile was used, also yielded a single crystal, 341b, of different morphology which was suitable for X-ray structure determination.

The reaction of 337 with copper chloride in methanol, over a peroid of hours, furnished crystals of two different colours - an orange/brown complex, 342a, in 38%

yield, and a green/yellow complex, 342b, in 53% yield. While 342a analyses as [337.$(CuCl_2)_2$], 342b analyses as [337.$(CuCl_2)_2$.2CH_3OH]. As the reason for the different colours of 342a and 342b is unclear from these analyses, the X-ray crystal structures of both these complexes were determined.

Crystal Structures of 341b, 342a and 342b

The silver complex, 341b, crystallises in the monoclinic space group $P2_1/c$, the asymmetric unit of which is shown (fig. 3.36). This unit contains three silver atoms and one and a half tetrakis(pyrazolylmethyl)benzene ligands, a different stoichiometry to the 1:1 metal/ligand ratio of 341a. There are also two nitrate anions and a cyanide anion, the latter of which arises from the use of undistilled acetonitrile, in which cyanide ions are a known impurity.

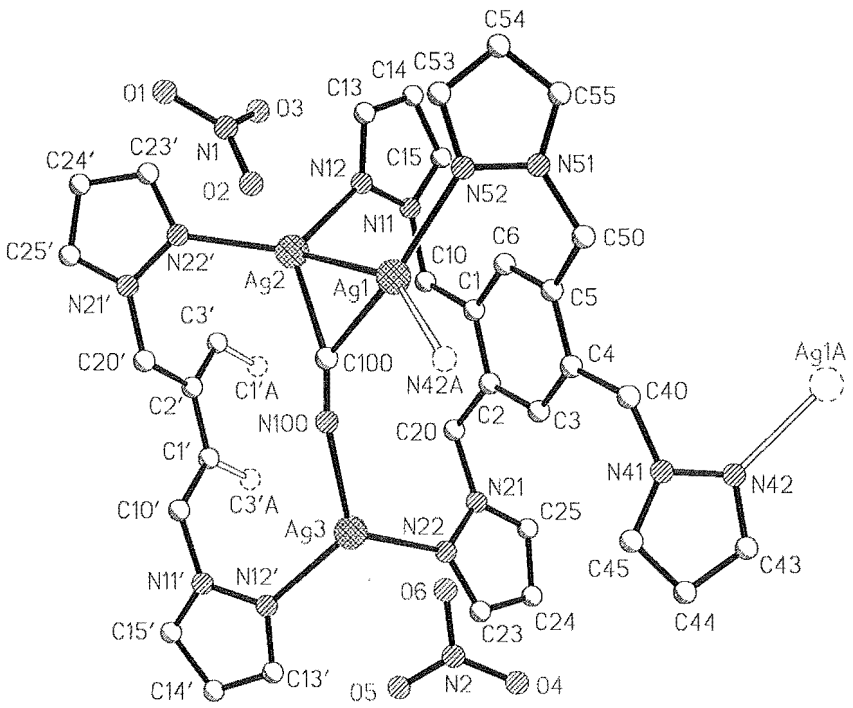


Fig. 3.36 Perspective view and atom labelling of the asymmetric unit of 341b with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1-Ag2 2.7767(7), Ag1-N42A 2.321(4), Ag1-N52 2.220(4), Ag1-C100 2.196(5), Ag2-N12 2.280(4), Ag2-N22' 2.286(4), Ag2-C100 2.194(5), Ag3-N12' 2.254(4), Ag3-N22 2.319(4) , Ag3-N100 2.188(4); Ag2-Ag1-N42A 150.4(1), Ag2-Ag1-N52 105.3(1), Ag2-Ag1-C100 50.7(1), N42A-Ag1-N52 104.1(2), N42A-Ag1-C100 101.5(2), N52-Ag1-C100 151.6(2), Ag1-Ag2-N12 100.4(1), Ag1-Ag2-N22' 151.5(1), Ag1-Ag2-C100 50.8(1), N12'-Ag3-N22 101.3(1), N12'-Ag3-N100 124.4(2), N22-Ag3-N100 122.1(1).

The silver atoms Ag1 and Ag2, as well as being strongly bonded to each other (Ag1-Ag2 2.7767(7)Å), are both coordinated to two pyrazole nitrogens and to the carbon of the cyanide anion. The geometry around both is highly distorted tetrahedral, the small Ag-Ag-C100 angles causing this distortion. The third silver atom, Ag3, is coordinated to the nitrogen of the cyanide group as well as two pyrazole nitrogens and has a distorted trigonal coordination geometry.

While the six pyrazole rings are each planar (maximum displacement from plane 0.009(6)Å) the complete benzene ring of the asymmetric unit is measurably distorted towards a boat conformation in that C2/C5 are 0.030(6)/0.037(6)Å above the plane defined by the other four carbons of the ring. The methylene groups, C20 and C50, attached to these two displaced carbons show an even greater distortion of 0.113(6) and 0.135(6)Å away from coplanarity with the benzene. This boat distortion arises from the strain associated with the metalloparacyclophane containing by the Ag1-CN-Ag3 bridge. The inclinations of the pyrazole rings to their respective benzene rings range between 69.7(5) and 110.1(5)°.

An interesting feature of this structure is the coordination of the cyanide group. Among the few structures containing tridentate cyanide groups that have been reported,[188-191] two cyanide orientations have been found: one with the carbon bifurcated and the nitrogen singly coordinated; and the other with nitrogen coordinated to two metals and the carbon to only one (fig. 3.37). The structure of 341b appears to contain the cyanide ion in the former orientation. The structure was modelled with the cyanide in both orientations and the thermal parameters for the two atoms compared. With the bicoordinate atom as nitrogen, the thermal parameters of this atom are significantly larger than those of the monocoordinate carbon. With a bicoordinate carbon, the thermal parameters of this atom are only slightly smaller than those of the monocoordinate nitrogen. The latter observations imply a better model as the thermal vibration of a bicoordinate atom would be expected to be smaller than that of the monocoordinate atom. The bifurcated carbon model is therefore proposed for 341b.

The overall structure of 341b is that of a two-dimensional metallopolymeric network of large macrocyclic units. Each of the large macrocycle units (fig. 3.38)

Fig 3.37

incorporates one or more silver atoms from six different Ag_3 trimers, with the largest dimension of the macrocycle being 24.133(1)Å. These macrocycles interlock with the adjacent units to give the two-dimensional polymeric network (fig. 3.39).

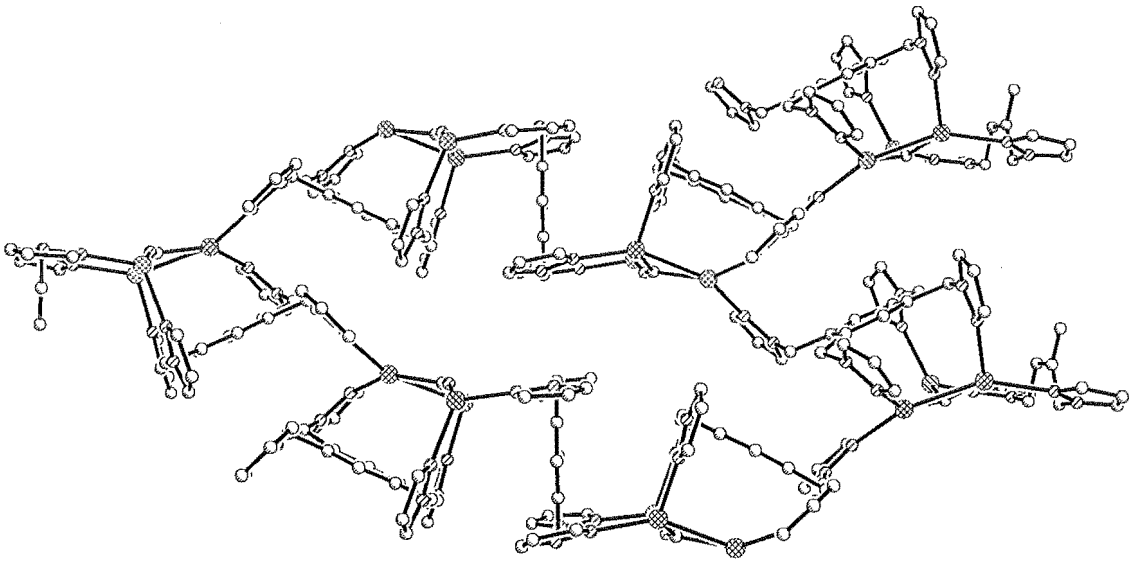


Fig. 3.38 Perspective view of the large macrocyclic unit of 341b.

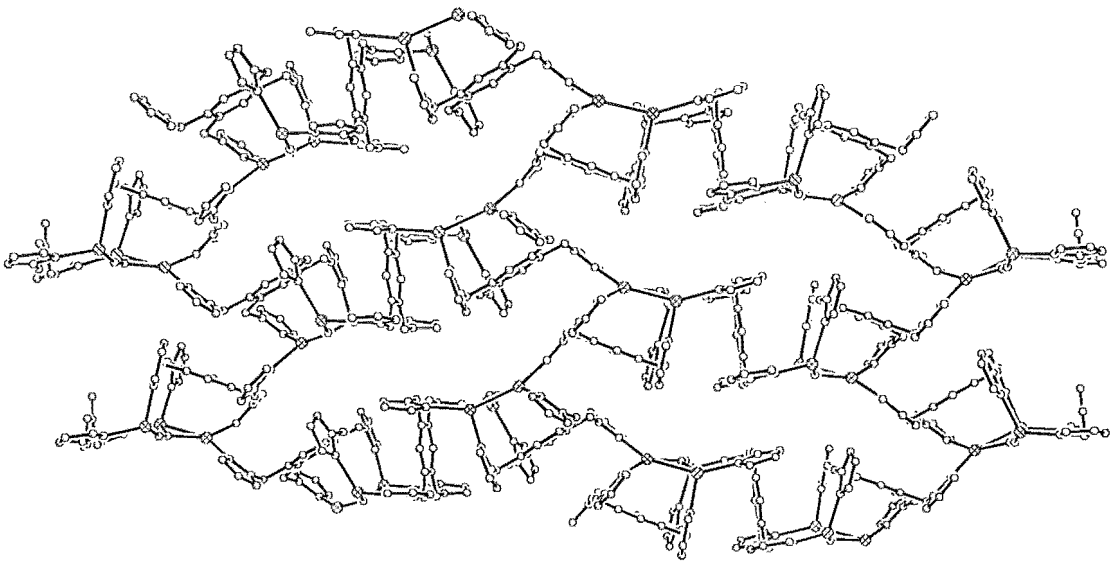


Fig. 3.39 Perspective view of the interlocking pattern of macrocycles in 341b.

The copper complex, 342a, crystallises in the monoclinic space group $P2_1/n$, the asymmetric unit of which contains half a $[337(CuCl_2)_2]$ unit (labelled in fig. 3.40), with the other half related to it by a centre of inversion. The copper atom is coordinated to two pyrazoles linked (through the methylenes) in an ortho- relationship to the benzene ring. It is also coordinated to two chlorine atoms with the copper-donor distances consistent with related structures.[134,180] The coordination geometry around the copper is strongly distorted tetrahedral (largest distortion N12-Cu1-N22 142.7(1)°).

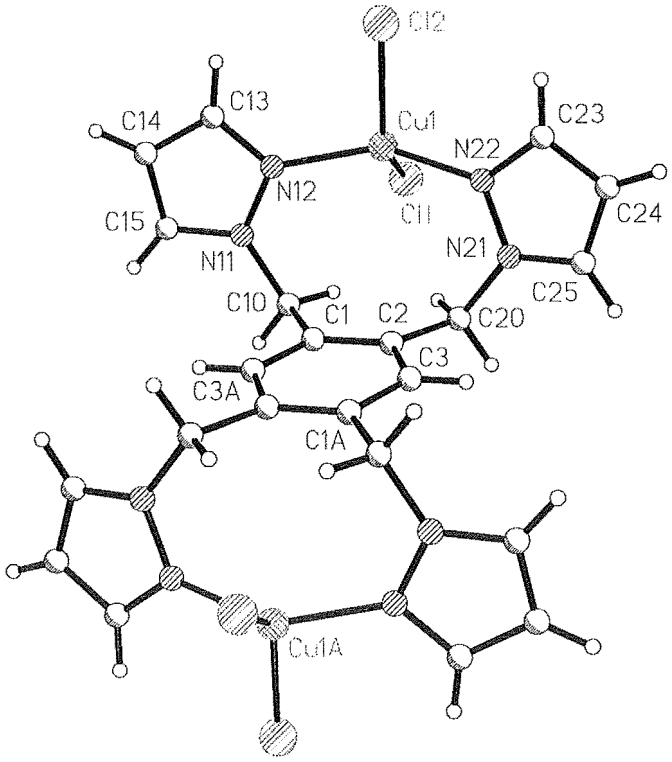


Fig. 3.40 Perspective view and atom labelling for 342a. Selected bond lengths (Å) and angles (°): Cu1-N12 1.958(3), Cu1-N22 1.965(3), Cu1-Cl1 2.261(1), Cu1-Cl2 2.245(1); N12-Cu1-N22 142.7(1), N12-Cu1-Cl1 96.9(1), N12-Cu1-Cl2 98.6(1), N22-Cu1-Cl1 100.7(1), N22-Cu1-Cl2 95.4(1), Cl1-Cu1-Cl2 129.10(4).

The benzene and pyrazole rings are each planar (maximum displacement from plane 0.008(5)Å) with the pyrazole rings inclined at angles of 99.1(3) and 102.5(3)° to the benzene, and at 20.7(3)° to each other.

The copper complex, 342b, also crystallises in the monoclinic space group $P2_1/n$, the asymmetric unit of which, like 342a, contains half a $[337(CuCl_2)_2]$ unit (labelled in fig. 3.41), although there is also a methanol in the asymmetric unit in accordance with the combustion analysis of the crystals. There is a hydrogen bond between Cl2 and the alcohol hydrogen (Cl-H 2.45(1)Å). As for 342a, the copper atom is coordinated to two

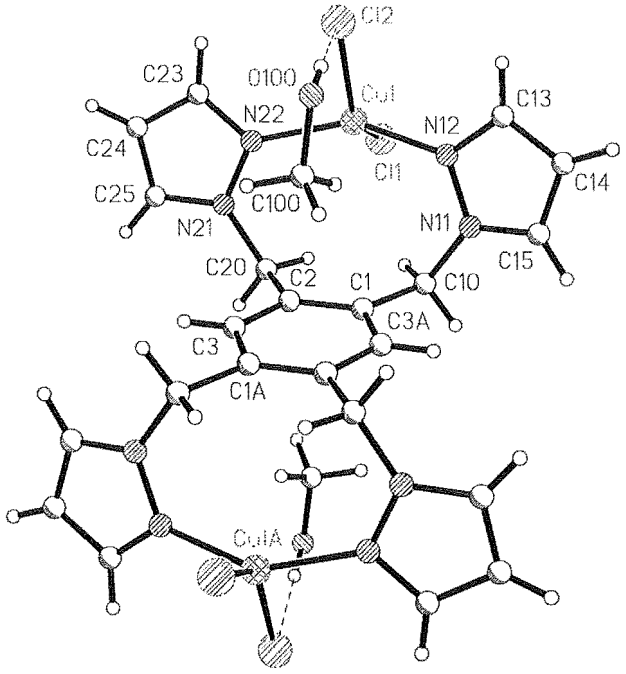


Fig. 3.41 Perspective view and atom labelling for 342b. Selected bond lengths (Å) and angles (°):Cu1-N12 1.961(3), Cu1-N22 1.961(2), Cu1-Cl1 2.2422(9), Cu1-Cl2 2.258(1); N12-Cu1-N22 145.2(1), N12-Cu1-Cl1 97.47(8), N12-Cu1-Cl2 95.66(8), N22-Cu1-Cl1 97.07(8), N22-Cu1-Cl2 94.23(8), Cl1-Cu1-Cl2 138.20(4).

ortho-pyrazoles and two chlorine atoms. The benzene and pyrazole rings are planar (maximum displacement from plane 0.009(4)Å) with similar plane inclinations as in 342a (pyrazole/benzene 100.9(3) and 101.9(3)°, pyrazole/pyrazole 15.9(3)°).

The different colour of the two crystals arises from the subtle influence of the methanol-chlorine hydrogen bond present in 342b, but not 342a. As seen in a side view (fig. 3.42), in 342b the chlorine atom, Cl2, is pulled towards H10C which in turn makes the Cl-Cu-Cl angle significantly larger than in 342a (Cl-Cu-Cl: in 342b 138.20(4)°, in 342a 129.10(4)°). The N-Cu-N angle is also more flattened out (N-Cu-N: 342b 145.2(1)°, 342a 142.7(1)°). The coordination geometry in 342b is, therefore, closer to square planar than in 342a. This change in geometry leads to different orbital energies for the two complexes, and as a consequence, the colour of the two compounds is different. Heating the green/yellow crystals of 342b, resulted in a vigorous disintegration of this compound to give an orange/brown solid. This is assigned to the loss of methanol, thus confirming the influence of the methanol on the copper coordination geometry.

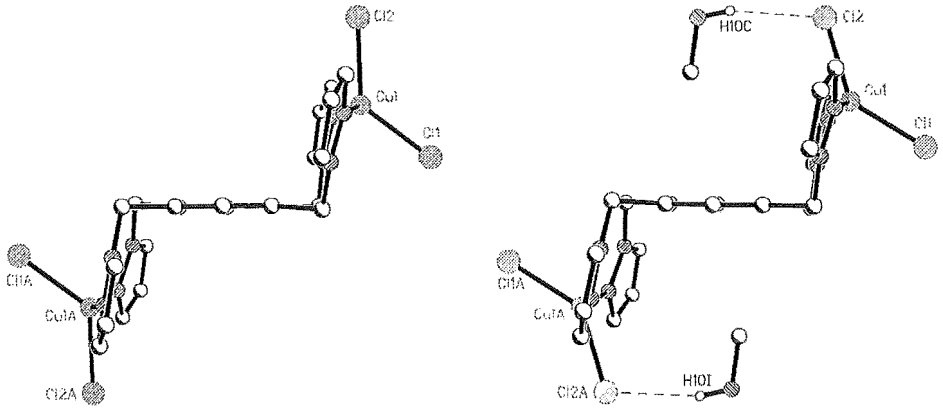


Fig. 3.42 Perspective view showing the different Cl-Cu-Cl geometry in 342a (left) and 342b (right).

While no attempt was made to prepare palladium, silver or copper coordination complexes of 1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338, a cyclopalladated complex of this ligand was synthesised (see chapter 5).

Palladium, silver and copper complexes, 343-345, of 1,2,4,5-tetrakis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 339, were prepared. The palladium complex, 343, was isolated in excellent yield and analyses as [339.$(PdCl_2)_4$.CH_3OH]. The most likely structure for this complex involves cis-coordination of each of the four pyridylpyrazole moieties to different palladium atoms. Further characterisation of this complex was not possible due to its insolubility in all solvents. The silver complex, 344, precipitated as small crystals from an aqueous/methanolic reaction mixture. These crystals analyse as [$(339)_2$.$(AgNO_3)_5$.$2H_2O$]. Despite this intriguing stoichiometry this complex was not able to be further characterised. The copper complex, 345, analyses as [339.$(CuCl_2)_4$.$4H_2O$] but, like 343, was highly insoluble and unable to be characterised further. As for the palladium complex, cis-coordination of each of the four pyridylpyrazole moieties to different metal atoms is the probable structure of 345.

Chapter 4

Complexes of Tri- and Hexapodal Ligands

Complexes of Tri- and Hexapodal Ligands

4.1 Introduction.

The coordination and organometallic chemistry of heterocyclic tripodal ligands has been extensively investigated over the last three decades.[192] The vast majority of this research has centred on geminal tri-heterocyclic ligands, as represented by the generalized structure in fig. 4.1, in which the three nitrogen-containing heterocycles are bonded at the adjacent position to the nitrogen, to the same atom.[9,193-199] While a number of different central atoms have been used (B, C, P, Ga, Al, In) and the heterocycle has been varied (pyrazole, imidazole, tetrazole and pyridine), the anionic tris(pyrazolyl)borates (Y=BH^-, heterocycle = pyrazole), in particular, have developed into much-used and highly versatile ligands.

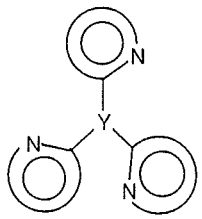
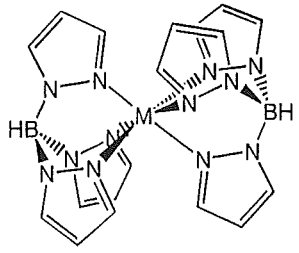
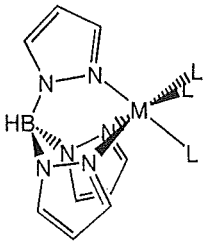


Fig. 4.1

Tris(pyrazolyl)borate ligands have been known for over twenty five years, over which time their predicted importance has come to fruition, as discussed in a number of extensive reviews.[9,192,193,196] The coordination chemistry of tris(pyrazol-1-yl)borate and tris(3,5-dimethylpyrazol-1-yl)borate has been the most extensively investigated and, as such, complexes of these have been reported for almost all transition metals. With octahedral metal centres, "full sandwich" (4.2a) or "half-sandwich" (4.2b) complexes are typical, while for metals favouring square planar geometry these ligands usually coordinate to the metal through only two pyrazole groups.[9]

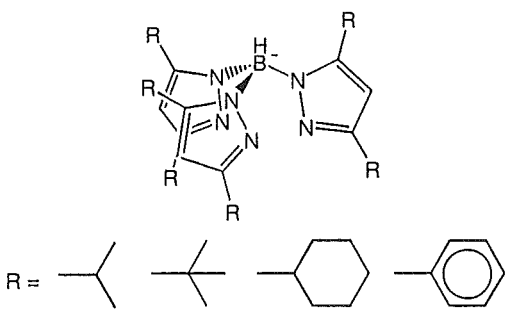


4.2a

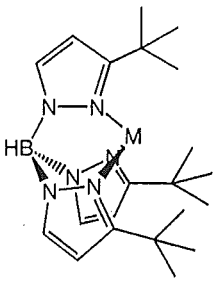


4.2b

Fig. 4.2



4.3a



4.3b

Fig. 4.3

The investigation of tris(pyrazolyl)borate ligands has been further extended over the last decade to the so-called second generation derivatives. These differ from the prototypical ligands in that sterically bulky substituents are appended to the pyrazole, most commonly in the 3 and 5 positions of the ring (4.3a). Upon coordination of these ligands, steric effects, in particular of the bulky 3- substituents, alter the properties of the metal complexes and place the coordinated metal in a highly protected environment (4.3b). The use of this second generation has allowed for the isolation and investigation of a number of complexes with novel structures and interesting properties. The areas of organometallic and bioinorganic chemistry have also benefitted from such studies.[195]

The neutral analogues of tris(pyrazolyl)borates, the tris(pyrazolyl)methanes (fig. 4.4) have received less attention. Although investigation of their organometallic chemistry with palladium and platinum has developed steadily,[196] more general investigation of the coordination chemistry of these compounds is now being studied.[197,200] The synthesis and investigation of the second generation tris(pyrazolyl)methanes has only recently been reported,[200] an indication of the slower development of this area compared to the related borate ligands.

Other tris(pyrazolyl) ligands, with three-fold symmetry and with the three pyrazole groups being nongeminal, have been reported (4.5a-d), although these are not as extensively studied as the geminal examples above. Several transition metal complexes of 4.5a (R=Me) have been characterised, in which, the three pyrazoles and the central

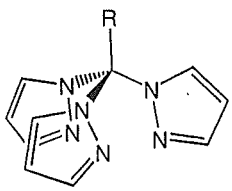
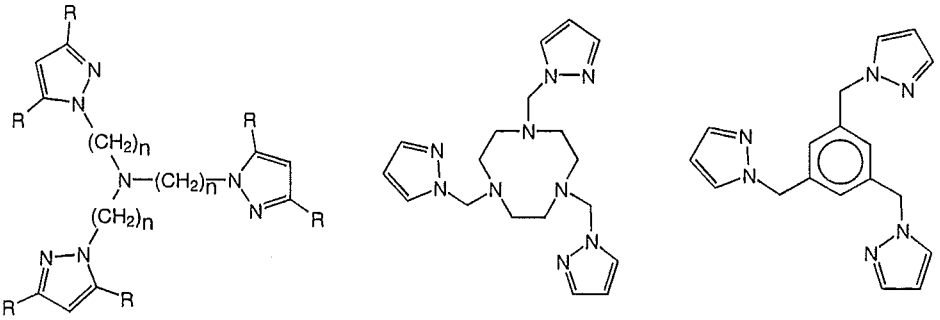


Fig. 4.4



4.5a : n=1
4.5b : n=2

4.5c

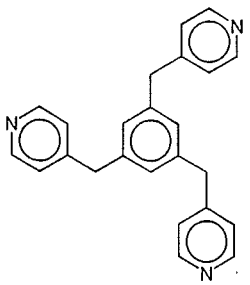
4.5d

Fig. 4.5

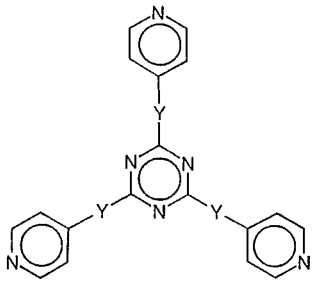
amine nitrogen are coordinated to the same metal centre. The coordination chemistry of ethylene linked tris(pyrazolyl)amine systems, 4.5b, has also been investigated, although with a larger array of metals and counterions.[9] The macrocyclic ligand, 4.5c, acts as a six coordinate ligand with additional coordination of the three nitrogen atoms in the macrocyclic ring.[201]

Of particular relevance to the ligands and complexes discussed here is the recently reported synthesis and coordination chemistry of 1,3,5-tris(pyrazol-1-ylmethyl)benzene, 4.5d. Three copper(II) complexes and a heteronuclear copper(II)/cobalt(II) complex were characterised, three by X-ray crystallography. In contrast to the tris(pyrazolyl) systems above, in none of these complexes do multiple pyrazole groups from one ligand coordinate to the same metal. Instead, a $[Cu(4.5d)_2(ClO_4)(H_2O)_2]ClO_4$ monomer, with coordination of a pyrazole from each ligand to the copper, and three metallopolymeric complexes were reported.[202]

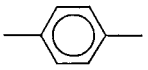
The incorporation of an aromatic ring as the core of a tripodal ligand is not limited to pyrazole-containing compounds. The complexes - in particular the palladium(II) complexes - of tris(4-pyridyl) systems (4.6a-d) have also been investigated of late. A palladium complex of 4.6a was found to be a $[Pd_3(4.6a)_2]$ cage with a central cavity of sufficient size to accomodate a guest molecule. Indeed, this cage was found to assemble in high yields only in the presence of certain substrates, an observation attributed to "induced-fit" recognition, whereby the substrate guest induces the organisation of the $[Pd_3(4.6a)_2]$ host.[65] A palladium complex of 4.6b, shown to be of $[Pd_6(ligand)_4]$ stoichiometry, is a supramolecular cage with nanosized dimensions as shown by X-ray crystallographic characterisation of a clathrate complex. The palladium complexes of 4.6c and 4.6d, by incorporation of phenylene and biphenylene spacers, respectively, gave $[Pd_6(ligand)_4]$ cage complexes with even larger molecular sizes than the complex of 4.6b.[23]



4.6a



4.6b : Y = none

4.6c : Y = 

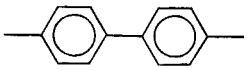
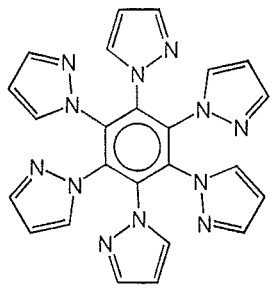
4.6d : Y = 

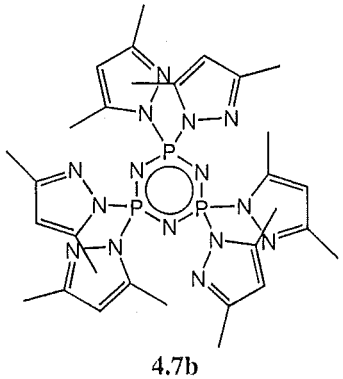
Fig. 4.6

In contrast to tripodal ligands described above, hexapodal heterocyclic ligands have received far less attention. Compounds of this type (4.7a,b), each containing six pyrazole groups, have been reported. The synthesis of hexakis(pyrazol-1-yl)benzene, 4.7a, was published recently,[203] but the coordination chemistry of this ligand thus far remains uninvestigated. Complexes of the hexakis(3,5-dimethylpyrazol-1-yl) ligand, 4.7b, have been characterised, wherein chelation of two geminal pyrazole groups to palladium(II) and platinum(II) halides is observed, while two nongeminal pyrazole groups and a cyclophosphazene nitrogen have been shown to coordinate to a copper(II) halide centre.[204]

In this chapter, the coordination chemistry of tris- and hexakis(pyrazolyl) ligands will be discussed. In keeping with the structural motif described in previous chapters, these ligands have the structures shown (fig. 4.8) with pyrazole units linked, through methylene groups, to a central benzene ring. Both pyrazole and 3,5-dimethylpyrazole will be used in the 1,3,5-tris(pyrazolylmethyl) ligands, as well as three different alkyl substituent sets in the 2, 4, and 6 positions of the benzene; only pyrazole will be used in the hexapodal ligands. The discussion of these ligands and their complexes includes six

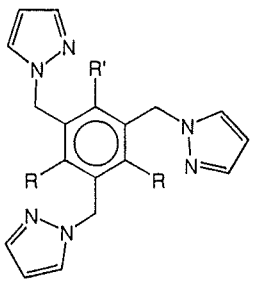


4.7a



4.7b

Fig. 4.7



R = R' = Me
R = R' = Et
R =Me, R' = H

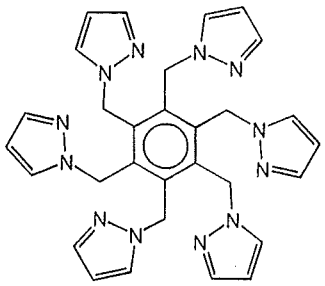
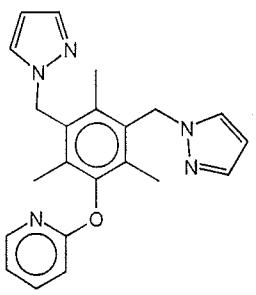
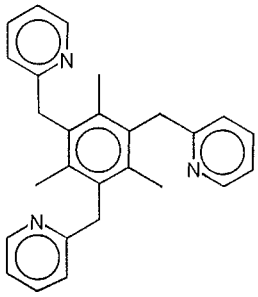


Fig. 4.8

X-ray crystal structure determinations displaying a variety of modes of coordination for the ligands. These include tripodal coordination to a metal, metal-benzene interaction and coordination to form a cage complex. Also discussed in this chapter will be the syntheses of other tris(heterocyclic) ligands incorporating a benzene core: the synthesis of a tripodal ligand system containing both pyrazole and pyridine groups (4.9a) will be described, along with the attempted synthesis of 1,3,5-tris(2-pyridylmethyl)-2,4,6-trimethylbenzene (4.9b).



4.9a



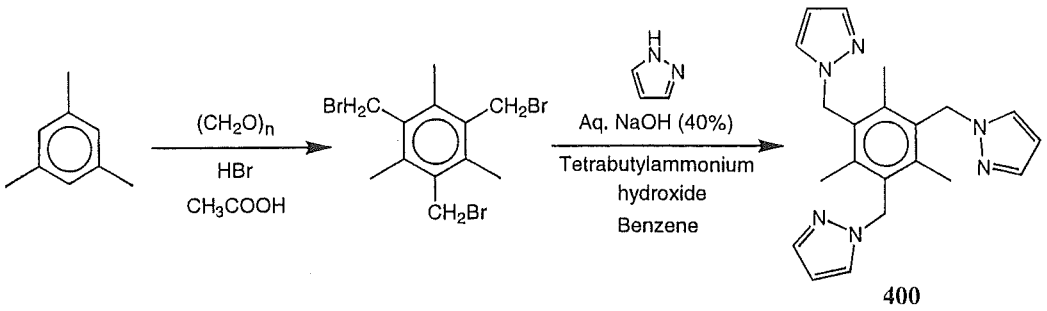
4.9b

Fig. 4.9

4.2 Synthesis and Complexes of Tris- and Hexakis(pyrazol-1-ylmethyl)benzene Ligands.

Investigation of this group of ligands began by examining the coordination chemistry of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene, 400. This ligand was synthesised in work undertaken prior to this thesis,[166] by tris-bromomethylation of 1,3,5-trimethylbenzene and subsequent phase-transfer-catalysed alkylation of pyrazole (fig. 4.10).

Palladium, silver, and copper complexes, 401-403, of this ligand have now been prepared. The palladium complex, 401, was isolated in excellent yield and analyses as $[(400)_2.(PdCl_2)_3.CH_3OH.2½H_2O]$. ^1H N.M.R. of this complex shows that there exists an



400

Fig. 4.10

equilibrium between noncoordinated ligand, 400, and the complex, 401, the nature of which is undetermined. The copper complex, 403, analyses as [400.$CuCl_2$.2½H_2O], a 1:1 metal/ligand stoichiometry as opposed to the 3:2 composition of the palladium complex, 401. A previously reported copper complex of 1,3,5-tris(pyrazol-1-ylmethyl)benzene, also displaying a 1:1 stoichiometry, was found by X-ray structure characterisation to be a metallopolymer.[202] The low solubility of 403 implies that this complex is also metallopolymeric, the structure of which (fig. 4.11) is therefore proposed to be similar to that of the previously characterised copper complex.

Reaction of silver nitrate with 400 gave a silver complex, 402, which analyses as [400.$AgNO_3$]. Slow evaporation of an acetonitrile solution of this complex yielded crystals of 402 suitable for single crystal X-ray structure determination. Given that the silver complexes of bis- and tetra(pyrazol-1-ylmethyl)benzene ligands were all found to be metallopolymeric (see chapter 3), a polymeric structure was also expected for 402. As the ligand, 400, is tris-heterocyclic the possibility arises that a metallopolymer of this ligand will be multi-dimensional as was observed in 341b, a silver complex of tetrakis(pyrazol-1-ylmethyl)benzene. To examine this possibility, the structure of 402 was determined.

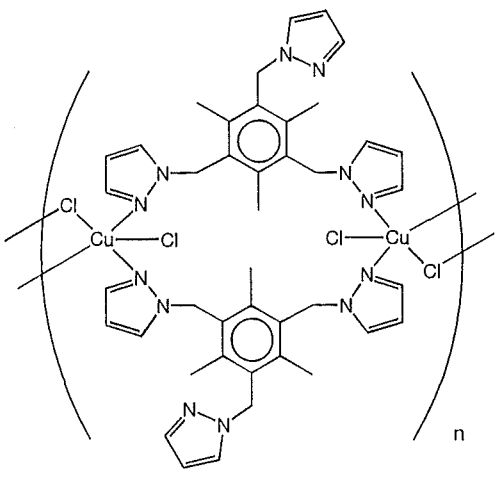


Fig 4.11

Crystal Structure of 402.

The complex crystallises in the monoclinic space group $P2_1/n$ and is a metallopolymer, the asymmetric unit of which, [(400)$AgNO_3$], is shown (fig. 4.12); the extended polymeric structure of the complex is also shown (fig. 4.13). The silver atom, Ag1, is coordinated to two pyrazole groups from the same ligand to give a ten-membered chelate ring and also to a third pyrazole from a different ligand. This ligand then bridges to another silver atom where its two other pyrazole groups are chelated, and so on to give a metallopolymeric structure. Each ligand is, therefore, both bridging and chelating. The silver-nitrogen distances are within the range of previously observed values,[80,161,167,170] although the Ag1-N12 distance (2.352(5)Å) is at the long end of this range. An oxygen of the nitrate ion is also weakly coordinated to the silver (Ag1-O3 2.804(5)Å) and, as indicated by a dashed bond, there is also a silver-benzene interaction (Ag1-C2 2.771(6)Å).

While the three pyrazole rings are planar (largest out of plane distance N12 0.011(8)Å) the benzene ring is slightly boat distorted with C2 and C5 out of the benzene mean plane by 0.037(8) and 0.044(8)Å respectively. The attached alkyl carbons at these positions show even more pronounced deviations from the benzene plane (out of plane distortion for C20 0.194(8)Å, C50 0.207(8)Å). The added strain of these distortions presumably relieves steric strain associated with the hexa-substituted benzene ring. An alternating pattern of substituents above and below the benzene is often observed to

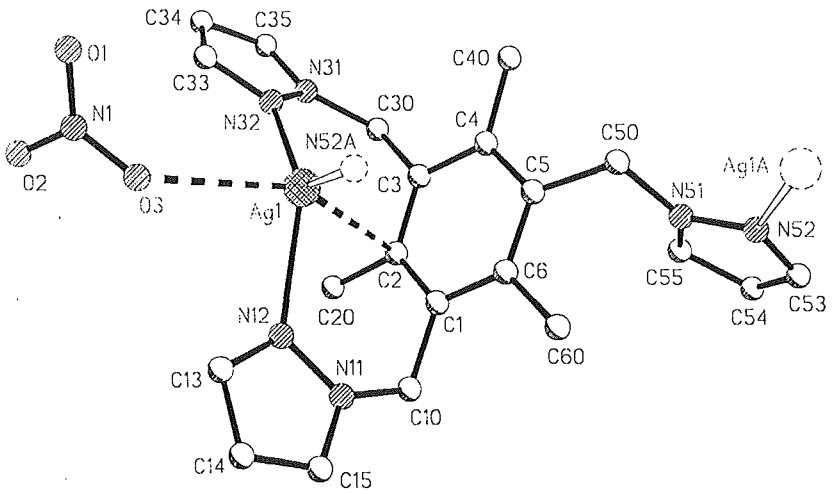


Fig. 4.12 Perspective view and atom labelling of 402. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Ag1-N12 2.352(5), Ag1-N32 2.217(5), Ag1-N52A 2.238(5); N12-Ag1-N32 133.5(2), N12-Ag1-N52A 93.5(2), N32-Ag1-N52A 132.5(2).

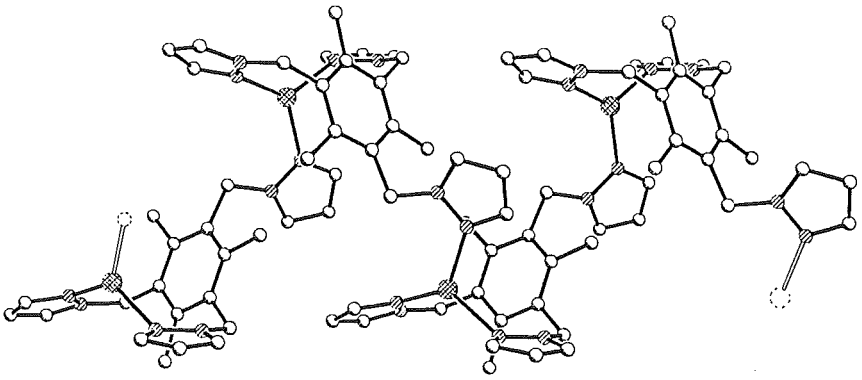


Fig. 4.13 Perspective view of the polymeric structure of 402.

relieve such strain. In this case, however, the steric relief resulting from two pyrazole groups being above one face of the benzene and the third above the other face also contributes, thereby leading to a boat rather than chair distortion.

The meanplanes of the two chelated pyrazole rings are inclined at angles of 65.8(6)° and 104.4(6)° to the meanplane of the benzene ring, and at 28.4(6)° to each other. The bridging pyrazole is inclined at angles of 77.9(6) and 108.9(6)° to the other pyrazoles and at 43.2(6)° to the benzene ring. The silver atom lies out of the extended planes of the coordinated pyrazole rings by between 0.168(5) and 0.979(5)Å, the latter value being unusually large.

An interesting feature of this structure is the silver-benzene interaction mentioned above. Silver complexes with benzene rings have been known to exist for many decades.[205] Such complexes were predicted, and later shown by structural characterisation, to have the silver coordinated to two carbons of an aromatic ring, rather than exhibiting η^6 benzene ring coordination. More specifically, it has been found that silver commonly coordinates to these two carbons in an unsymmetrical fashion, where one Ag-C bond is short (typically 2.45-2.49Å) with the second Ag-C bond being longer (2.6-2.9Å).[205,206] The shortest Ag-C distance in 402 is 2.771(6)Å which implies that, while the benzene is not strongly coordinated, there is nonetheless a significant silver-benzene interaction. Interestingly, the silver atom is positioned almost directly above a benzene carbon (C2) (fig. 4.14), rather than lying between this and a neighbouring carbon (C1 or C3). Such η^1 benzene coordination has previously been observed for a silver complex, and was attributed to electronic effects of other ligands present.[205] In 403, η^1 benzene-silver interaction is enforced by the chelation of two pyrazole groups, as this restrains the silver to lie over C2 rather than being displaced towards either C1 or C3.

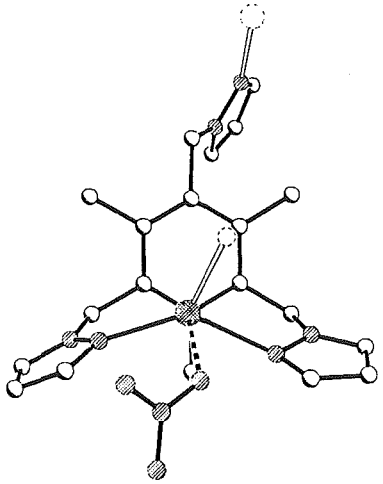
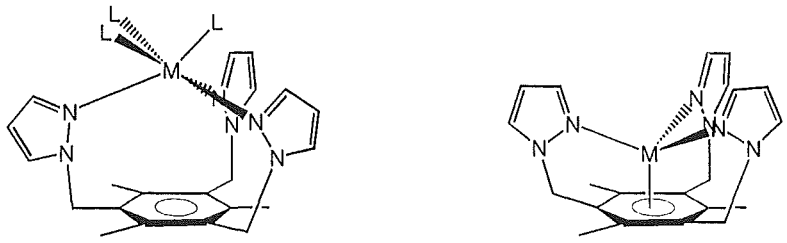


Fig. 4.14 Perspective view of the η^1 silver-benzene interaction in 402

A ruthenium complex, 404, of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene, 400 was first synthesised in work undertaken prior to this thesis.[166] From a reaction of 400 with dichloro-tetrakis(dimethylsulfoxide)ruthenium(II) in ethanol/water, a complex, 404, was isolated as its hexafluorophosphate salt. Although no composition was found that totally matched the analysis of this complex, it did, none the less, imply a 1:1 ruthenium/400 ratio. ^{1}H N.M.R. of this complex shows all three pyrazole groups of the ligand to be equivalent. Given these observations, two possible structures for 404 were proposed (fig. 4.15). One of these involves 400 acting as a tripodal chelating ligand (4.15a), with the second also involving tripodal chelation but with additional η^6 coordination to the benzene ring (4.15b). Despite exhaustive attempts to grow single crystals of this complex, no further characterisation of this complex was possible at that time.

Further investigation of the nature of 404 has been carried out in the present work. Electrochemical measurements, and UV/Vis and ^{13}C N.M.R. spectra have been



4.15a **4.15b**

Fig. 4.15

obtained for the hexafluorophosphate salt, all of which are consistent with an $N_3(\eta^6$-benzene) coordination sphere for ruthenium(II).[207-210] Most notably, large upfield shifts of around 30ppm for the arene carbons are observed, a clear indication of their coordination to the ruthenium. The same reaction between 400 and dichloro-tetrakis(dimethylsulfoxide)ruthenium(II) has been repeated, and counterions other than hexafluorophosphate used in attempts to isolate the complex. Removal of the reaction solvent gives crude 404 as its chloride salt. FABMS of this salt shows a set of highest mass ions centred around 497 Daltons which corresponds to $[(400).Ru.Cl]^+$. This salt was dissolved in water and filtered. Zinc chloride (2 equiv.) and hydrochloric acid were then added to the filtrate, which, over a period of weeks, yielded crystals of the tetrachlorozincate salt of 404 suitable for single crystal X-ray structure determination.

Crystal Structure of 404.

The complex crystallises in the triclinic space group P-1, the cation of which, [(400)Ru], is shown (fig. 4.16). The ruthenium atom is indeed coordinated to all three pyrazole groups and the benzene ring of the ligand. This is the first time such simultaneous tripodal and benzene ring coordination from within the same ligand has

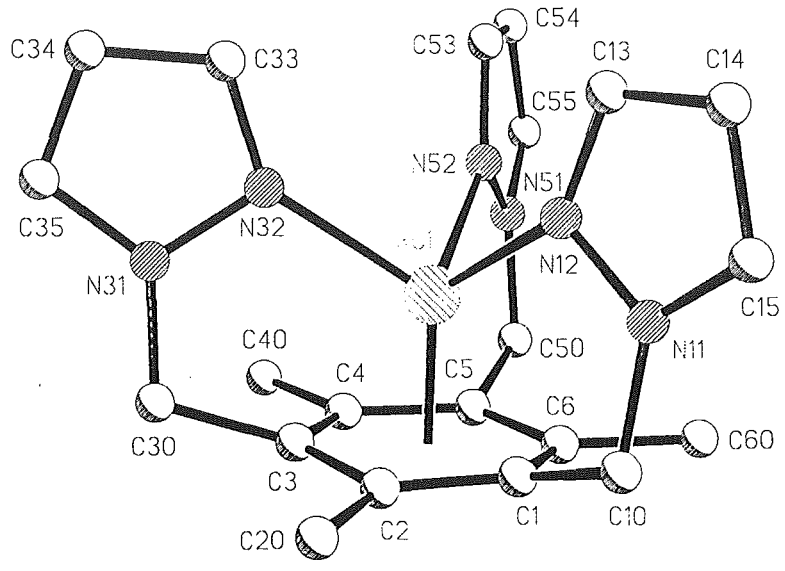


Fig. 4.16 Perspective view and atom labelling of 404. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1-N12 2.107(8), Ru1-N32 2.091(8), Ru1-N52 2.094(8), Ru1-C1 2.103(9), Ru1-C2 2.186(9), Ru1-C3 2.096(9), Ru1-C4 2.156(9), Ru1-C5 2.083(9), Ru1-C6 2.149(9); N12-Ru1-N32 96.7(3), N12-Ru1-N52 94.5(3), N32-Ru1-N52 92.6(3).

been observed. By coordinating in this manner, the ligand encapsulates the ruthenium and, as such, the name 'coelenterands' is coined for this new class of ligand. This name is taken from the animal phylum Cœlenterata, from the Greek for "hollow stomach". While the ruthenium-nitrogen distances are within the range of previously observed values,[207-209,211-213] the ruthenium atom lies 1.579(9)Å from the centroid of the benzene ring. In previously reported structures containing a $RuN_3(\eta^6$-benzene) interaction,[207,208,211-213] Ru-centroid distances are all in the range 1.67-1.70Å. This indicates a strong metal-arene interaction in 404, no doubt reinforced by multiple chelate effects in the structure. Another change in the geometry of 404 relative to that of the related structures is in the bond angles around the ruthenium. In the previous structures the N-Ru-N angles are generally acute, while in 404 these angles are obtuse (N-Ru-N 96.7(3), 94.5(3), 92.6(3)°). This arises from the coordinated nitrogens being in the same ligand as the benzene in 404. No coordinating nitrogen is in the same ligand as the benzene in any of the previously reported structures. This N-benzene connectivity difference also results in the configuration of the structure being eclipsed (fig. 4.17), as opposed to the staggered, piano-stool type arrangement common to the related $RuN_3(\eta^6$-benzene) complexes.

While the three pyrazole rings are planar (largest out of plane distance N12 0.01(1)Å) the benzene ring is chair distorted with the pyrazolylmethyl-substituted carbons displaced towards the ruthenium atom by an average of 0.03(1)Å. The attached methylene carbons at these positions show even more pronounced deviations from the benzene plane (average out of plane distortion for C10, C30, C50 0.47(1)Å), clearly

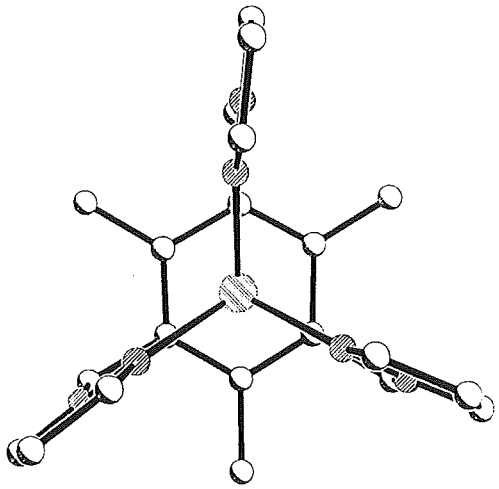


Fig. 4.17 Top view of 404 showing the eclipsed configuration of the pyrazolylmethyl substituents and their attached benzene carbons.

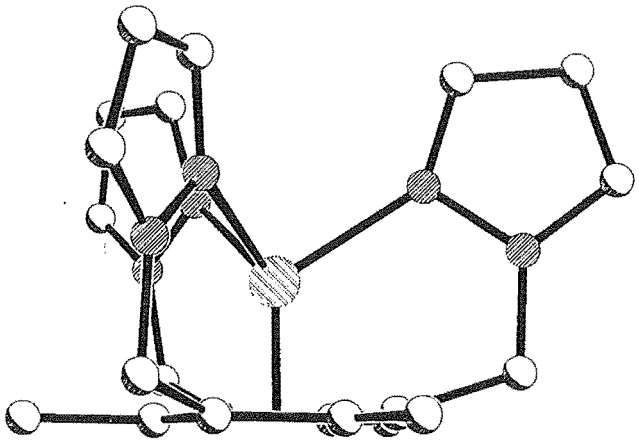


Fig. 4.18 Side view of 404 showing the displacement of the methylene substituents from the plane of the benzene ring.

seen in a side view of the $[(400)Ru]^{2+}$ cation (fig. 4.18). The three pyrazole rings are approximately orthogonal to the benzene ring (inclination range to the benzene plane 86.1(9)-95.4(9)°), and are inclined at angles between 107.0(9)° and 133.6(9)° to each other, giving the cation approximate C_{3v} symmetry.

Along with (previously discussed) tripodal chelation, π-arene complexes of transition metals have also received much attention. In particular, $Ru(\eta^6\text{-benzene})_2^{2+}$ is a robust compound that has played an important role in the development of organometallic chemistry;[214,215] half-sandwich complexes of ruthenium, $Ru(\eta^6\text{-benzene})L_3^{2+}$, are less well studied.[207,214-216] Thus, the coordination of 400 brings together two important areas of chemistry for the first time.

In order to assess the generality of the structure of 404, other ligands containing the 1,3,5-tris(pyrazol-1-ylmethyl)benzene moiety were synthesised. The first of these was 1,3,5-tris(pyrazol-1-ylmethyl)-2,4-dimethylbenzene, 405, the coelenterate complex of which might be expected to display interesting chemistry at the unsubstituted position of the benzene ring. The 3,5-dimethylpyrazolyl analogue, 406, of this ligand was also prepared. These two ligands were each synthesised in two steps from 1,3-dimethylbenzene (fig. 4.19). The starting material is first tris-bromomethylated[217] to give 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene, 407, which is then used in a phase transfer alkylation of pyrazole, or 3,5-dimethylpyrazole to give 405 and 406, respectively.

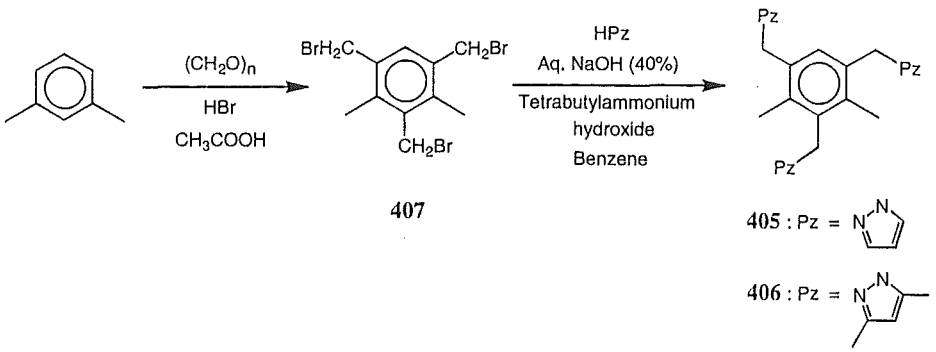


Fig. 4.19

While assignments of the ^{1}H and ^{13}C N.M.R. spectra of 405 and 406 were trivial, the benzene proton of 406 is at the remarkably highfield shift of 5.28ppm. A similar high chemical shift was observed for the benzene hydrogens of 1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338. As for the latter compound, the highfield chemical shift of this hydrogen in 406 is caused by the shielding effect of the adjacent pyrazoles. Again, methyl substituents are required on the pyrazole group to twist these groups so that significant shielding occurs - the shift of the benzene hydrogen in 405 is at the more normal position of 6.64ppm.

A ruthenium complex, 408, was then prepared in a reaction of 405 with dichloro-tetrakis(dimethylsulfoxide)ruthenium(II) in ethanol/water. Removal of the reaction solvent gives crude 408 as its chloride salt. FABMS of this salt shows a significant set of highest mass ions centred around 483 Daltons which corresponds to $[(405).Ru.Cl]^{+}$. This salt was dissolved in water, filtered and ammonium hexafluorophophate added giving a precipitate of 408 as its hexafluorophophate salt in low yield. The ^{1}H N.M.R. spectrum of this complex shows the two-fold symmetry of the ligand to be maintained, with coordination induced shifts of between -0.06 and 0.89ppm, with the induced shifts for the three pyrazole rings being similar. The methylene signals are a singlet for the 3-substituent, while the 1- and 5-substituents are a pair of sharp geminally coupled doublets. This implies that both of these methylenes have hydrogens locked in nonequivalent environments. This evidence is consistent with a coelenterate structure for 408 (fig 4.20). Attempts to grow single crystals of a salt of 408, suitable for X-ray structure determination, were unsuccessful.

As has been noted above, in the structure of the silver complex, 402, of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene, the three pyrazole rings are arranged so that the two chelated rings are above one side of the benzene, while the bridging pyrazole lies above the opposite side of the benzene. Speculation arose as to whether three pyrazole groups could be pre-organised to lie above the same face of the benzene.

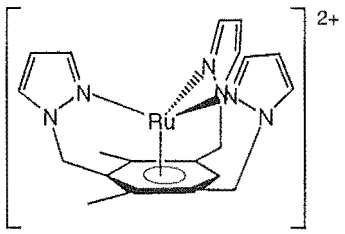


Fig. 4.20

Such an arrangement may make tripodal chelation to a metal more favourable, either with or without additional η^6-benzene coordination.

To investigate this possibility 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 409, and the 3,5-dimethylpyrazolyl analogue, 410, were prepared. These two ligands were each synthesised in two steps from 1,3,5-triethylbenzene (fig. 4.21). The starting material is first tris-bromomethylated[217] to give 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene, 411, which is then used in a phase-transfer-catalysed alkylation of pyrazole, or 3,5-dimethylpyrazole, to give 409 and 410, respectively. During the course of this work, other workers synthesised 411 under similar conditions but using zinc bromide catalyst.[218] It was stated that without the catalyst present only bis-bromomethylated products are observed. In fact, with extended reaction times, tris-bromomethylation does proceed, allowing for isolation of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene in satisfactory yield. Significantly, an X-ray crystal structure of a 1,3,5-substituted 2,4,6-triethylbenzene was also reported,[218] in which the 1,3,5-substituents were all found to lie above one side of the benzene plane.

Palladium, silver, and copper complexes, 412-414, of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene were then prepared. The copper complex, 414, was isolated in excellent yield and analyses as $[(409)_2.(CuCl_2)_3.1½H_2O]$. This stoichiometry is different from the 1:1 metal ligand ratio observed for 403, the copper complex of the

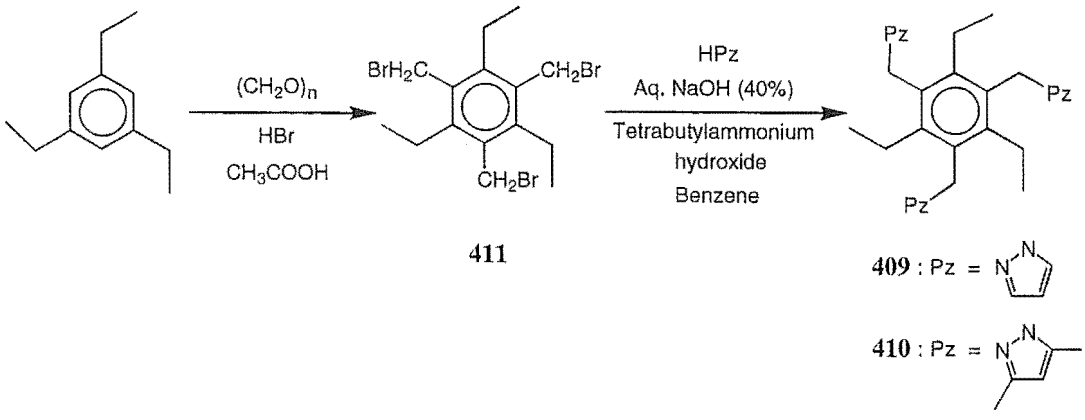


Fig. 4.21

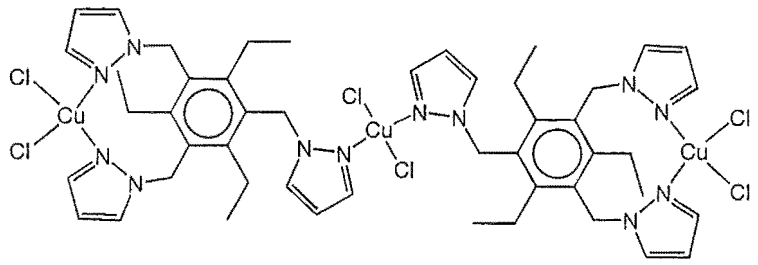


Fig. 4.22

analogous 2,4,6-trimethyl ligand. While the exact nature of 414 is not known, possible structures for this complex include $[L_2M_3]$ or $[L_4M_6]$ cage complexes, or an $[L_2M_3]$ complex in which two coppers are bis-chelated, while the third is bis-monocoordinated through the remaining pyrazole of each ligand (fig. 4.22).

Reaction of silver nitrate with 409 yielded crystals of a silver complex, 413, suitable for single crystal X-ray structure determination. These crystals analyse as $[409.(AgNO_3)_2]$ as opposed to the 1:1 metal/ligand ratio observed for 402, the silver complex of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene. The structure of 413 was determined to investigate the relative orientations of the three pyrazole rings and, if the three rings are pre-organised, the influence that this has on the structure of 413 relative to that of 402.

The palladium complex, 412, precipitated from its reaction mixture in excellent yield. The ^1H N.M.R. spectrum of this complex in DMSO shows that the three-fold symmetry of the ligand is maintained in 412. Coordination induced shifts for the complex range between -0.38 and 1.03ppm, clearly indicating incorporation of 409 into a complex of some sort. The symmetry observed in the complex was surprising given the combination of a tripodal ligand with a square planar metal, such as palladium(II), and was difficult to explain in terms of a palladium complex of low nuclearity. Of the various attempts to grow single crystals of 412, vapour diffusion of acetone into a DMSO solution of the complex yielded crystals suitable for X-ray crystal structure determination. These analyse as $[(409)_2.(PdCl_2)_3.2DMSO.4H_2O]$, a composition consistent with several possible structures. Upon isolation from the solvent mixture, these crystals underwent rapid decomposition. Only after many attempts was a crystal able to be transferred to the low temperature stream of the diffractometer with suitably minimal decomposition.

Crystal Structures of 413 and 412.

The silver complex, 413, crystallises in the triclinic space group P-1, the asymmetric unit of which, [(409)($AgNO_3$)$_2$], is shown (fig. 4.23). The silver atom, Ag1, is coordinated to two pyrazole groups from the same ligand to give a ten-membered chelate ring, as was observed in 402. Similarly, there is also a silver-benzene interaction of the same order as that in 402 (Ag1-C2 2.785(6)Å in 413, 2.771(6)Å in 402). However, in contrast to 402, Ag1 is not coordinated to a third pyrazole; rather, it is (semi-)coordinated to two nitrate oxygens (Ag1-O2A 2.681(4), Ag1-O4B 2.634(8)Å) to give a pseudo-trigonal bipyramidal geometry around Ag1. The ligand bridges to the second silver atom, Ag2, to which is coordinated a pyrazole nitrogen, a full occupancy nitrate oxygen (Ag2-O2 2.459(4)Å), and a second nitrate which is disordered over a bidentate site (Ag2-O4 2.48(1), Ag2-O5 2.328(8)Å) and a monodentate site (Ag2-O5A 2.367(8)Å). The silver-nitrogen distances are each within the range of previously observed values.[80,161,167,170]

Although the [(409)($AgNO_3$)$_2$] moiety is a discrete unit rather than being polymeric, the Ag-Ag bridging coordination of the nitrate ions leads to a pseudo-polymeric nature in the structure (fig. 4.24).

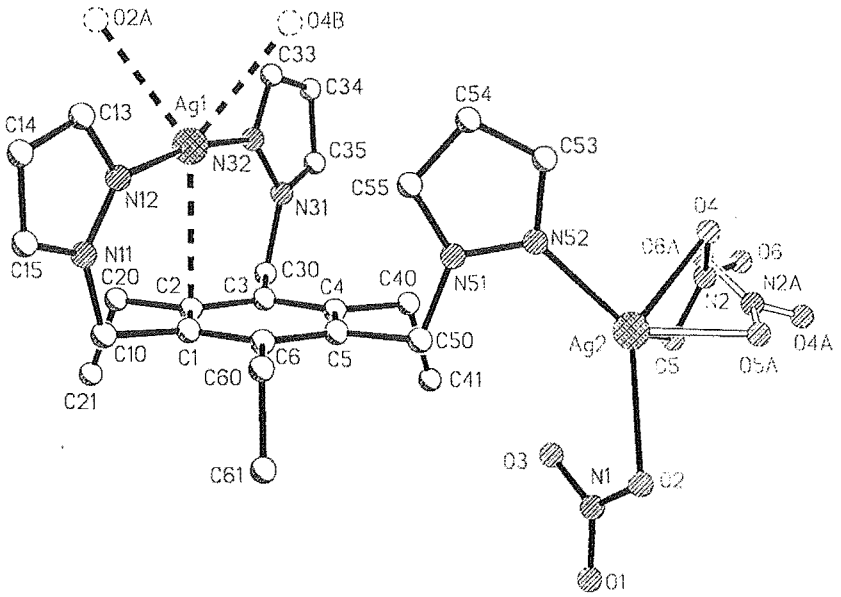


Fig. 4.23 Perspective view and atom labelling of 413. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Ag1-N12 2.215(4), Ag1-N32 2.236(4), Ag2-N52 2.204(4), Ag2-O2 2.459(4), Ag2-O4 2.48(1), Ag2-O5 2.328(8), Ag2-O5A 2.367(8); N12-Ag1-N32 170.1(2), N52-Ag2-O2 128.9(2), N52-Ag2-O4 96.3(3), N52-Ag2-O5 124.7(4), N52-Ag2-O5A 141.2(2), O2-Ag2-O4 134.8(2), O2-Ag2-O5 93.4(3), O2-Ag2-O5A 89.3(2), O4-Ag2-O5 51.9(3).

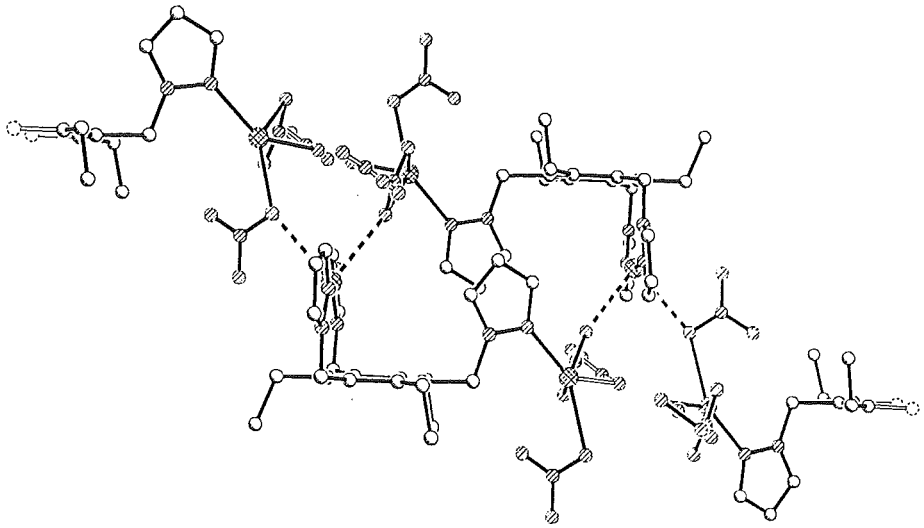


Fig. 4.24 Perspective view of the Ag-Ag bridging coordination of nitrate ions in 413

Significantly, the three pyrazole rings lie above one side of the benzene ring, while the ethyl groups all lie on the other side to give an alternating substituent pattern around the benzene. Such an arrangement was predicted and is attributed to the pre-organisation effect of using ethyl rather than methyl substituents. While the benzene and three pyrazole rings are each planar (largest out of plane distance C6 0.010(7)Å), the attached alkyl carbons, C10 and C30, in the chelate ring deviate from the benzene plane (average out of plane distortion 0.116(7)Å).

The meanplanes of the two chelated pyrazole rings are inclined at angles of 90.4(4)° and 96.7(4)° to the meanplane of the benzene ring, and at 8.6(4)° to each other. The third pyrazole is inclined at angles of 125.7(4) and 119.4(4)° to the other pyrazoles and at 90.9(4)° to the benzene ring. The silver atom lies out of the extended planes of the coordinated pyrazole rings by between 0.081(4) and 0.310(4)Å.

Despite the three pyrazole rings being above the same side of the benzene, tripodal chelation to a single silver atom was not observed. For this to occur, the silver atom, Ag1, would need to sit approximately over the centre of the benzene ring to allow coordination of N52. The nature of silver-benzene interactions makes such a silver position unfavourable. As discussed above, silver prefers η^1/η^2 coordination to a benzene ring, whereas η^6 interaction has never been observed. Therefore, upon coordination to the first two pyrazoles the silver atom interacts with C2, rather than moving towards the third pyrazole, as this would result in a less favourable η^6 silver-benzene interaction.

The palladium complex, 412, crystallises in the triclinic space group P-1; the major component of the asymmetric unit is shown (fig. 4.25). The complex is an $[M_6L_4]$ metallosupramolecular cage consisting of six trans-$PdCl_2$ units bridged, through trans-nitrogen coordination, by four molecules of 409. In addition to the cage complex shown, the asymmetric unit also contains eight DMSO and eight water molecules, many of which are disordered. One of these DMSO molecules, with its sulfur atom disordered over two sites, is contained in the central cavity of the cage.

The range of palladium-nitrogen distances (1.95(1)-2.06(2)Å) and the palladium-chlorine distances (2.266(5)-2.305(5)Å) are consistent with previously reported trans-Cl_2N_2 palladium distances.[176,177] For all six palladiums there is a tetrahedral distortion from square planarity; for example for Pd1 the trans angles (N12A-Pd1-N12B 176.0(7)°, Cl10-Pd1-Cl11 172.4(2)°) and the $PdCl_2N_2$ plane (out of plane distortions N12A -0.10(1), N12B -0.10(1), Cl10 0.117(5), Cl11 0.116(5)Å) are significantly removed from square planar geometry.

The six palladium atoms are arranged in a pseudo-octahedral array (fig. 4.26) with the diagonally opposite palladiums having separations of between 13.257(3) and 15.540(3)Å. The four molecules of 409 form a tetrahedral aromatic core (fig. 4.26) with an internal radius of approximately 4.7Å. The potential Td symmetry is destroyed not only by the DMSO guest and the different Pd···Pd separations discussed above, but also by differing conformations of the ethyl groups in the four ligands (fig. 4.27). While one of the three ligands has all three methyl groups directed towards the inner core, the other three ligands have one methyl group directed outside the core. In contrast, there is symmetry observed in the ^{1}H N.M.R. spectrum of this complex which, along with the broadened signals for methyl and methylene protons, indicates that this complex does have significant conformational freedom in solution.

Significantly, although the substituents in three out of the four ligands are not alternating above and below the benzene, the three pyrazole rings still lie above one side of the benzene ring in each ligand. It is assumed that these pyrazole groups are organised in this manner by the ethyl groups, but formation of the cage complex leads to a change in ethyl group conformation, thus destroying an alternating substituent pattern in the ligand. The twelve pyrazole and four benzene rings are planar (largest out of plane distance C5D 0.04(2)Å). The three pyrazole rings in each ligand are approximately orthogonal to their respective benzene rings (average displacement from orthogonality 4(1)°), and are inclined at angles of approximately 120° to each other.

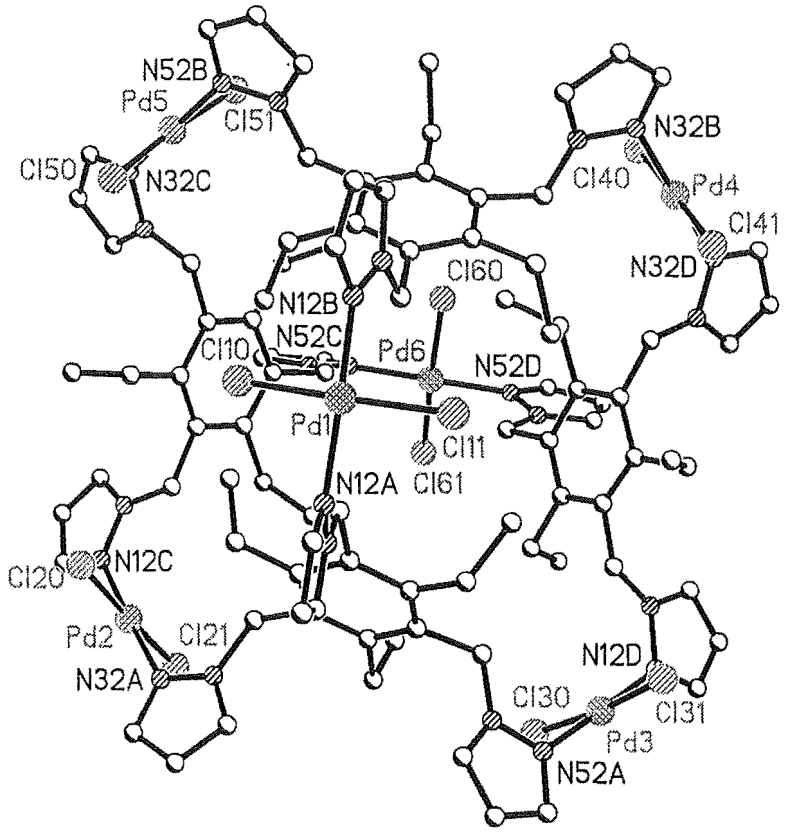


Fig. 4.25 Perspective view and atom labelling of of 412 with hydrogen atoms omitted for clarity. Palladium-donor bond lengths (Å) :Pd1-N 1.98(1), 2.06(2), Pd1-Cl 2.291(5), 2.289(5), Pd2-N 1.95(1), 1.99(2), Pd2-Cl 2.266(5), 2.305(5), Pd3-N 1.99(1), 1.99(1), Pd3-Cl 2.279(5), 2.303(5), Pd4-N 2.00(1), 2.03(2), Pd4-Cl 2.287(4), 2.300(4), Pd5-N 1.95(1), 2.01(2), Pd5-Cl 2.286(5), 2.294(5), Pd6-N 1.97(1), 2.02(1), Pd6-Cl 2.278(5), 2.297(4).

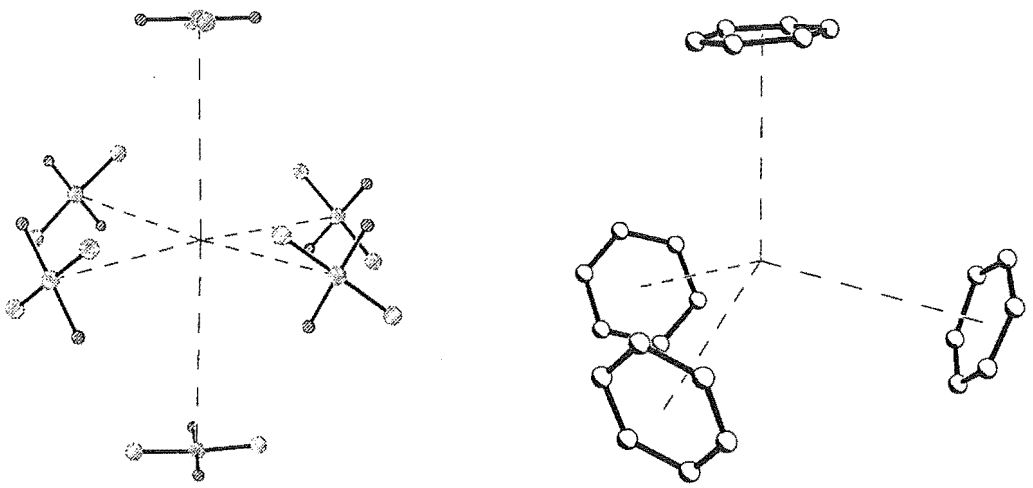


Fig. 4.26 Perspective view of the approximate octahedral arrangement of the palladium centres (left) and tetrahedral arrangement of the ligands (right) in 412.

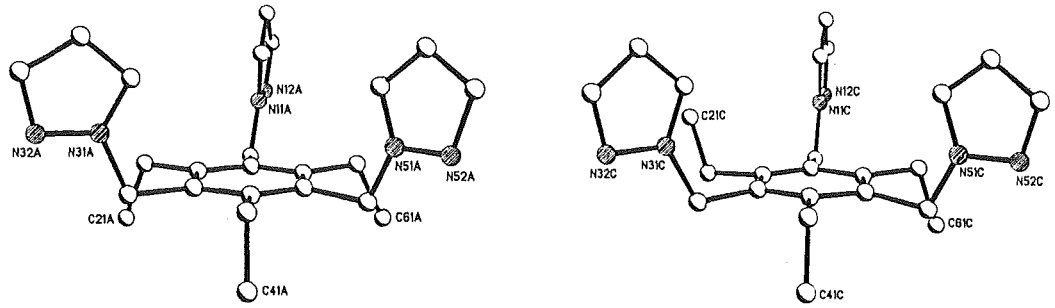


Fig. 4.26 Perspective view of the different conformation of one ligand (left) from those of the other three ligands (one of which is shown on the right) in 412.

This complex represents only the second structurally characterised example of an M_6L_4 supramolecular cage,[219] although stoichiometrically inverted M_4L_6 compounds are also known.[220,221] It is, however, the first X-ray structure of a free cage of this sort; in the previous example a low-precision X-ray structure of a clathrate complex with four adamantanyl carboxylate ions was determined. Despite the constitutional similarity between 412 and the previous adamantanoid M_6L_4 cage, 412 is quite different in shape. This is primarily a consequence of the different coordination geometries of palladium atoms in the two complexes. In the previously reported complex, the bridging ligands are obligatorily cis-coordinated to the palladiums, due to the presence of chelating ethylenediamine ancillary ligands; in the present case the ligands are trans-coordinated, which has the effect of making the palladiums more exposed on the surface of the cage. Furthermore, the presence of the methylene spacer groups in 409 imparts greater flexibility to the ligand and allows for more compact packing within the cage; in the previous example the diagonally opposite palladiums are separated by *ca* 19Å.

The internal core of four tetrahedrally arranged benzene rings is reminiscent of that in the recently synthesised $C_{36}H_{36}$ spheriphane molecule (fig. 4.28), which has covalently bonded ethylene bridges linking the benzenes and a radius of the internal cavity (as measured from the centroids of the rings) of 2.84Å.[222-224] In 412 the nature of the bridges expands this core to a radius of approximately 4.7Å and allows for

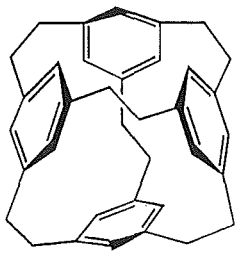


Fig. 4.28

incorporation of the DMSO guest molecule. The octahedral arrangement of the six metals is also related to that in the hexacoordinated palladium and platinum complexes of C_{60}, wherein the diagonally opposite metals are separated by *ca* 11.2Å and the internal core has a radius of 3.51Å.[225,226]

Palladium, silver and copper complexes, 415-417, of 1,3,5-tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 410, were also prepared. The palladium complex, 415, precipitated from the reaction mixture as small crystals upon slow evaporation of the solvent. The ^{1}H N.M.R. spectrum of this compound showed the symmetry of the ligand to be maintained on incorporation into 415. The coordination induced shifts are relatively small (≤ 0.16ppm). No change in chemical shift is observed for either the methylene or methyl signals of the ethyl groups. The change is also small for the methyl substituents of the pyrazole rings. Combustion analysis of the compound gives a [($H_2$410).(Pd_2Cl_6).½H_2O.¼CH_3OH] composition. Given these observations, the structure of 415 probably involves protonated nitrogens on the ligand and a non-coordinated chloropalladium counterion (fig. 4.29). The small differences in chemical shift between the free ligand and 415 are consistent with protonation, rather than palladium coordination to the pyrazoles, a conclusion supported by the largest change in shift being for the pyrazole hydrogen, H4', for which a protonated nitrogen would have the greatest effect. The symmetry in the N.M.R. spectrum of 415 results from this protonation being fluxional, so that, in solution, each pyrazole is rapidly protonating and deprotonating, and therefore equivalent on the N.M.R. timescale.

Upon mixing of an aqueous solution of silver nitrate and a methanolic solution of 410, a colourless solution resulted. A silver complex of 410 was not able to be isolated as the nitrate salt from this reaction mixture due to its high solubility. Addition of excess

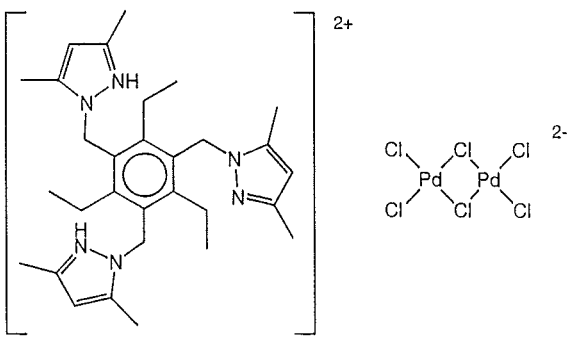


Fig. 4.29

sodium perchlorate solution did however precipitate a silver complex, 416, as a perchlorate salt. Microanalysis of this complex was consistent with [410.$AgClO_4$.2¼H_2O] for 416.

Mixing of methanolic solutions of copper(II) chloride and 410 gave a green solution. Diffusion of diethyl ether into this reaction mixture furnished crystals of 417, analysing as [410.$CuCl_2$.H_2O.½CH_3OH], which were suitable for single crystal X-ray structure analysis. The solubility of this complex in methanol, the 1:1 metal/ligand ratio and the expected pre-organised conformation of the three pyrazole rings, are each consistent with a triply-chelated structure for 417. The structure of this complex was therefore determined, to investigate whether this mode of coordination to a copper centre had been realised.

Crystal Structure of 417.

The copper complex, 417, crystallises in the triclinic space group P-1, the asymmetric unit of which contains two [(410)$CuCl_2$.H_2O] units and a methanol solvate, in accordance with the microanalysis of the compound; one of the [(410)$CuCl_2$.H_2O] units is labelled and shown (fig. 4.30). In each of the two independent complexes in the

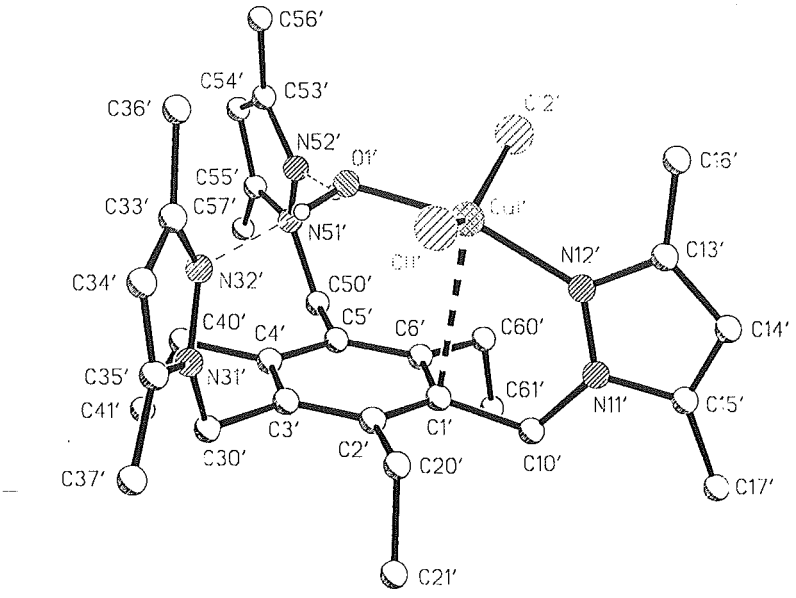


Fig. 4.30 Perspective view and atom labelling of 417. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°) for Cu1', Cu1 molecules: Cu1'-N12' 1.983(5), 1.961(5), Cu1'-Cl1' 2.250(2), 2.241(2), Cu1'-Cl2' 2.243(2), 2.268(2), Cu1'-O1' 1.946(4), 1.951(5); N12'-Cu1'-Cl1' 94.8(2), 94.8(2), N12'-Cu1'-Cl2' 93.2(2), 92.8(2), N12'-Cu1'-O1' 163.6(2), 166.1(2), Cl1'-Cu1'-Cl2' 145.62(9), 148.83(9), Cl1'-Cu1'-O1' 91.0(2), 89.5(2), Cl2'-Cu1'-O1' 90.7(2), 90.2(2).

asymmetric unit, the copper atom is coordinated to only one pyrazole group along with two chlorine atoms and a water molecule. The copper-donor bond distances are consistent with those of related structures.[134,180,181,202] The hydrogens from the coordinated water molecule are hydrogen bonded to nitrogens of the other two pyrazole groups of the ligand (N···H distances 1.98(8) and 1.95(8)Å for the molecule shown). In both [(410)$CuCl_2.H_2O$] units, one hydrogen of the water was found in a difference electron density map, although these were later fixed to ride on the coordinates of the attached oxygen.

As for the previous two triethyl substituted compounds for which X-ray structures were determined, the three pyrazole rings lie above one side of the benzene ring in each ligand. The benzene and three pyrazole rings in each molecule are approximately planar (largest out of plane distance C2 0.022(8)Å). The three pyrazole rings in each ligand are approximately orthogonal to their respective benzene rings (average displacement from orthogonality 8.6(6)°). The coordinated pyrazole group is inclined to the other two pyrazoles of the ligand at angles of 86.6(6) and 45.0(6)° (for the Cu1 molecule 90.6(6) and 52.0(6)°) with the latter two inclined to each other at an angle of 41.8(6)° (for the Cu1 molecule 38.9(6)°). In fact, the two [(410)$CuCl_2.H_2O$] molecules have very similar geometry overall, although the methanol solvate destroys any symmetry that may have been present.

A distance of 2.954(6)Å separates the copper from C1'. While this separation is too long to be considered as coordination (typical distances 2.15-2.45Å),[227,228] there is evidence of an interaction between the benzene π-orbitals and the copper atom. The N-Cu-O angle, 166.1(2)°, is less bent than the Cl-Cu-Cl angle, 148.83(9)°. The straightening of this bond helps to dispose the copper atom to arene interaction (fig. 4.31). It can also been seen that the methylene carbon linking the benzene and the

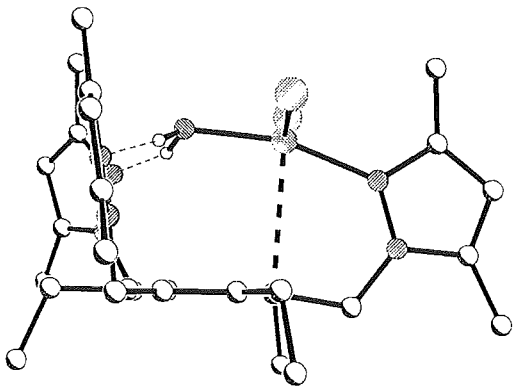


Fig. 4.31 Side view of 417 showing the N-Cu-O and methylene distortions associated with the Cu-benzene interaction

coordinated pyrazole group is displaced below the plane of the benzene (out of plane distance 0.232(8)Å). This moves the whole [Cu(pyrazole)(H_2O)Cl_2] moiety closer to the benzene ring, clearly indicating an attractive intramolecular Cu-arene interaction.

Of particular interest with regard to the 1,3,5-tris(pyrazol-1-ylmethyl)benzene ligands, 400, 405 and 409, has been the $N_3(\eta^6$-benzene) coelenterate mode of coordination. An extension of this type of metal encapsulation would be to encapsulate a metal on each side of a benzene ring to give an inverse sandwich complex (fig. 4.32).[229-231]

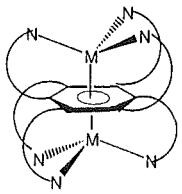
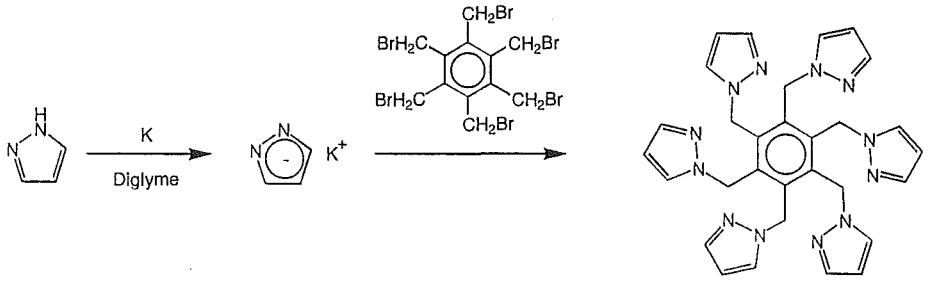


Fig. 4.32

Hexakis(pyrazol-1ylmethyl)benzene, 418, a ligand that may be capable of such coordination, was synthesised in work undertaken prior to this thesis,[166] by bromination of hexamethylbenzene and subsequent phase-transfer-catalysed alkylation of pyrazole. The alkylation step proved to be a difficult reaction from which to isolate 418 in good yield. Consequently, a different reaction has been used in this work to prepare 418 (fig 4.33). The potassium salt of the pyrazolate ion is first generated using diglyme as the solvent, hexakis(bromomethyl)benzene added, and the mixture is then heated for a prolonged period. After work-up of the reaction mixture, 418 was isolated in 43% yield. Recrystallisation of this compound from a diethyl ether/ethyl acetate mixture afforded crystals of 418 suitable for single crystal X-ray structure determination. In order to confirm the structure of 418 and to investigate the relative orientations of the pyrazolylmethyl substituents, the X-ray crystal structure of 418 was determined.



418

Fig. 4.33

Crystal Structure of 418.

The compound crystallises in the triclinic space group P-1, the asymmetric unit of which contains two independent half molecules. Each of these half ligands is positioned about a centre of inversion through which are generated the other half of the ligands; a complete ligand is shown with atoms labelled (fig. 4.34).

The bonding geometry is very similar in each of the two independent molecules. However, the two hexasubstituted benzene rings differ significantly in their degree of planarity; in one molecule the mean deviation from the plane of the six carbons is 0.010(2)Å, while the corresponding value for the other molecule is 0.005(2)Å. The difference between the two molecules is more significant when considering the deviations of the attached methylene carbons from the benzene. While for one molecule these deviations are 0.154(2), -0.195(2) and 0.147(2)Å, the corresponding values for the second molecule are only 0.057(2), -0.041(2) and 0.050(2)Å. In both molecules the six pyrazolylmethyl substituents describe an alternating pattern above and below the benzene ring. This pattern is consistent with the tris(pyrazolylmethyl)-triethylbenzene structures discussed above, as well as previously reported hexasubstituted benzenes,[232,233] although exceptions do exist.[234,235] Significantly, this alternating arrangement is exactly that required for encapsulation of two metal atoms.

Aside from different benzene meanplane distortions in the two molecules, they also differ in the conformational orientations of the pyrazole rings. While the planes of all

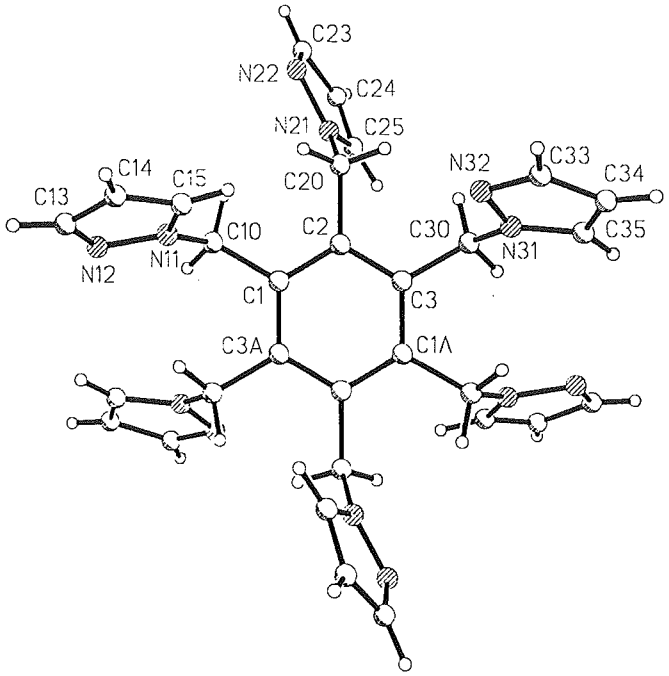


Fig. 4.34 Perspective view and atom labelling of 418.

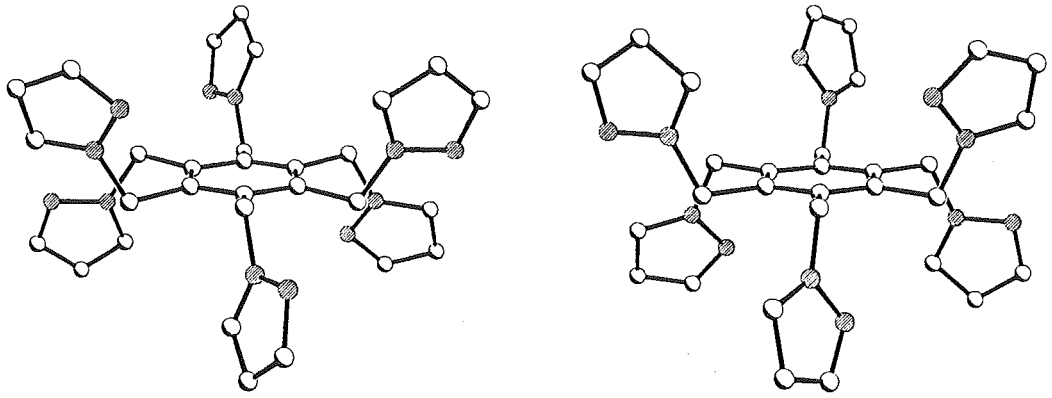


Fig. 4.35 Perspective view showing the different conformational orientations of pyrazole groups in the two independent molecules of 418.

pyrazole rings are approximately orthogonal to their respective benzene ring, one molecule has four out of six potentially coordinating nitrogens directed inwards towards the benzene ring, but the other only has two such inwardly directed nitrogens (fig. 4.35).

A ruthenium complex, 419, was then prepared in a reaction of 418 with two equivalents of dichloro-tetrakis(dimethylsulfoxide)ruthenium(II) in ethanol/water. The complex - a red/brown powder - precipitated from the reaction mixture. This compound analyses as $[(418)Ru_2Cl_4]$, a composition consistent with an inverse sandwich structure. The complex is insoluble in common solvents, thus preventing characterisation by N.M.R. or UV/Vis spectroscopy. All attempts to obtain the complex in a more soluble form also failed. A mass spectrum of 419 was obtained by suspension of a finely ground sample in a para-nitrobenzyl alcohol matrix which was subsequently injected into the mass spectrometer. The highest set of ion masses observed was centred around 867 Daltons, a mass corresponding to $[(418)Ru_2Cl_3]^+$. Given this, and the ideal ligand conformation shown in the structure of 418, this complex is thought to be the inverse sandwich complex shown (fig. 4.36).

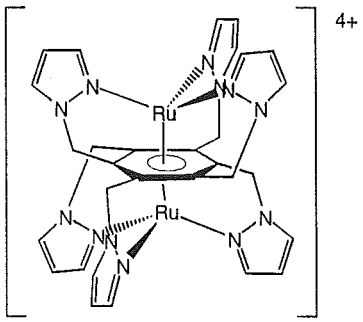


Fig. 4.36

4.3 Synthesis of Tripodal Pyridine-Containing Ligands.

The synthetic target of 2-substituted pyridine rings linked through one atom to a benzene has been achieved using oxygen as the linking atom, as discussed above. However, the relative ease of synthesis of poly(methylthiopyridyl)benzenes also gave rise to a synthetic pathway for the analogous carbon linked compounds. The general reaction scheme for conversion of a 2-pyridylsulfanylmethylbenzene into a 2-pyridylmethylbenzene is shown (fig. 4.37). The sulfide is first oxidised to a sulfoxide using meta-chloroperbenzoic acid. Upon isolation the sulfoxide is then treated with a Grignard reagent, which leads to a σ-sulfarane intermediate. This intermediate then under goes ligand coupling, eliminating the sulfur atom, to give the 2-pyridylmethylbenzene. Importantly, it has been shown by isotopic labelling experiments that the benzene in the sulfoxide is carried through to the product - there is no incorporation of the benzene of the Grignard reagent into the pyridylmethylbenzene product.[236] This being the case, poly(2-pyridylsulfanylmethyl)benzene compounds should therefore act as precursors to the analogous poly(2-pyridylmethyl)benzenes, as the integrity of the ligand is maintained upon elimination of sulfur.

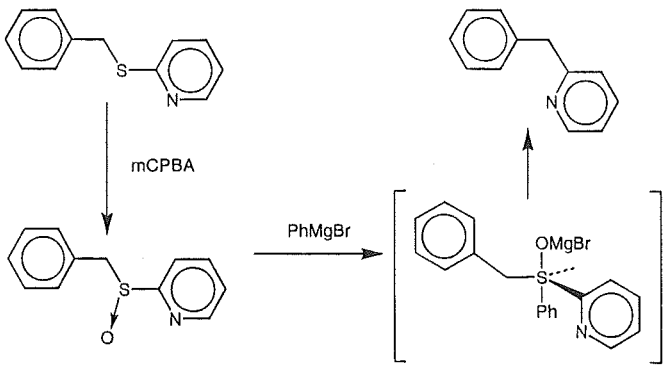


Fig. 4.37

The starting sulfide compound 1,3,5-tris(2-pyridylsulfanylmethyl)-2,4,6-trimethylbenzene, 420, was synthesised as for the thiopyridine compounds described previously, in a reaction of the trisbromomethyl compound with 2-mercaptopyridine. This was isolated and then oxidised to 1,3,5-tris(2-pyridylsulfinylmethyl)-2,4,6-trimethylbenzene, 421. This compound was isolated and shown by ^{1}H NMR spectroscopy to be the expected mixture of two diastereoisomers. This was then dissolved in THF and added dropwise to a THF solution containing excess phenylmagnesium bromide. Work-up of the reaction mixture yielded an orange oil shown by ^{1}H NMR spectroscopy to contain a number of different compounds. A mass

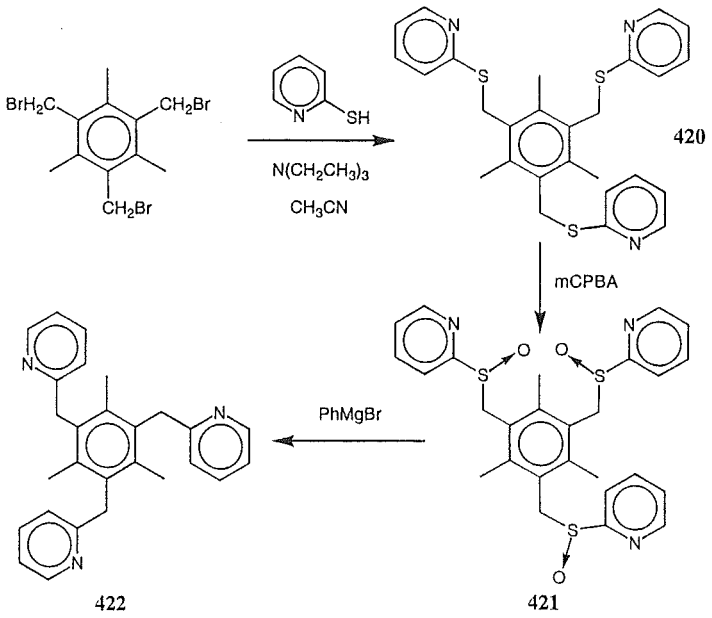


Fig. 4.38

spectrum of this oil showed a peak (m/z ca 393) corresponding to 1,3,5-tris(2-pyridylmethyl)-2,4,6-trimethylbenzene, 422 (fig. 4.38), but this was only a minor component of the mixture. Given the relative ease of synthesis of poly(2-pyridoxy)benzene compounds, this reaction was not further investigated.

Given the ease of appending 2-pyridoxy groups to a benzene, attempts were made to incorporate such a group into unsymmetrical tripodal compounds. The approach used to synthesise these ligands employs 2,4,6-trimethylphenol as the starting material (fig. 4.39). The first step involves reaction of the aromatic alcohol group with 2-bromopyridine[78] to give 2,4,6-trimethyl-1-(2-pyridoxy)benzene, 423, which is then bis-

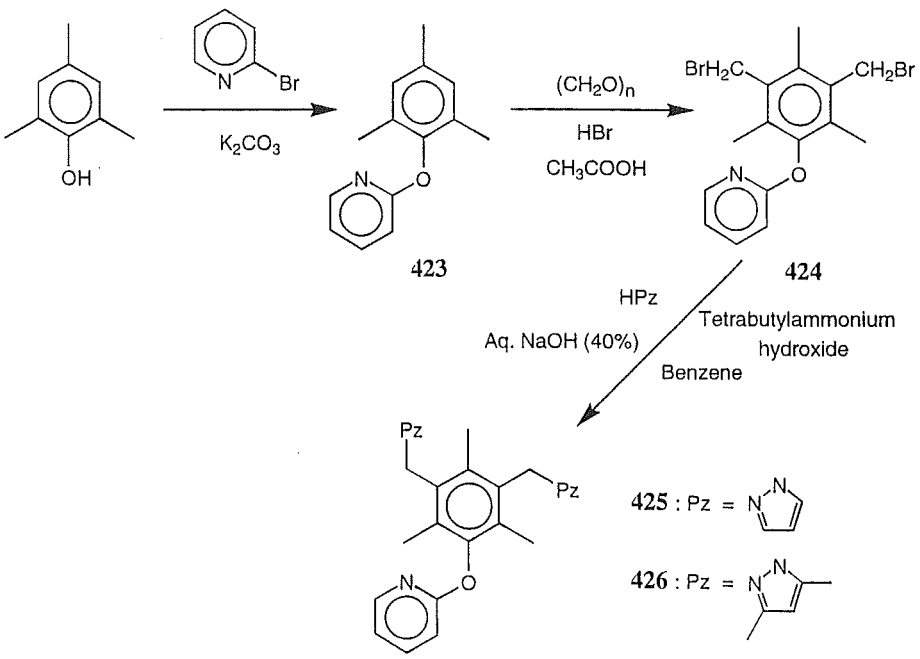


Fig. 4.39

bromomethylated[217] in the second step to give 3,5-bis(bromomethyl)-2,4,6-trimethyl-1-(2-pyridoxy)benzene, 424. This was then used in a phase-transfer-catalysed alkylation of pyrazole, or 3,5-dimethylpyrazole, to give 425 and 426, respectively. While these two compounds were both isolated in satifactory yields, no complexes of 425 or 426 were characterised.

Chapter 5

Cyclometallated Complexes

Cyclometallated Complexes

5.1 Introduction.

Cyclometallated complexes, as depicted by 5.1a, are distinguished from chelated coordination compounds, 5.1b, in that a carbon-metal bond is incorporated in the cyclic structure resulting from coordination of the ligand to the metal.

5.1a **5.1b**

Fig. 5.1

In the extensive studies of cyclometallation undertaken during the past three decades, a variety of metals have been used in these metallocycles.[237-240] The cyclometallated complexes involving one metal in particular - palladium - have been the subject of great interest.[241-243] The formation of a cyclopalladated complex was first reported more than three decades ago[244] and a vast number of such compounds have been reported since that time. As well as this extension of the catalogue of known cyclopalladated compounds, much research has also been devoted to the examination of their chemistry. Resulting from this, these compounds have found various applications as organometallic intermediates in organic synthesis, including regio- and stereoselective reactions.[241-243,245,246] More recently, cyclopalladated compounds have proved to have applications in other areas as well, including liquid crystals, optical devices, photochemistry and anti-tumour agents.[242,243,247]

Of particular interest in the area of cyclopalladation chemistry has been that of ortho-palladated compounds.[248] This class of compound, represented by figure 5.2, incorporates a palladium-carbon bond to the aromatic ring at the ortho position to a substituent coordinated to the palladium. Such complexes constitute the majority of known palladacycles, and have been found to be of particular use in regioselective additions to the metallated aromatic substrates.[249]

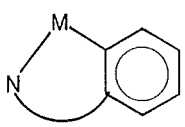
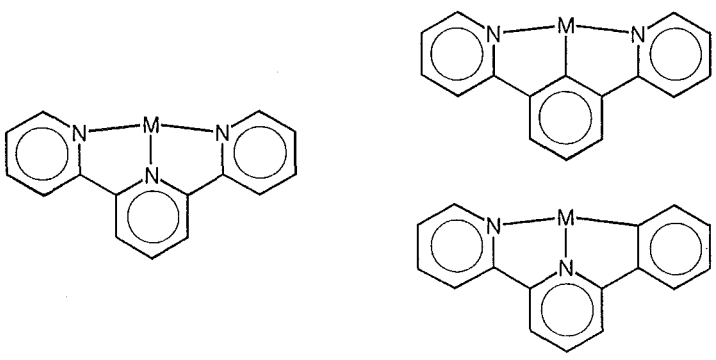


Fig. 5.2

Aside from the particular metal involved, other structural classifications of cyclometallated compounds can be made. The ring size formed in the metallocycle is one means of classification. Chelate ring sizes can vary between three and nine members, although by far the most common of these are the five membered metallocycles.[247,250] Six membered metallocycles are the most abundant of the other ring sizes, but while the last five years has seen an increase in the rate of articles published in this area,[247,251-257] reports of structures of this type remain comparatively rare.

Ligands are not limited to a bidentate mode of coordination in the formation of metallocycles, thereby offering further means of distinction between cyclometallated compounds. Many metallocycles are known where the ligand coordinates to a metal through a carbon as well as two (or more) other donor atoms to give a fused-ring system. As such, these metallocycles constitute cyclometallated analogues of more extensively studied tridentate coordination complexes, an example of which, 2,2',6',2"-terpyridine, and two cyclometallated analogues, are shown (fig. 5.3). This class of metallocycle has received much attention in recent years and a variety of donor sets have been incorporated in the design of such ligands.[239,241,251,258-260]

Double cyclometallation of ligands offers a further extension to the range of known palladocycles and a number of reports of this type of compound have been made. While many such compounds containing two palladated phenyl rings are known,[101,243,246,261-264] relatively few compounds have been reported where two different sites on the same benzene ring have been cyclopalladated.[242,248,265-267] Doubly cyclometallated complexes have also attracted much recent interest in the area of molecular electronic devices due to the significant electronic coupling between the two metal centres in such systems.[6,239,248] Doubly cycloruthenated complexes are of particular interest, as the 1 electron Ru^{II}-Ru^{III} oxidation/reduction couple is more amenable to electrochemical studies than is the 2 electron Pd^{II}-Pd^{IV} couple.



Coordination Complex Fused-ring Metallated Analogues

Fig. 5.3

This chapter reports the synthesis of cyclometallated compounds incorporating the structural features described above. Ligands included in this study (fig. 5.4) all incorporate a 1,3-bis(pyrazol-1-ylmethyl)benzene fragment, although each contains structural modification to this basic system. The discussion of the cyclometallation reactions of these ligands includes four X-ray structural determinations: two orthopalladated complexes in which coordination of the metal gives two fused six membered palladacycles; a doubly orthopalladated complex with the metals as 1,4-substituents on the same benzene ring, where coordination of each metal gives two fused six membered palladacycles; and an orthoruthenated complex where coodination of the ruthenium gives two fused six membered ruthenocycles. The dynamic behaviour of the cyclopalladated complexes will also be discussed.

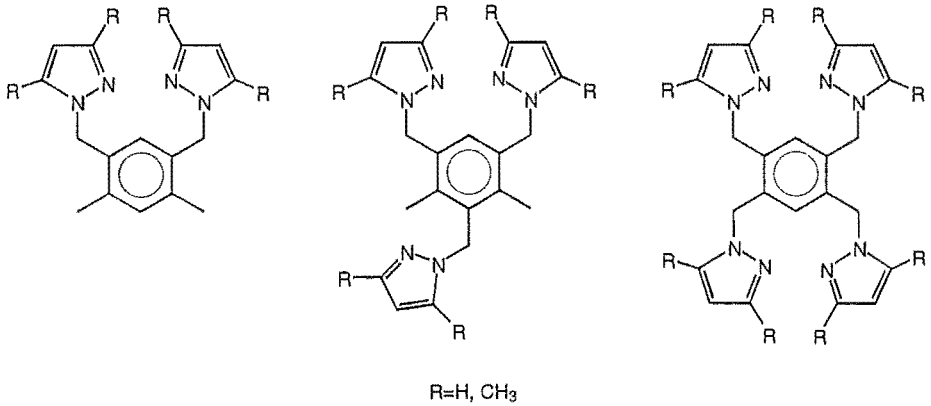


Fig. 5.4

5.2 Synthesis of Ligands.

The 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzenes, 337 and 338, and the 1,3,5-tris(pyrazol-1-ylmethyl)benzenes, 405 and 406, had previously been synthesised for other parts of this research. As discussed in chapter three, the synthesis of 1,3-bis(pyrazol-1-ylmethyl)benzene has previously been reported; also reported was the cyclopalladation of this ligand.[135] Before any attempt was made to cyclometallate 337, 338, 405 and 406, it was important to reconfirm that a 1,3-bis(pyrazol-1-ylmethyl)benzene system would cyclometallate without the complication of the extra pyrazole substituents in the tri- and tetra-substituted compounds. If this bis-heterocyclic compound cyclometallated, investigation of the cyclometallation of the more substituted systems could then take place. Cyclopalladation reactions of other 1,3-substituted benzenes have been shown to give both the 2-monopalladated fused ring system, 5.5a,

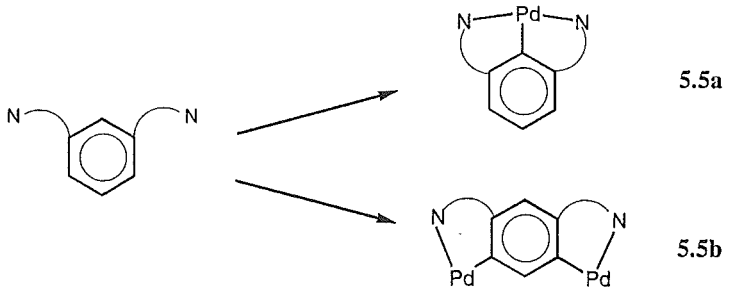


Fig. 5.5

and the 4,6-bis-cyclopalladated system, 5.5b.[242,243,248,268] To avoid bis-cyclopalladation of the model 1,3-bis(pyrazol-1-ylmethyl) system, methyl substituents were used to protect the 4 and 6 positions of the benzene ring.

The first step in the synthesis of the 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene system (fig. 5.6) is the preparation of its bromomethyl precursor 1,3-bis(bromomethyl)-4,6-dimethylbenzene, 500. This was carried out by bromomethylation of 1,3-dimethylbenzene using paraformaldehyde and hydrobromic acid in acetic acid.[217] Although this also produced 1,3-bis(bromomethyl)-2,4-dimethylbenzene, 501, steric factors lead to a 3:1 ratio of the desired 500 to 501. The latter impurity was easily removed by recrystallisation to give 500 in satisfactory yield.

Attempts to substitute pyrazole groups for bromine using the phase transfer conditions employed for previous ligand syntheses were unsuccessful, and gave mainly products with only one bromine replaced. Consequently, an alternative procedure using potassium carbonate in dimethylformamide was used to give the 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzenes, 502-505.

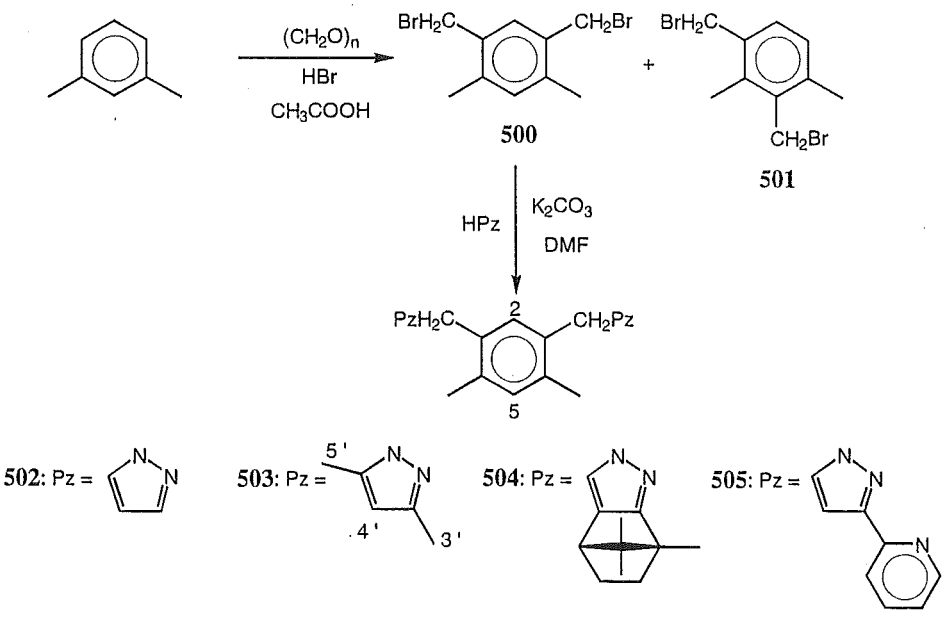
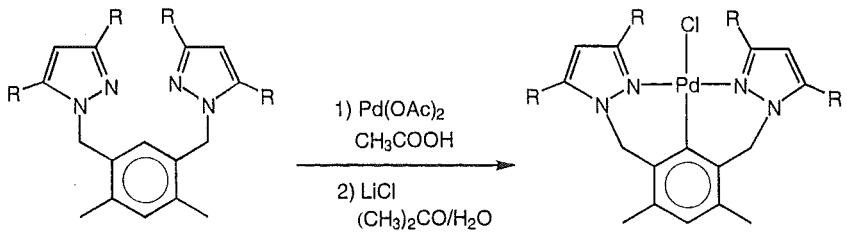


Fig. 5.6

While the assignments of the ^{1}H N.M.R. spectra of 502, 504 and 505 were trivial, that of 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)-4,6-dimethylbenzene, 503, was more involved. The methyl groups in the ^{1}H N.M.R. spectrum of 503 were unambigously assigned using difference nOe experiments, wherein irradiation of H4' resulted in approximately equal enhancements of the 3'-CH_3 and 5'-CH_3 signals (both 0.5%). Irradiation of the methylene signal resulted in enhancements for the adjacent aryl methyl group (2.6%) and for the 5'-CH_3 group (1.7%). The latter irradiation also allowed for assignment of the aryl proton signals as a 12.6% enhancement was observed for one (H2) compared to the absence of any enhancement of the other signal (H5). The proton on the 2 position of the benzene ring of 503 has an exceptionally high field chemical shift of 5.43ppm, consistent with the earlier observation of high field shifts of aromatic protons in 1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338, and 1,3,5-tris(3,5-dimethylpyrazol-1-ylmethyl)benzene, 406. Once again this can be attributed to the 3',5'-substituent-induced shielding arrangement of the pyrazole rings with respect to H2.

5.3 Cyclopalladated Complexes.

For reasons outlined previously initial cyclopalladation reactions were carried out using the bis-pyrazolyl ligands 502 and 503. A mixture of the ligand and palladium acetate was stirred in refluxing glacial acetic acid to give acetato-cyclopalladated complexes which were transformed to the chloro- complexes, 506 and 507, using lithium chloride (fig. 5.7). These chloro- compounds were characterised using microanalysis as well as ^{1}H and ^{13}C N.M.R. spectroscopy. The number of signals in the ^{1}H spectra, along with observed downfield shifts for the palladated carbon in 506 (143.97ppm) and 507 (147.33ppm) consistent with those in known cyclopalladated systems,[243] confirmed the palladated structures. As with the ^{1}H N.M.R. spectra of the



506 : R = H
507 : R = CH_3

Fig. 5.7

ligands 502 and 503, the ease of assignment of the ^1H spectra of the respective cyclopalladated complexes differed. While assignment in the less substituted 506 was trivial, the spectrum of 507 required difference nOe experiments to assign signals in the methyl region. As for 503, irradiation of the signals for the methylene and H4' protons allowed for the unambiguous assignment of the signals for the three different methyl environments.

Only one previous report (with two examples) has described X-ray crystal structures of orthopalladated complexes in which coordination of the metal gives two fused six membered palladocycles.[252] As a result, and in order to fully confirm the cyclopalladated structures above, various recrystallisation techniques were used which eventually resulted in crystals of both 506 and 507, suitable for single crystal X-ray structure analyses.

Crystal Structures of 506 and 507.

The cyclopalladated complex of 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene, 506, crystallises in the monoclinic space group $P2_1/c$ and contains one cyclopalladated molecule and a disordered dimethylsulfoxide solvate in the asymmetric unit. The structure and atom labelling of the metallated unit is shown (fig. 5.8).

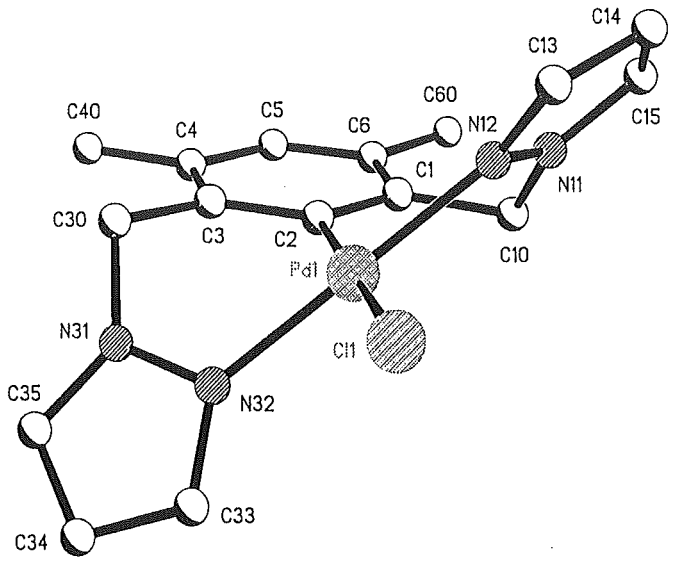


Fig. 5.8 Perspective view and atom labelling of 506. The hydrogen atoms and disordered solvate are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C2 1.993(4), Pd1-N12 2.008(3), Pd1-N32 2.007(3), Pd1-Cl1 2.429(1); C2-Pd1-N12 88.8(1), C2-Pd1-N32 88.7(1), Cl1-Pd1-N12 91.2(1), Cl1-Pd1-N32 91.4(1), C2-Pd1-Cl1 176.0(1), N12-Pd1-N32 177.3(1).

The palladium atom has approximately square planar coordination to the N, C, N, Cl donor set. The plane of coordination is twisted 37.1(3)° out of the plane of the benzene placing the two pyrazole rings on opposite sides of the extended plane of the benzene ring. There is evidence of a slight tetrahedral distortion from square planarity around the palladium as the mean plane defined by Pd1 (deviation from the plane of 0.023(2)Å), Cl1 (-0.046(3)), C2 (-0.058(5)), N12 (0.040(5)) and N32 (0.040(5)) shows alternating displacement of the donor atoms above and below the plane. This is supported by the trans-coordination angles (177.3(1) and 176.0(1)°). This tetrahedral distortion and the disordered dimethylsulphoxide in the structure destroy any potential crystallographic C_2 symmetry arising from the cyclopalladated unit. The palladium atom is 0.067(2) to 0.108(2)Å out of the planes of the three donor rings, but there is minimal distortion of the planarity of the rings themselves (maximum displacement from a ring mean plane = 0.008(5)Å for N31). While the Pd1-C2, Pd1-N12 and Pd1-N32 bond lengths are within the range of lengths found in related structures, the Pd1-Cl1 distance (2.429(1)Å) is relatively long. It is however consistent with other structures where the Cl is trans to a σ-bonded carbon. Such Pd-Cl bond lengthening has previously been attributed to the trans influence of the low electronegativity of the C^- donor.[248,269]

The fused six-membered metallocycles each exist in a boat conformation: Pd1 and C10 are 0.734(2) and 0.592(5)Å, respectively, above the mean plane defined by C1, C2, N11, N12; and Pd1 and C30 are 0.813(2) and 0.594(5)Å, respectively, below the mean

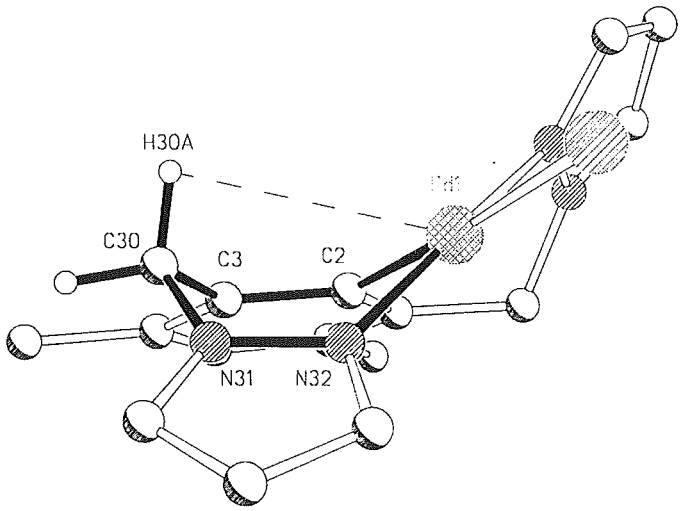


Fig. 5.9 Perspective view of 506 highlighting the boat conformation of one of the palladacycles and the Pd1-H30A agostic interaction. All hydrogens except those of the methylene group are omitted for clarity.

plane defined by C2, C3, N31, N32. This conformation allows for a weak agostic interaction between the palladium and a hydrogen from each methylene group (Pd1-H10A 3.14(2)Å, Pd1-H30A 3.05(2)Å), one of which is shown in figure 5.9.

The cyclopalladated complex of 1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)-4,6-dimethylbenzene, 507, crystallises in the monoclinic space group $P2_1$, the asymmetric unit of which contains two cyclopalladated molecules (fig. 5.10). There is some ambiguity associated with the space group of this compound as the two independent molecules appear to be related by a crystallographic glide plane. However, all attempts to solve or refine the structure of 507 in a higher symmetry space group were unsuccessful.

The geometry of each molecule is similar to that of 506; again there is evidence of slight tetrahedral distortion of the square planarity around the respective palladium atoms, although this distortion is different in 507 as the C-Pd-Cl angles (both 179.0(5)°) are only slightly non-linear while the N-Pd-N angles (174.3(6) and 174.6(6) °) are more bent than in 506. The Pd-Cl bond lengths (2.441(6) and 2.438(6)Å) again reflect the

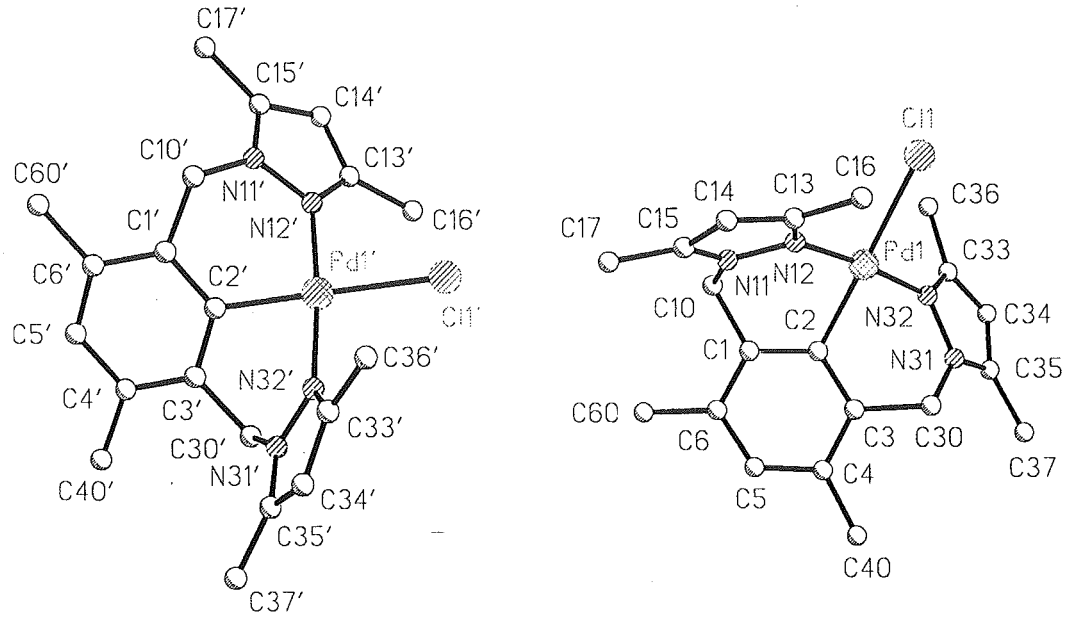


Fig. 5.10 Perspective view and atom labelling of 507. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for Pd1 molecule, Pd1' molecule : Pd1-C2 1.98(2), 1.99(2); Pd1-N12 2.04(1), 2.01(1); Pd1-N32 2.01(1), 2.06(1); Pd1-Cl1 2.441(6), 2.438(6); C2-Pd1-N12 88.1(7), 87.0(7); C2-Pd1-N32 86.9(7), 88.5(7); Cl1-Pd1-N12 91.5(4), 93.2(5); Cl1-Pd1-N32 93.5(5), 91.5(4); C2-Pd1-Cl1 179.0(5), 179.0(5); N12-Pd1-N32 174.3(1), 174.6(6).

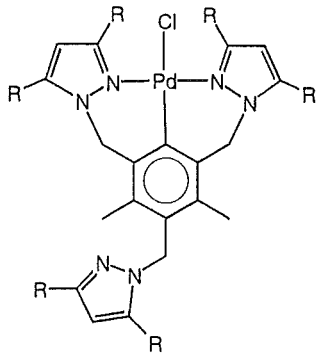
trans- influence of the σ-bonded C^- donor.

Boat conformations are again observed for the metallocycles but the distances of the palladium and methylene groups out of the plane of the boat are significantly greater for 507 (average Pd/CH_2 distance out of plane for 507 = 0.77(2)Å, for 506 = 0.683(4)Å). As a result, shorter Pd-H(methylene) distances are observed for 507 (Pd-H_{Av} 3.0(1)Å) than for 506 (3.10(2)Å). While stronger than in 506, this agostic interaction remains relatively weak.

Significant differences in comparing the two molecules of 507 with 506 can also be seen in the relative orientations of the pyrazole groups with respect to each other and the benzene ring, as well as the twist angle of the Pd, N, C, N, Cl coordination planes with respect to the benzene rings. The mean planes of the two pyrazoles in 506 are inclined at an angle of 51.2(3)° to that of the benzene. In 507 the pyrazole-benzene angles range from 64(1)° to 68(1)°. Likewise, the angle of the coordination plane to the benzene ring increases to 44.9(8) and 45.2(8)° in the two molecules of 507. This increase in the twist angle of the pyrazoles and coordination planes relative to the benzene is due to the presence of the methyl substituents, C16 and C36, on the 3 position of the pyrazole rings in 507. By twisting the pyrazole rings further from the plane of the benzene, the distance between these methyl groups and the proximate coordinated chlorine is increased, thereby relieving steric compression between the two. These methyl groups are also distorted out of the plane of their respective pyrazole rings (0.04(2)-0.12(2)Å) to further increase the methyl-chlorine distance.

Once it had been established that the 1,3-bis(pyrazol-1-ylmethyl)benzene unit cyclopalladated in the manner predicted, palladation reactions for the 1,3,5-tris(pyrazol-1-ylmethyl)benzene and 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene systems were then investigated.

The chloro-cyclopalladated compounds, 508 and 509 (fig. 5.11), of the 1,3,5-tris(pyrazol-1-ylmethyl)benzenes, 405 and 406 respectively, were synthesised using similar reaction conditions to those employed for 506 and 507. These chloro-compounds were characterised using microanalysis, as well as ^1H and ^{13}C N.M.R. spectroscopy. As for the previous palladacycles, the number of signals in the ^1H spectra, along with observed downfield shifts for the palladated carbon in 508 (144.85ppm) and 509 (147.83ppm) confirmed the palladated structures.



508 : R = H

509 : R = CH_3

Fig. 5.11

The syntheses and isolation of the bis-cyclopalladated complexes of the tetrapyrazolyl systems, 337 and 338, proved to be more difficult. Although the chloro-bis-cyclopalladated complex 510 (fig. 5.12) was synthesised using two equivalents (or in excess of two equiv.) of palladium acetate, it proved awkward to isolate from palladium impurities formed during the extended period of reflux in acetic acid. To combat this problem, the chloro-monocyclopalladated complex, 511 (fig. 5.12), was synthesised using one equivalent of the ligand, 337, to a half equivalent of palladium acetate. This ensured that a minimal amount of the palladium starting material formed impurities instead of metallating the benzene ring. The crude monocyclopalladated 511 was purified in low yield for the purposes of characterising the compound (microanalysis, ^{1}H and ^{13}C N.M.R. spectroscopy), but was used in the crude form for

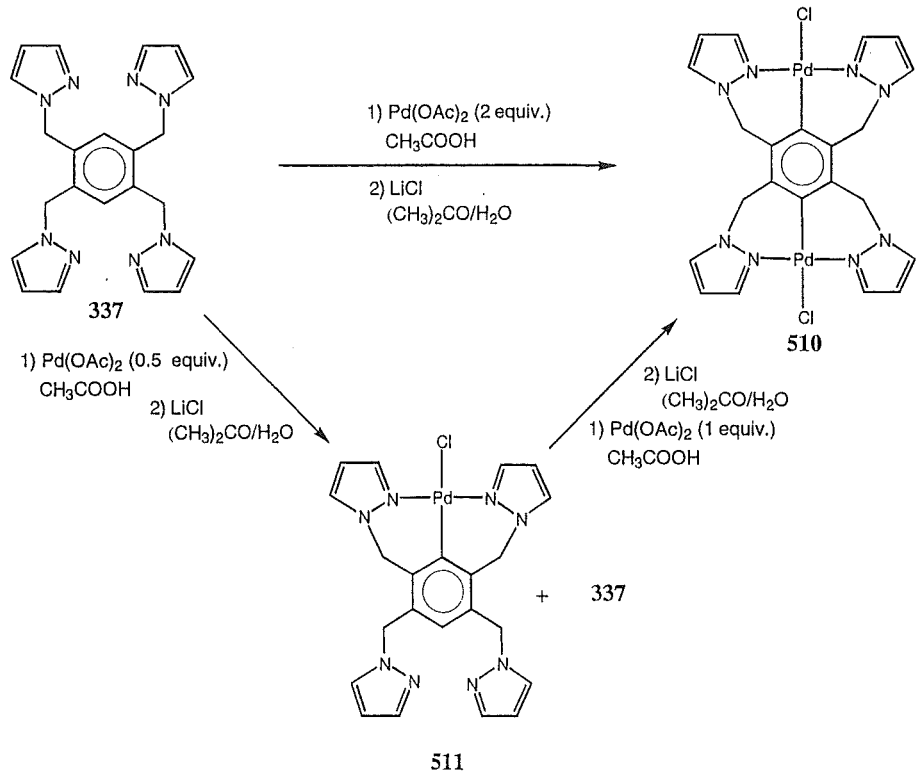
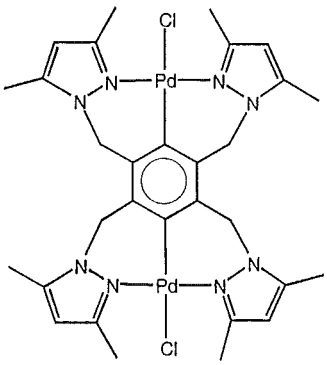


Fig. 5.12

subsequent reactions. The excess ligand was recovered with good efficiency from the reaction mixture. This monocyclopalladated species was reacted with one equivalent of palladium acetate and worked up to give 510 as a white solid. This is in contrast to the dark brown solid produced using the one-step bis-cyclopalladation. Microanalysis along with ^{1}H and ^{13}C N.M.R. spectroscopy confirmed that the doubly orthopalladated complex had been synthesised.

Efficient synthesis, rather than isolation, of the doubly metallated complex was a significant problem in the preparation of 512 (fig 5.13). Regardless of the duration of reflux, or of the ratio of reactants, the reaction never appeared to go to completion as only a proportion of the ligand, typically 40-50%, doubly cyclometallated. The solubility of this compound was significantly better than that of 510, and did allow for the isolation of 512 from the reaction mixture. Although this was achieved in only modest yield, it did however afford crystals of 512 suitable for single crystal X-ray structure analysis. The chemical shift of the metallated carbons was again consistent with that of a cyclopalladated structure (143.10ppm).



512

Fig. 5.13

Crystal Structure of 512.

The complex crystallises in the triclinic space group P-1, the asymmetric unit of which contains two bis-cyclopalladated molecules along with four methanol solvate molecules, two of which are disordered. The presence of these solvates destroys any potential intramolecular C_2 symmetry, along with any possible intermolecular symmetry relation between the two palladated molecules. Furthermore, the mean planes of the two independent binuclear palladacycles are inclined at an angle of 50.7(7)°. One of the two cyclometallated molecules in the asymmetric unit is shown with atom labelling (fig. 5.14). Selected bond lengths and angles for the second molecule (which has the same labelling but with primes (')) are given with those of the molecule shown.

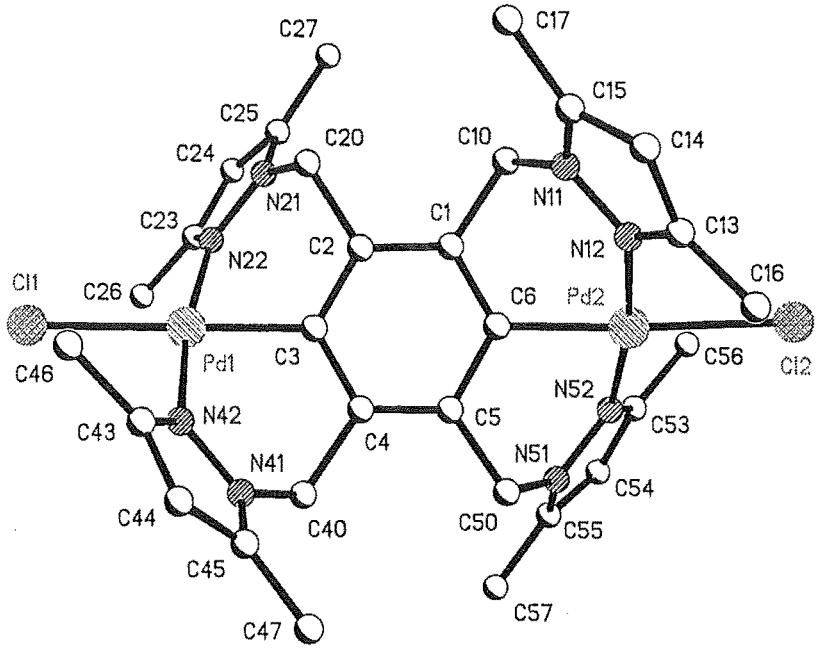
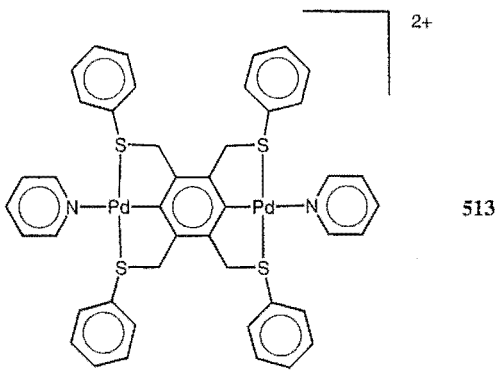


Fig. 5.14 Perspective view and atom labelling of 512. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for Pd1 molecule, Pd1' molecule: Pd1-C3 1.969(8), 1.984(8); Pd1-N22 2.023(7), 2.027(7); Pd1-N42 2.037(7), 2.041(7), Pd1-Cl1 2.461(2), 2.460(2); Pd2-C6 1.973(8), 2.002(8); Pd2-N12 2.037(7), 2.045(7); Pd2-N52 2.018(6), 2.031(7); Pd2-Cl2 2.473(2), 2.458(2); C3-Pd1-N22 85.5(3), 85.1(3); C3-Pd1-N42 85.2(3), 85.9(3); Cl1-Pd1-N22 94.8(2), 94.9(2); Cl1-Pd1-N42 94.5(2), 94.1(2); C3-Pd1-Cl1 179.3(3), 178.7(2); N22-Pd1-N42 170.5(2), 171.0(3); C6-Pd2-N12 85.4(3), 86.3(3); C6-Pd2-N52 86.0(3), 85.4(3); Cl2-Pd2-N12 94.6(2), 94.3(2); Cl2-Pd2-N52 94.1(2), 94.0(2); C6-Pd2-Cl2 176.7(3), 179.1(2); N12-Pd2-N52 171.3(2), 171.6(3).



513

Fig. 5.15

The only previous structurally characterised example, 513 (fig. 5.15),[265] of a 1,4-bis-palladated aromatic ring has some structural features in common with 512. As well as the metal being palladium, fused-ring metallocycles are formed and the aromatic ring is benzene. However, the structures are distinctly different as the palladacycles in the earlier case are only five membered and planar, and no significant distortion from planarity of the benzene ring was observed. Coordinated to each of the palladiums was a S, C, S, N donor set with the nitrogen trans to the metallated carbon, rather than the N, C, N, Cl set of 512 (with the chlorine trans to the carbon). As such the comparisons that can be made between the two structures are limited to the palladium-carbon bond lengths and the Pd-Pd separation across the metallated ring.

The four palladium-carbon bond lengths of 512 range between 1.969(8)Å and 2.002(8)Å (average = 1.982(8)Å) which are of comparable length to that of 513 (2.02Å), and those of 506 (1.993(4)Å) and 507 (1.98(2)Å, 1.99(2)Å). The similar Pd-C distances in 512, 506 and 507 indicate that the presence of a second palladium attached to the para- carbon has little effect on the bond strength of each. The Pd-Pd separations for 513 are 6.730(1)Å and 6.734(1)Å compared to 6.785Å in 513.

The Pd1 molecule has the Pd1, N22, C3, N42, Cl1 coordination plane twisted 49.9(4)° with respect to the benzene ring plane, while the Pd2, N12, C6, N52, Cl2 plane is twisted 49.2(4)° from the benzene plane, but in the opposite direction. The result is an alternating pattern of the pyrazole rings above and below the plane of the benzene ring to give a saddle-shaped structure. The other independent palladacycle in the asymmetric unit also has the alternating pyrazole pattern, with the coordination planes twisted

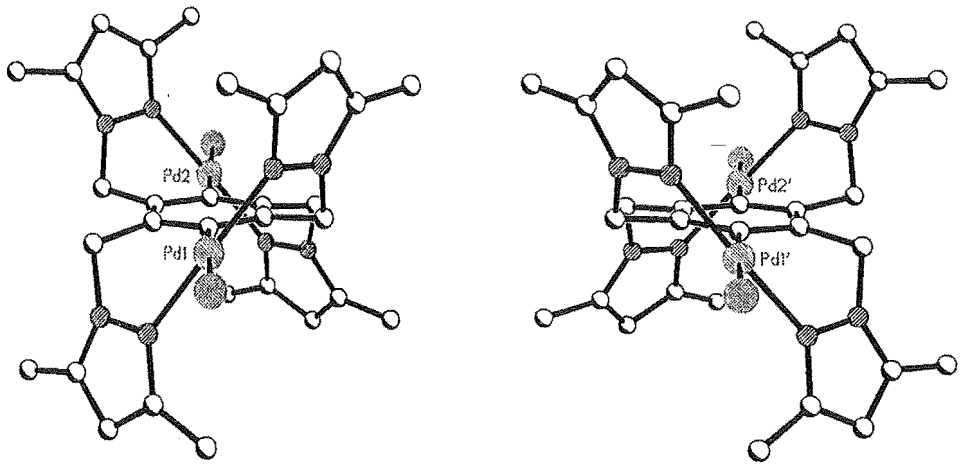


Fig. 5.16 Perspective view of the two independent molecules in the asymmetric unit of 512, highlighting the alternating pattern of the pyrazole groups.

from the benzene plane by 49.3(4)° and 49.1(4)° in opposite directions with respect to the benzene ring (fig. 5.16).

The larger angle between the coordination planes and the benzene ring, compared to 506 and 507, is in part facilitated by a distortion of the planarity usually observed in and around a benzene ring. The benzene rings are slightly distorted towards a twist-boat in that C1/C4 (C1'/C4') are 0.04(1)/0.03(1)Å (0.03(1)/0.02(1)Å) out of the mean plane of the benzene, and likewise C2/C5 (C2'/C5') are an average of 0.03(1)Å (0.03(1)Å) on the other side of the benzene plane. In each case the distortion pulls the carbon towards the attached pyrazolyl substituent. The methylene groups show an even greater distortion, ranging between 0.17(1) and 0.26(1)Å away from coplanarity with the benzene. The added strain of these distortions presumably relieves ring strain in the palladocyclic ring, and/or steric strain by allowing a greater distance between the 3-methyl of the pyrazole and the coordinated chlorine. As for 507, this steric strain is also relieved by an out of (pyrazole) plane distortion of the C16, 26, 36, etc. methyl groups (Average distance out of plane 0.07(1)Å).

As for 506 and 507, the palladium atoms each have approximately square planar coordination to the N, C, N, Cl donor set, with a slight tetrahedral distortion from this geometry. This can again be seen in the alternating pattern above and below the plane defined by Pd and the four coordinated atoms. As for 507, the trans-coordination angles for the four C-Pd-Cl sets (average angle 178.5(3)°) are less distorted from linearity than the N-Pd-N sets (average angle 171.1(3)°). Like the palladium-carbon distances discussed earlier, the Pd-N distances, ranging from 2.018(6) to 2.045(7)Å, are unremarkable. The palladium-chlorine distances are longer than those in 506 and 507, with distances between 2.458(2) and 2.473(2)Å. Few structurally characterised examples exist with larger bond lengths from a palladium atom to a non-bridging chlorine atom.[270-274] The palladium atoms lie between 0.043(7) and 0.436(7)Å out of the planes of the donor rings, an increase from the previous structures, but unlike the respective benzene rings there is little extra distortion from planarity in the pyrazole rings.

Boat conformations are again observed for the metallocycles with the distances of the palladium and methylene groups out of the plane of the boat of 512 being slightly larger than those of 507 (average Pd/CH_2 distance out of plane for 512 = 0.80(1)Å , for 507 = 0.77(2)Å) The Pd-H(methylene) distances observed for 512 (Pd-H_{Av} 2.91(3)Å) indicate a semi-agostic interaction as for the structures described above.

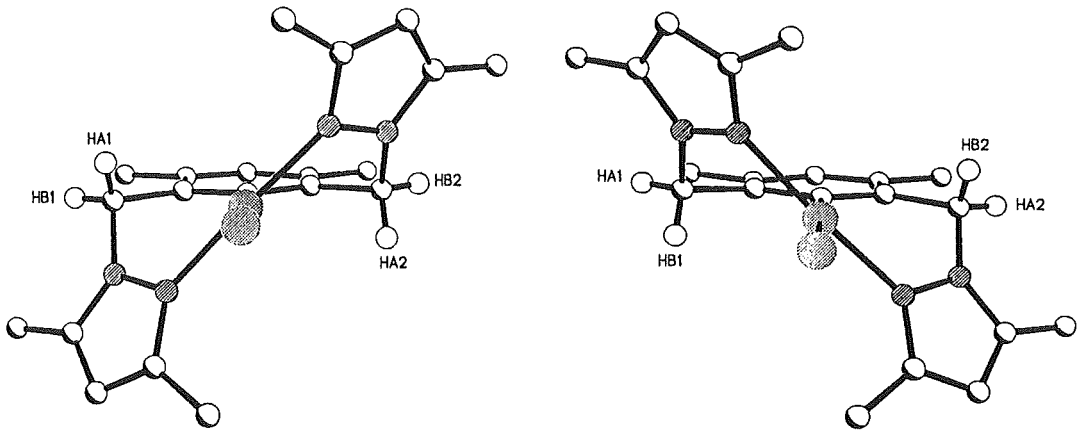


Fig. 5.17 Perspective view of the two independent molecules in the asymmetric unit of 507 highlighting the exchange of hydrogen environments upon inversion of the palladacycles. All hydrogens except those of the methylene groups are omitted for clarity.

A result of the boat conformations of the palladacycles in the above compounds is the non-equivalence of the methylene hydrogens. The two different environments of these hydrogens, H_A and H_B, are shown in the crystal structure of 507 (fig. 5.17). However, in solution the structure is not locked and as a result, a specific hydrogen does not remain in the same environment. By twisting the coordination plane in the opposite direction with respect to the benzene ring, inversion of the boat conformers occurs and H_A and H_B switch environments. Isolated examples of this dynamic behaviour of six-membered palladacycles exist in the literature;[247,250,252,257] however structure dependent studies of this phenomenon have only involved variation of the non-metallated ligands coordinated to the palladium. The compounds synthesised in this work allow for a structure dependent investigation by variation of the cyclopalladated ligand itself.

The inversion of six-membered palladacycles can be observed using ^{1}H N.M.R. spectroscopy. When this inversion is slow, two signals are observed for the diastereotopic methylene hydrogens. As the speed of this inversion progressively increases, these signals broaden, collapse to become one broad signal which then becomes sharper as the rate of inversion increases further. This rate can be controlled and studied using variable temperature N.M.R. techniques. The temperature at which the two broad signals become one, the coalescence temperature, can be used to find $\Delta G^{\#}$, the free energy of activation for the inversion of the palladacycles - the higher the

coalescence temperature, the greater the energy of activation. Using this methodology, the dynamic behaviour of the various palladacycles can be compared.

The first distinction between the palladacycles investigated is in the effect of the methyl substituents on the pyrazole rings in 507, 509 and 512. In the process of inversion of boat conformers the methyl groups on the 3-position of the pyrazole come into close proximity to the coordinated chlorine atom. For this reason, the inversion of these palladacycles is slowed to the extent that the coalescence temperature is above the maximum temperature attainable in these experiments. As such, the methylene hydrogen signals for these compounds are an AB quartet at both typical (23°C) and raised (up to 80°C) temperatures. For the four palladacycles with unsubstituted pyrazoles - 506, 508, 510 and 511 - broadening of signals and coalescence occurred either below or within the accessible temperature range, as the absence of the methyl groups means that conformational inversion is not sterically hindered to the same extent.

Within the four less substituted palladacycles listed above, variation in the shape of the N.M.R. signal(s) for the methylene hydrogens at 23°C was observed (fig 5.18). One broad signal was observed for 506, while two signals of varying separation and broadness were observed for the methylenes attached to coordinated pyrazoles of 508, 510 and 511. The methylene regions in the spectra of 508 and 511 are complicated by the presence of sharper

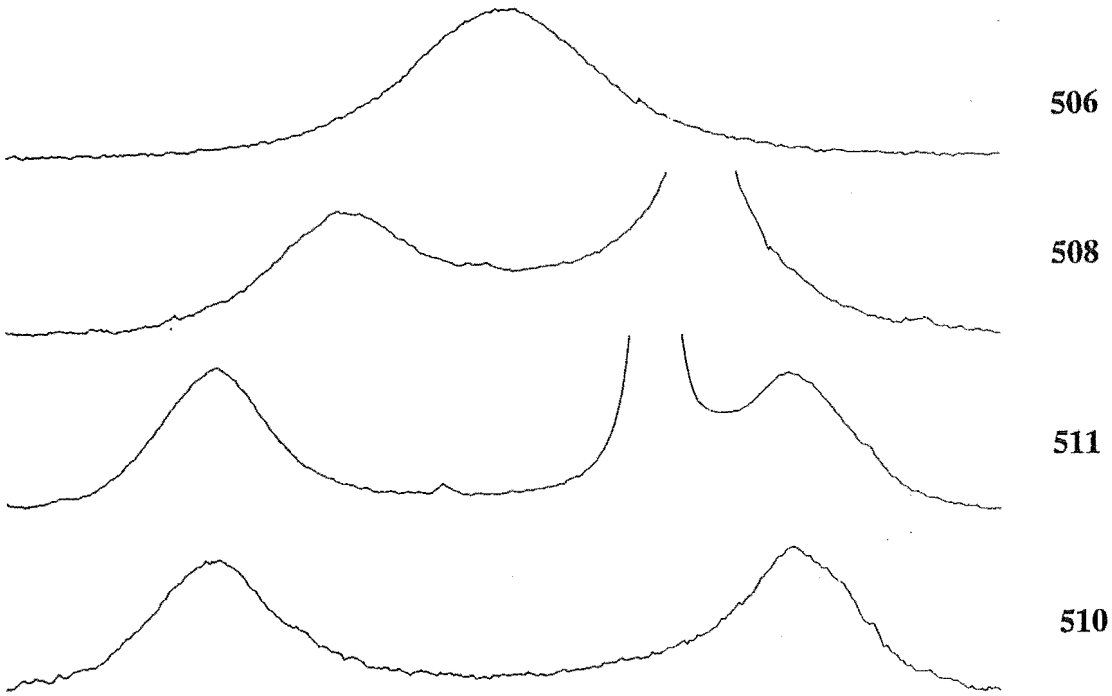


Fig. 5.18 The different ^{1}H N.M.R. methylene signal patterns of 506, 508, 511 and 510 at 23°C.

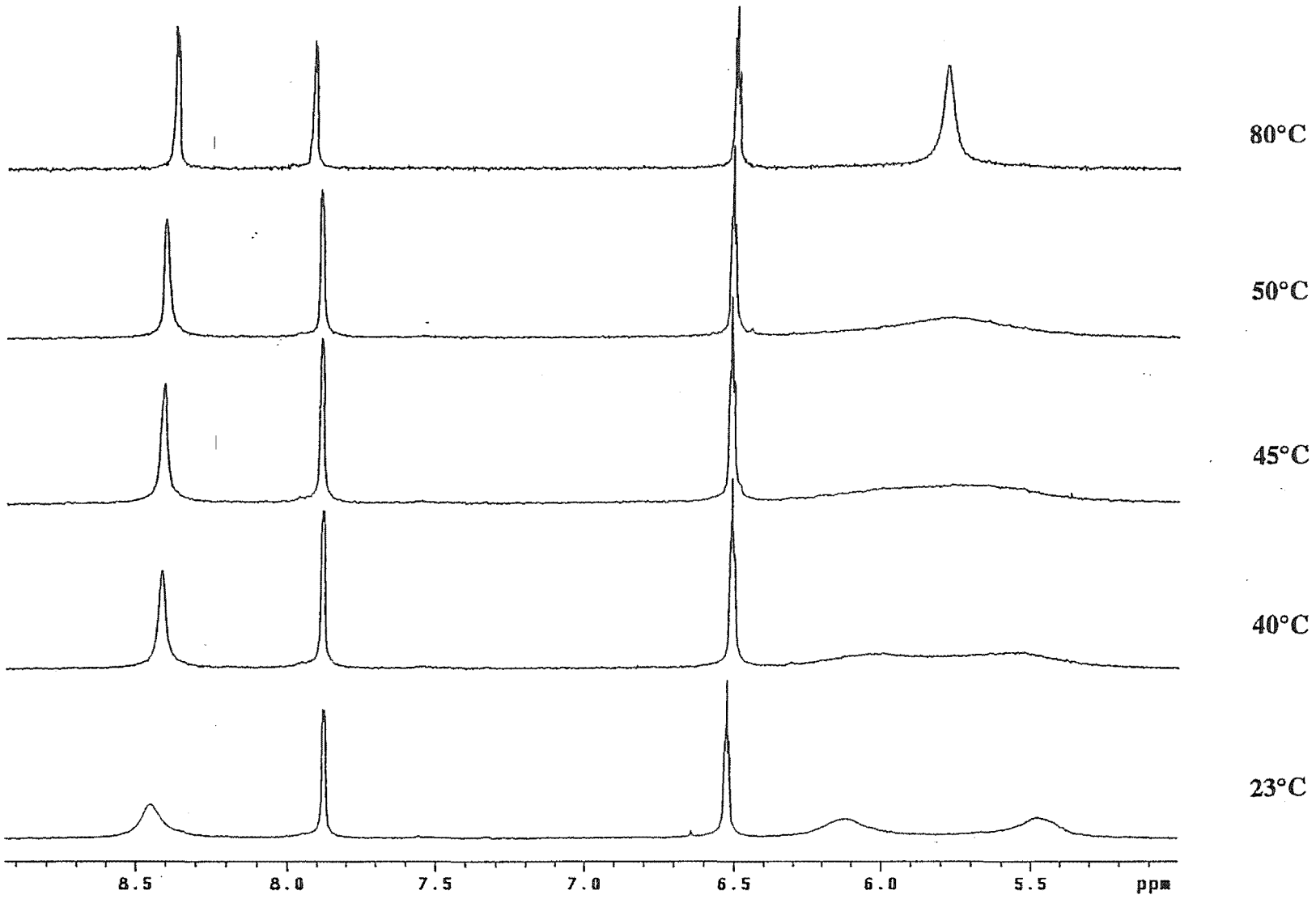


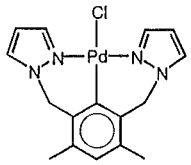
Fig. 5.19 Variable temperature ^{1}H N.M.R. spectra of 510.

signals due to the non-coordinated pyrazolylmethyl substituents. Variable temperature N.M.R. experiments were carried out for the three latter compounds to find the respective coalescence temperatures. An array of the variable temperature ^{1}H N.M.R. spectra of one of the compounds, 510, is shown (fig. 5.19).

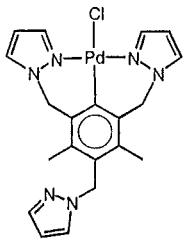
The experiments were carried out on d_6-DMSO solutions of the complexes due to the poor solubility of 508, 510 and 511 in other solvents. As a result, experiments wherein solutions were cooled were not possible. Hence the coalescence temperature of 506 is estimated on the basis of comparison between signal shape at 23°C of 506 with the same peak shape of other compounds. The temperature at which these signal shapes were similar to those of 506 was typically around 10°C above the coalescence temperature. Hence, a coalescence temperature of 13°C was estimated for 506.

To determine $\Delta G^{\#}$, both the coalescence temperature and the difference in frequency of the two hydrogen signals when inversion is slow, $\Delta\upsilon$, are required. For 510, at 23°C the two signals are sufficiently separated for $\Delta\upsilon$ to be approximately known. However, for 506, 508 and 511 the signals are not as separate, and as the solutions can not be cooled, $\Delta\upsilon$ for these compounds can not be found. Instead, the assumption is made that $\Delta\upsilon$ for these three compounds will be similar to that of 510. Using the coalescence temperatures found, and the same $\Delta\upsilon$ for the four complexes, $\Delta G^{\#}$ has been calculated for each. The overall results of these experiments are listed (table 5.1).

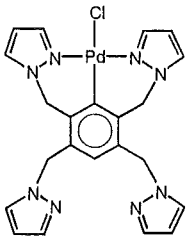
A $\Delta G^{\#}$ of 56.0 kJmol^{-1} has previously been reported for the inversion of a six-membered palladacycle,[257] a value consistent with those calculated here. The range of coalescence temperatures observed can be accounted for by considering the different structural features of the four cyclopalladated compounds. 506 has the lowest free energy of activation for inversion, while at the opposite end of this series 510, which differs from 506 in that it has the extra fused-ring palladacycles on the opposite side of the benzene ring, has the highest $\Delta G^{\#}$. If the two palladacyclic systems of 510 inverted independently of each other, then the activation energy of the compound could be expected to be the same as that of 506. The higher free energy of activation therefore indicates that inversion around the palladiums at the two sides of the benzene is correlated - as one fused palladacyclic pair inverts, the other must also invert. The alternating pattern of pyrazole around the benzene ring, as observed in the crystal structure of 512, is likely to be the lowest energy conformation, either for steric reasons or because the twist boat distortion of the benzene ring is the most energetically favourable geometry available. For this reason, the inversions are correlated as this



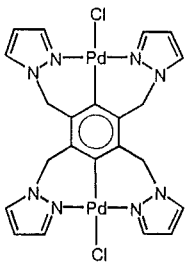
506



508



511



510

Compound	506	508	511	510
Coalescence Temp.,T_c (°C)	13*	27	37	45
$\Delta G^{\#}(=RT_c(22.96+\ln(T_c/\Delta\upsilon)$ (kJmol^{-1})	55.4	58.2	60.3	61.9

* estimated

$\Delta\upsilon$ = 204Hz (using chemical shifts of 6.15 and 5.47ppm on a 300MHz spectrometer)

Table 5.1

maintains the structure of minimum energy.

The other two compounds only contain one fused ring system, but still have a higher activation energy than 506. Surprisingly, the $\Delta G^{\#}$ of 508 is noticably higher than that of 506. The only difference between the two compounds is the presence of a pyrazolylmethyl substituent in the para- position to the palladated carbon. This site is too remote for a direct steric influence on the inversion of the palladacycles which would suggest more subtle influences are contributing. Instead, more indirect steric influences are proposed to explain this observation. In the process of palladacyclic inversion it is proposed that some lateral distortion of the methyl groups occurs (fig. 5.20). In 508 this is less feasible than in 506, as this methyl group distortion is towards the non-coordinated pyrazolylmethyl group. As a result, the methyl groups can not provide as much space for the inversion, thereby raising the activation energy of the process.

The $\Delta G^{\#}$ of 511 is only 1.6 kJmol^{-1} lower than 510 where a theory of correlation of inversion explained the observations. Instead for this compound, steric arguments explain the coalescence temperature observed. In 511 two pyrazolylmethyl substituents are not coordinated and are therefore free to rotate. This extra freedom leads to steric bulk in closer proximity to the palladacycle providing extra steric hindrance to the inversion. As a consequence the activation energy of the process is raised above that of 506 where these substituents are not present. The bis-cyclopalladated complex, 510, has

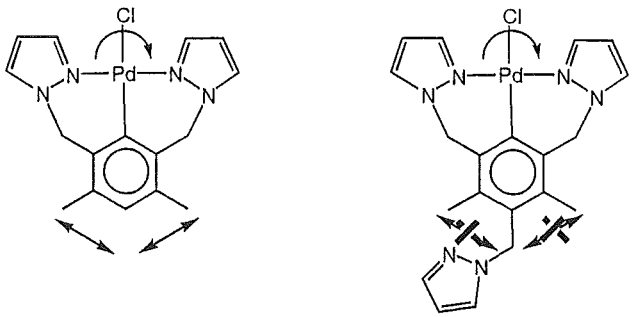


Fig. 5.20 Abilities for the methyl groups of 506 and 508 to laterally distort during palladacyclic inversion.

all the pyrazolylmethyl substituents tethered into palladacycles, thereby reducing the steric effect of the noncoordinated pyrazole groups present in 511. Despite this decrease in steric congestion in 510, it still has the highest activation energy/coalescence temperature. The previously proposed correlation of the ring inversions accounts for this observation.

5.4 Cycloruthenated Complexes.

The investigation of the cycloruthenation of these ligands was begun in a similar manner to that of cyclopalladation. The compounds of most interest are the doubly cycloruthenated complexes of 337 and 338, as the two ruthenium atoms metallating the same benzene ring should be strongly interacting. However, as for the cyclopalladation chemistry discussed above, before synthesis of these doubly cycloruthenated complexes was investigated it was important to ensure that ruthenation of the simplest 1,3-bis(pyrazolylmethyl)benzene systems, 502 and 503, gave the desired singly cycloruthenated product. Such mononuclear models would also be useful for comparison of reduction potentials with those of the desired dinuclear complexes.

The reaction scheme used for ruthenating 502 employs methodology previously used in the cycloruthenation of other heterocycle-substituted benzene rings.[6] The (terpyridine)tris(acetone)ruthenium intermediate is generated, then reacted with the ligand to give the cycloruthenated complex which can be isolated from the reaction mixture as the hexafluorophosphate salt (fig. 5.21). When using 502 as the ligand, filtration of the reaction mixture led to the isolation of a brown solid, while addition of ammonium hexafluorophosphate to the filtrate did not give the expected precipitate. Upon washing the isolated solid with water, addition of ammonium hexafluorophosphate to the filtrate gave a precipitate. ^{1}H N.M.R. spectroscopy showed

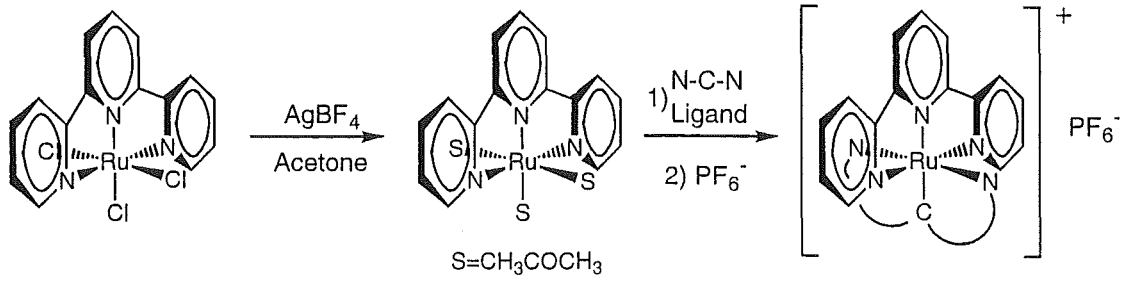
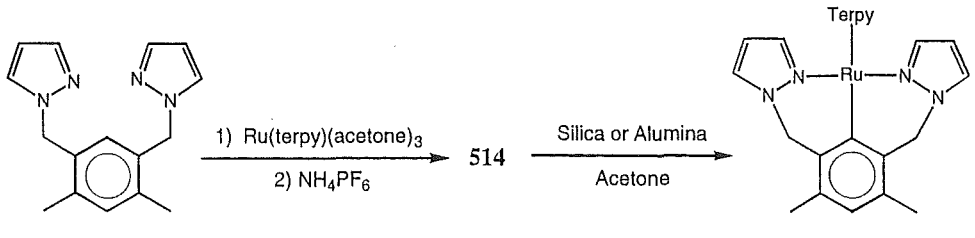


Fig. 5.21 General reaction scheme for the synthesis of cycloruthenated compounds.

this to be a mixture of two compounds: a compound resembling the ruthenium starting material; and, a compound, 514, with an unsymmetrical terpyridine ligand, the pyrazolyl ligand coordinated with the two pyrazole groups equivalent and both benzene hydrogens still present.

A variety of purification techniques were employed in an attempt to isolate the unsymmetrical product. The first of these was silica gel chromatography, wherein elution of the compound down the column gave an increasingly large and intense purple band. Such a colour is characteristic of Ru(II) in a CN_5 cyclometallated coordination environment.[275-278] The ^1H N.M.R. spectrum of the compound isolated, 515, matched this observation - the terpyridine ligand was now symmetrical and only one benzene hydrogen signal was observed. As such, the spectra of 514 and 515 are significantly different (fig. 5.22). Alumina chromatography gave the same result - development of the purple band and subsequent changes in the ^1H N.M.R. spectrum. Hence, the cycloruthenation of 502 proceeds through an intermediate, 514, the ortho-metallation of which, to give 515, is catalysed by silica or alumina (fig. 5.23). It was important, therefore, to ascertain the nature of the metallation intermediate, 514.

Ion exchange chromatography allowed for the isolation of 514 without the formation of the cycloruthenated product, 515. A variety of N.M.R. techniques were used to both assign the ^1H N.M.R. spectrum and to assist with the structure elucidation of 514. The spectra from COSY (fig. 5.24) and difference nOe experiments (fig. 5.25) are shown. The COSY spectrum, along with 1D TOCSY experiments (not shown)



502 **515**

Fig. 5.23

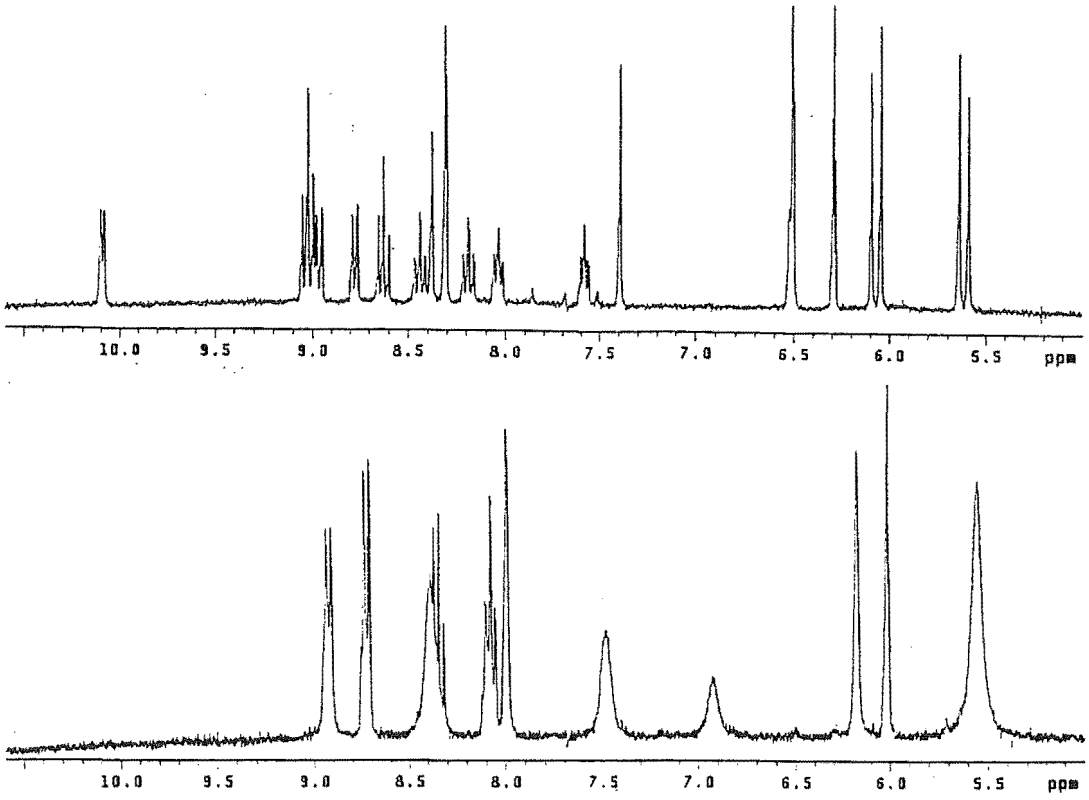


Fig. 5.22 Partial ^{1}H N.M.R. spectra of 514 and 515.

allowed for the assignment of the spectrum into the different ring systems of the complex. On the basis of these assignments, selected signals were irradiated in nOe experiments in order to examine the relative spacial arrangement of the terpyridine and 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene ligands, as well as to fully assign the ^{1}H N.M.R. spectrum of 514.

Irradiation of the methyl group signal (2.74ppm) gives the expected enhancement of one of the benzene protons (13.3%) which can then be assigned as H5 (spectrum A, fig. 5.25). Further enhancements are observed for one pair of geminally coupled methylene hydrogens (3.9%) and one of the pyrazole group hydrogens (1.3%). An enhancement with implications for terpyridine/pyrazolylbenzene orientation is also observed for a 6-position hydrogen on one of the terminal pyridines. Subsequent irradiations of the two methylene hydrogen signals confirmed the assignment of the benzene hydrogens and the methylene hydrogens themselves (spectra B and C, fig. 5.25). An enhancement of a pyrazole hydrogen (7.1%) when irradiating one pair of methylene hydrogens allowed for

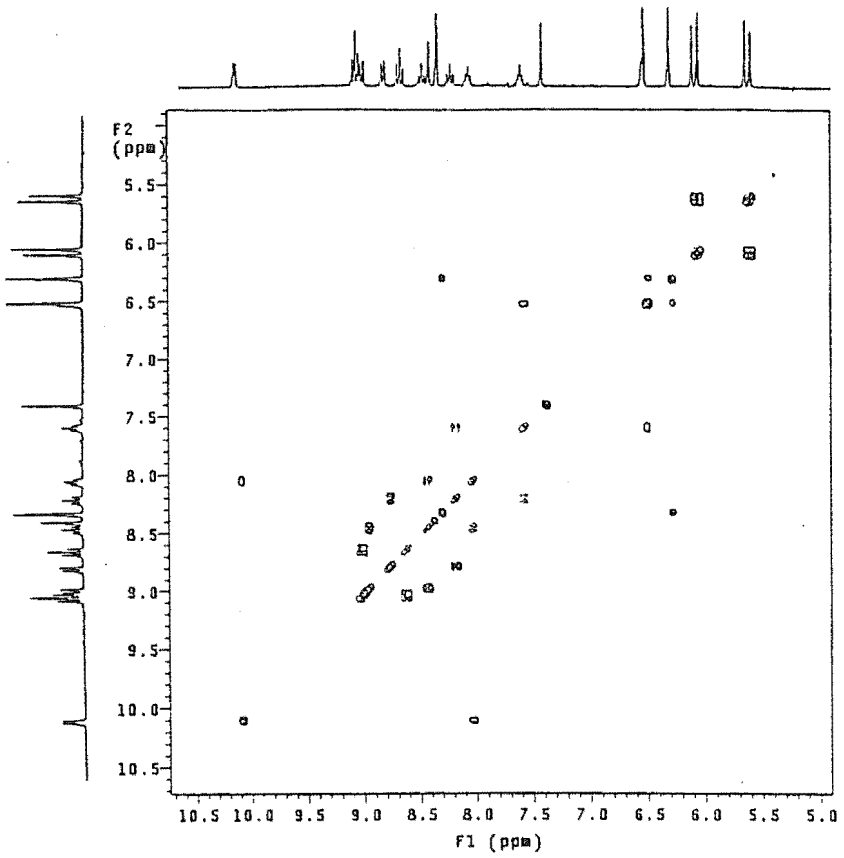


Fig. 5.24 COSY spectrum of 514

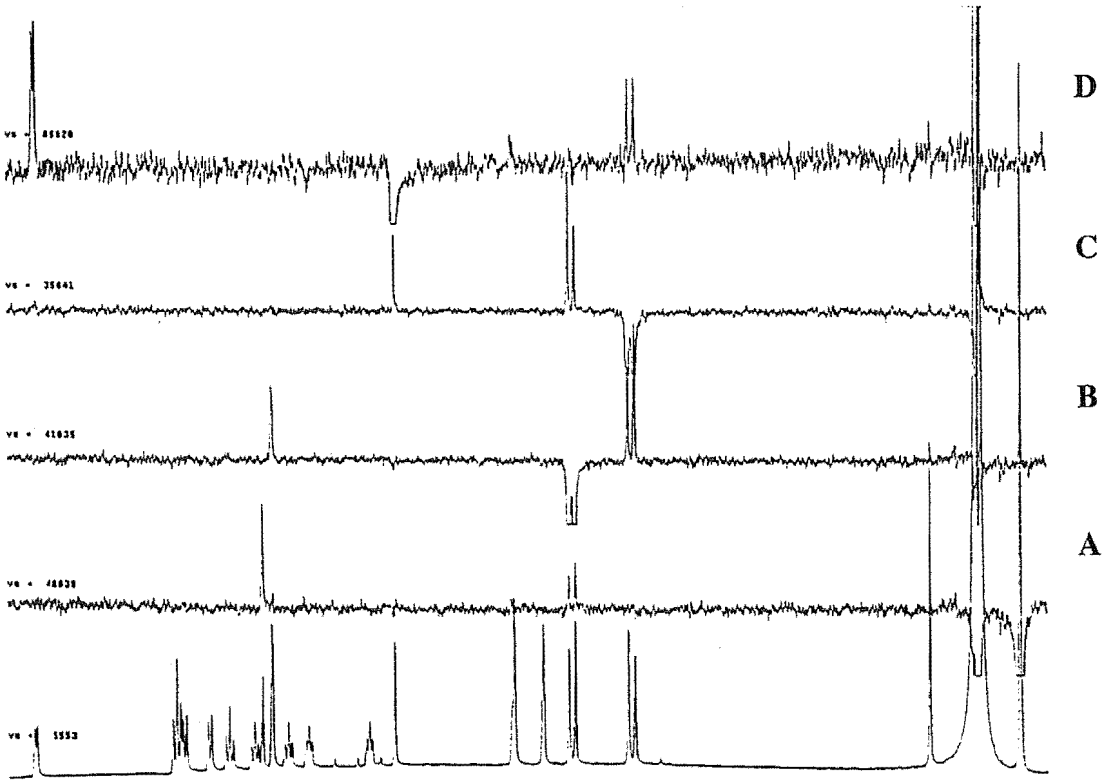


Fig. 5.25 Difference nOe spectra of 514

distinction and assignment of the signals for the 3- and 5-position hydrogens of the pyrazole. The absence of any such enhancement when irradiating the other methylene hydrogens gives further information regarding spacial arrangement of the different rings. One further nOe experiment provided significant information on the structure of 514. Irradiation of the benzene proton between the methylene groups enhanced signals for the following hydrogens (spectrum D, fig. 5.25): the signal of one pair of methylene hydrogens (4.3%); the 6-position pyridine signal previously enhanced by irradiating the methyl group signals (3.1%); and the 6-position signal of the other terminal pyridine ring (18.9%).

Given the results of these experiments a structure defining the terpyridine/pyrazolylbenzene orientation can be proposed for 514 (fig 5.26). H6" must be in close proximity to H2 given the large nOe enhancement observed. The other 6-position pyridine hydrogen, H6"", lies over the benzene ring as enhancement of the N.M.R. signal occurred on irradiation of both the methyl and H2 signals. The orientation of the pyrazole groups is also consistent with the N.M.R. observations, as irradiation of one of the methylene signals enhanced the methyl and H5' signals while no such enhancement was observed on irradiating the other methylene signal.

Some remarkable chemical shifts for 514 support this structure. The low field shift for H6" (10.09ppm) is due to the deshielding effect of the benzene ring. Conversely, H6"", which lies over the benzene ring, has an exceptionally high field shift (6.52ppm) as it is shielded by the benzene. The H3' signal (6.51ppm) also has a chemical shift higher than is typically observed, due to the shielding effect of the nearby central pyridine ring.

While the structure of the [(terpyridine)(1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene)ruthenium], or Ru(terpy)$(LH)^{2+}$, has been determined by N.M.R.

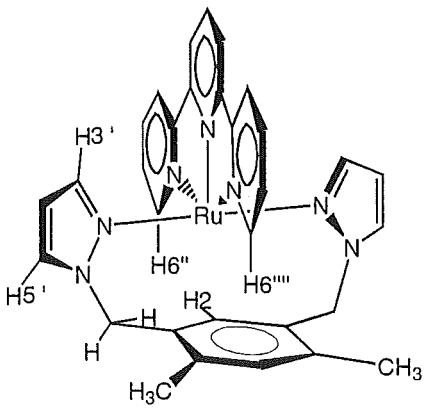


Fig. 5.26 Structure of 514

techniques, the ruthenium in this fragment is only five coordinate. On steric grounds, it is unlikely that any species other than the above ligands can occupy the sixth site of the octahedral ruthenium sphere. This is supported by HRFAB mass spectrometry where the highest mass found corresponds to $[Ru(terpy)(L)]^{2+}PF_6^-$. Given the propensity to cyclometallate in the presence of mild catalysts such as silica and alumina, 514 is clearly a very reactive species. Compounds with agostic 3-centre, 2 electron Ru-H-C interactions are known to be reactive intermediates en route to cycloruthenated compounds.[169,279] Indeed, the structure proposed for 514 appears to have the ruthenium and H2 arranged for such an interaction to exist. However, hydrogens involved in agostic interactions have remarkably high field chemical shifts; values up to -16ppm have been reported.[169,280] The shift of H2 is 7.39ppm, an unexceptional shift for an aromatic hydrogen, and not indicative of involvement in an agostic interaction. In X-ray crystal structures described in previous chapters, η^1 metal-carbon interactions have been observed when the metal is chelated by a 1,3-pyrazolylmethylbenzene moiety. Such an interaction is proposed for the sixth coordination site of the ruthenium in 514.

Attempts were made to confirm, and compare, the structures of 514 and 515 by X-ray crystal structure analysis. Despite the use of exhaustive recrystallisation techniques for both, only crystals of the cyclometallated compound, 515, were obtained that were suitable for single crystal X-ray structure determination.

Crystal Structure of 515.

The complex crystallises in the orthorhombic space group Pbca, the asymmetric unit of which contains one cycloruthenated molecule and a hexafluorophosphate counter-anion. The structure of the cycloruthenated monocation is shown in figure 5.27.

The coordination geometry around the ruthenium is approximately octahedral. Deviations from this geometry are due to the coordination of the terpyridine (N1'-Ru1-N3' 156.9(2)°), a typical feature of terpyridine coordination,[281-283] and tetrahedral distortion of the Ru1, N12, C2, N32, N2' coordination plane analogous to the distortions of the cyclopalladated complexes. The Ru-N(pyrazole) bond distances are within the range of distances expected, as are the Ru-N bond distances to the two terminal pyridine groups. The bond distance to a central pyridine ring in terpyridine metal complexes is generally around 0.1Å less than those to the terminal pyridines.[281-283] In the structure of 515 this distance (2.000(4)Å) is only around 0.07Å shorter due to the trans- effect of the coordinated carbon. The observed trans effect is small in this case as the central pyridine ring is harnessed by the coordination of the terminal pyridine rings of the ligand.

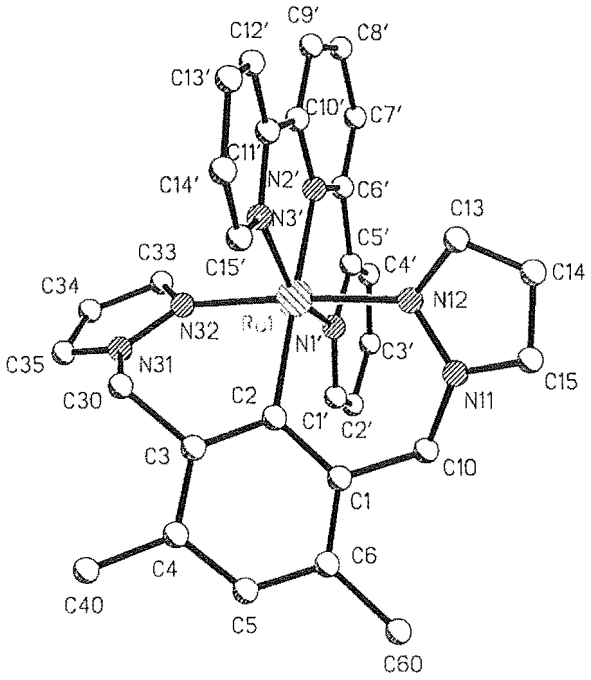


Fig. 5.27 Perspective view and atom labelling of 515. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-C2 2.073(4); Ru1-N12 2.073(4); Ru1-N32 2.079(4); Ru1-N1' 2.062(4); Ru1-N2' 2.000(4); Ru1-N3 2.081(4); C2-Ru1-N12 87.6(2); C2-Ru1-N32 87.8(2); C2-Ru1-N1' 100.1(2); C2-Ru1-N3' 103.0(2); N12-Ru1-N1' 96.0(2); N12-Ru1-N2' 92.5(1); N12-Ru1-N3' 84.9(1); N32-Ru1-N1' 96.0(2); N32-Ru1-N2' 92.1(1); N32-Ru1-N3' 96.3(1); N1'-Ru1-N2' 78.3(2); N3'-Ru1-N2' 78.6(2); C2-Ru1-N2' 178.4(2); N12-Ru1-N32 175.4(1); N1'-Ru1-N3' 156.9(2).

The ruthenium atom is 0.014(4) to 0.285(4)Å out of the planes of the six donor rings, with the largest of these distances being out of the planes of the pyrazole rings (0.285(4) and 0.226(4)Å). As for the cyclopalladated complex of the same ligand, there is minimal distortion of the planarity of the benzene and pyrazole rings themselves (maximum displacement from a ring mean plane 0.011(7)Å for C3). The mean plane of the terpyridine ligand is inclined at an angle of 65.5(4)° to the plane of the benzene ring. Within the terpyridine ligand the three pyridine rings are not coplanar with the two terminal rings being 7.8(4) and 8.9(4)° out of the plane of the central ring. This occurs to relieve the steric compression between the terminal pyridines and the methylene hydrogens (fig. 5.28).

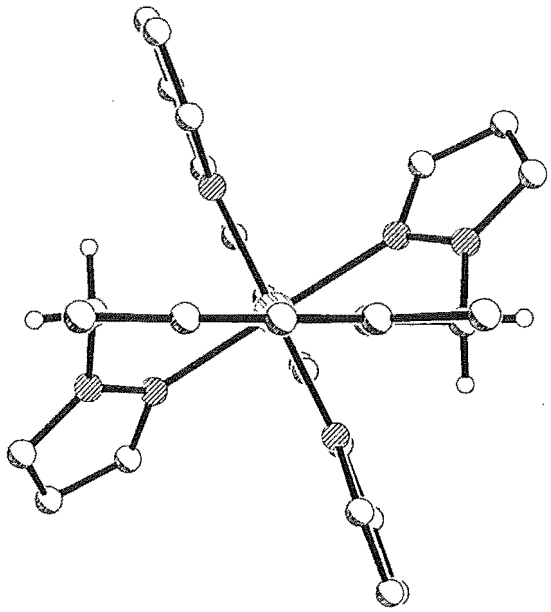
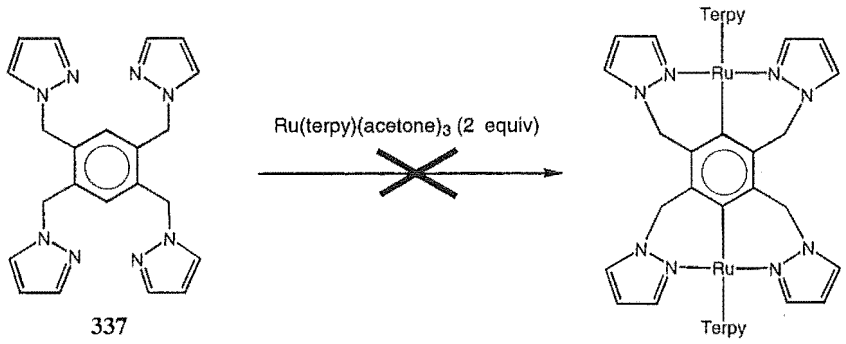


Fig. 5.28 Perspective view of 515 showing the distortion of the terminal pyridine rings away from the methylene hydrogens. All hydrogens except those of the methylene are omitted for clarity.

Once again boat conformations are observed for the fused metallocycles (0.605(7)-0.679(4)Å distortion of Ru/CH_2 out of the plane of the boat). The smaller average displacement from the plane of the boat, relative to the palladacyclic structures, is due to the absence of possible agostic interactions available to six coordinate ruthenium.

Although achieved by unexpected means, 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene does undergo cycloruthenation. Leading on from this, attempts were then made to synthesise 516 - the doubly cycloruthenated complex of 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene, 337 (fig. 5.29). Despite numerous attempts using a variety of modifications of the above reaction conditions - variation of solvent, concentration, reaction times and work-up procedures - only mixtures of complexes, none of which resembled the desired product, were obtained. It has been shown in previous chapters that a variety of modes of coordination are possible for 1,2-, 1,3- and 1,4-pyrazolylmethyl substituted ligands. All of these substituent relationships are present in 337, so consequently a wide range of complexes could form on reaction with ruthenium. Only in one of these cases, where there is first trans coordination of the 1,5 substituents to a ruthenium and trans coordination of the 2,4 substituents to a second ruthenium, will double cycloruthenation of 337 be possible. That this is only one of

many modes of coordination, and that formation of some of the others may be favoured, most likely leads to a small yield of metallated compound (or intermediate as for 514/515). As a result, even if the targeted product is present, it was not detected amongst the range of other compounds formed.



337 516

Fig. 5.29

Chapter 6

Conclusion

Conclusion

This thesis has described the syntheses and complexes of a series of nitrogen-containing poly-heterocyclic ligands. By building these ligands from a central benzene ring, a range of ligands was synthesised, not only by variation of the heterocycle and the linking atoms used, but also by appending different numbers of heterocycles to the benzene core. When two such groups are attached to the benzene, structural variation was also achieved using 1,2-, 1,3- and 1,4- substituent patterns on the benzene ring.

Pyridine groups were linked to the central benzene through a range of linking atoms. For the silver complexes of these ligands, the linking atom(s) used, in part, determine the mode of coordination in the complex. When solely an oxygen atom is used to link the benzene and pyridine rings, weak coordination of this oxygen to the proximate silver atom leads to a ligand conformation ideally disposed for [2+2] dimetallomacrocycle formation. Contributing to this [2+2] formation is an attractive π–π interaction between the benzene rings of the two ligands; a displaced arrangement of the two rings is observed where an atom of one ring lies over the centroid of the other.

Extension of the linking group to two atoms gives the ligand greater flexibility, resulting, in the majority of instances, in metallopolymer formation. Attractive π–π interactions contribute to the packing of these polymers. As for the [2+2] macrocycles, a displaced arrangement of the stacked aromatic rings is typically observed, confirming this orientation as the most favourable in such interactions.

Only methylene groups were used to link pyrazole groups to the benzene ring. In this case, ligands were varied by incorporating a range of substituted pyrazoles, use of different numbers of these pyrazole groups in different substituent patterns on the benzene, and also by varying the non-heterocyclic substituents on the benzene ring.

The incorporation of (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazole, a chiral pyrazole, into bis-heterocyclic ligands gave a ligand, 315, capable of chelation to a metal - an important property in its potential use in asymmetric catalysis - as well as a ligand, 313, that forms metallopolymeric and [2+2] dimetallomacrocyclic complexes. To date, host-guest chemistry is limited to hosts of high symmetry; the synthesis of chiral macrocyclic structures presents one means of reducing this symmetry and allowing for greater selectivity in the recognition of guest molecules.

One such high symmetry host molecule, 412, has been characterised in the present work by using a tris-pyrazolyl ligand, 409, in which the pyrazole groups are pre-

organised into a particular conformation. The cage complex formed with palladium chloride was shown, crystallographically, to enclose a cavity of *ca.* 4.7Å radius, in which was contained a dimethylsulfoxide guest molecule. The incorporation of (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazole in the place of the three pyrazole groups provides the prospect of a chiral host molecule upon complexation with palladium chloride.

Arising out of the incorporation of benzene into the ligands described in this work are different types of metal-benzene interactions that have been observed. For each of the metals used in this work - palladium, silver, copper and ruthenium - complexes have been structurally characterised in which metal-benzene interactions are present. Two silver complexes, 402 and 413, contain Ag-benzene interactions constrained to be η^1 by chelation of two pyrazole groups to the silver. In a copper complex, 417, the position of the copper atom is controlled by intramolecular hydrogen bonding as well as a η^1 copper-benzene interaction.

For the palladium complexes described, a palladium d_{z2} - benzene π orbital interaction contributes to the conformation of the complex, 210, where an agostic Pd-H interaction is not possible; a number of Pd-$C_{benzene}$ σ-bonded (cyclopalladated) complexes have also been characterised. While reactions of these cyclopalladated complexes were not investigated, the dynamic ^{1}H N.M.R. spectroscopy of these complexes, in which inversion of boat conformers occurs, was examined. Using variable temperature experiments, a relationship was found between structural features within the complexes and the energy barrier for inversion.

Perhaps the most interesting metal-benzene interactions observed occurred with ruthenium. In chapter 5, an intermediate product, 514, to a Ru-$C_{benzene}$ σ-bonded complex, 515, was isolated. The former is a highly reactive species that cyclometallates to give 515 under mild conditions. The intermediate, 514, was found, through ^{1}H N.M.R. spectroscopy, to contain a η^1 Ru-benzene interaction. A η^6 Ru-benzene complex, 404, has also been structurally characterised in which three coordination sites of the ruthenium are occupied by the benzene while the remaining three are occupied by pyrazole groups linked to the coordinated benzene. Tripodal coordination and η^6 Ru-arene chemistry are two major areas of chemistry that have received much attention. While the reaction chemistry of 404 was not investigated, it, and related structures, will none the less be examined by other workers.

The incorporation of benzene as a central building block for ligand design is not only versatile in the range of ligands that are possible, but also leads to π–π and metal-arene interactions. By gaining further appreciation of these features, ligands can be designed to give complexes with interesting reaction chemistry, and supramolecular species in which π–π and metal-arene interactions can be used to control the assembly of the complexes.

Experimental

Experimental

General Experimental

^{1}H N.M.R. spectra were recorded on a Varian 300 Unity spectrometer with a 3mm probe and operating at 300MHz. ^{13}C N.M.R. spectra were recorded on a Varian 300 Unity spectrometer or a Varian XL-300 spectrometer with a 3mm or 5mm probe operating at 75MHz. Spectra recorded in $CDCl_3$ were referenced relative to internal Me_4Si and those recorded in $(CD_3)_2SO$, $(CD_3)_2CO$, CD_2Cl_2 and CD_3CN were referenced against the solvent signals. When required, nOe, 1D TOCSY and COSY experiments were performed using standard pulse sequences and parameters available with the Unity 300 system.

UV/VIS absorption spectra were recorded using a Perkin Elmer Lambda 2 spectrophotometer.

Cyclic voltammetric measurements for 404 were made using a Par Model 173 potentiostat coupled to a home-built wave-form generator. The measurements were made for an acetonitrile solution of 1mmol 404 and 0.1M tetrabutylammonium hexafluorophosphate, using a scan rate of $100mVs^{-1}$ and a glassy carbon working electrode. Ferrocene was used as an internal standard.

Melting points were determined using an Electrothermal melting point apparatus and are uncorrected.

Mass spectra were recorded using a Kratos MS80RFA spectrometer with a Mac 3 data system. Electron Impact spectra were obtained at 70eV with a source temperature of 150°C. Fast Atom Bombardment (FAB) spectra were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN1FW FAB gun operated at 8KV and 2mA.

Elemental analyses were performed by the Chemistry Department, University of Otago, Dunedin.

Column chromatography was performed with silica gel (grade 923 100-200 mesh) or sephadex-SP C-25 ion exchange resin (40-120μ). Solvents were purified according to literature procedures.

Unless otherwise stated reagents were obtained from commercial sources and used as supplied. 1,2-Bis(bromomethyl)benzene,[163] 1,3-bis(bromomethyl)benzene,[163] 1,4-bis(bromomethyl)benzene,[163] 1,2,4,5-tetrakis(bromomethyl)benzene,[164] hexakis-(bromomethyl)-benzene,[284] (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole,[152] 3-(2'-pyridyl)pyrazole,[159] 1,4-bis(pyrazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene,[166] 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene,[166] 1,4-

benzenedimethanol,[285] 1-(2-pyridoxy)-4-methylbenzene,[78] dichlorotetrakis(dimethyl-sulphoxide)ruthenium(II)[286] and trichloro-(terpyridine)ruthenium(III)[287] were prepared according to literature procedures.

Preparation of Ligand Precursors

1,3,5-Tris(bromomethyl)-2,4-dimethylbenzene, 407.

A mixture of 1,3-dimethylbenzene (2.65g, 25mmol), paraformaldehyde (2.50g, 82.5mmol) and hydrobromic acid (40% solution in acetic acid, 17.5ml) was refluxed in acetic acid (12.5ml) for 72 hours. The resulting solution was poured into water and the solid filtered and washed with hot petroleum ether (2x50ml). Recrystallisation from petroleum ether/ethyl acetate (2:1) gave 407 (5.55g, 58%), m.p. 151-152°C (Found: C, 34.60; H, 3.25; Br, 62.19. $C_{11}H_{13}Br_3$ requires C, 34.32; H, 3.40; Br, 62.28). ^{1}H N.M.R. ($CDCl_3$) δ: 2.43, 6H, s, CH_3; 4.48, 4H, s, 1,5- CH_2; 4.57, 2H, s, 3- CH_2; 7.25, 1H, s, H6. ^{13}C N.M.R. ($CDCl_3$) δ: 14.87, CH_3; 29.00, 3- CH_2; 32.25, 1,5- CH_2; 132.10, C6; 134.38, C2,4; 136.40, C3; 137.85, C1,5.

1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene, 411.

A mixture of 1,3,5-triethylbenzene (2.03g, 12.5mmol), paraformaldehyde (1.25g, 41.3mmol) and hydrobromic acid (40% solution in acetic acid, 10ml) was refluxed in acetic acid (8ml) for 6 days, with additional hydrobromic acid (1ml) added every second day. Over this time a precipitate formed in the reaction mixture which was filtered while still hot. Recrystallisation of this solid from petroleum ether yielded 411 (2.52g, 46%), m.p. 173-174°C (Found: C, 40.47; H, 4.50; Br, 54.57. $C_{15}H_{21}Br_3$ requires C, 40.85; H, 4.80; Br, 54.35). ^{1}H N.M.R. ($CDCl_3$) δ: 1.34, 9H, t, CH_3; 2.93, 6H, m, 2,4,6- CH_2; 4.58, 6H, s, 1,3,5- CH_2. ^{13}C N.M.R. ($CDCl_3$) δ: 15.58, CH_3; 22.69, 2,4,6- CH_2; 28.54, 1,3,5- CH_2; 132.59, C2,4,6; 144.94, C1,3,5.

2,4,6-Trimethyl-1-(2-pyridoxy)benzene, 423.

A mixture of 2,4,6-trimethylphenol (11.43g, 84mmol), 2-bromopyridine (6.63g, 42mmol) and potassium carbonate (5.79g, 42mmol) was heated, with stirring, at 220-230°C for 8 hours. The resulting mixture was extracted repeatedly with diethyl ether, the extracts combined and concentrated to around 20ml. This was then washed with aqueous sodium hydroxide (405, 6x30ml), and then with water (2x30ml). Removal of solvent under reduced pressure and recrystallisation from petroleum ether yielded 423

(5.54g, 62%), m.p. 70-71°C (Found: C, 78.66; H, 7.10; N, 6.60. $C_{14}H_{15}NO$ requires C, 78.84; H, 7.09; N, 6.57).^{1}H N.M.R. ($CDCl_3$) δ: 2.08, 6H, s, 2,6-CH_3; 2.29, 3H, s, 4-CH_3; 6.81, 1H, d, H3'; 6.91, 1H, t, H5'; 6.91, 2H, s, H3,5; 7.64, 1H, t, H4'; 8.15, 1H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 16.36, 2,6-CH_3; 20.77, 4-CH_3; 109.55, C3'; 117.41, C5'; 129.32, C3,5; 130.56, C2,6; 134.54, C4; 139.22, C4'; 147.83, C6'; 147.97, C1; 163.27, C2'.

3,5-Bis(bromomethyl)-2,4,6-trimethyl-1-(2-pyridoxy)benzene, 424.

A mixture of 423 (2.27g, 11mmol), paraformaldehyde (1.3g, 44mmol), and hydrobromic acid (40% solution in acetic acid, 4.5ml) was refluxed in acetic acid (5ml) for 14 days, with additional hydrobromic acid solution (1ml) added every second day. The resulting solution was poured into water and the solid filtered and recrystallised from petroleum ether to give 424 (1.23g, 29%), m.p. 160-161°C (Found: C, 48.57; H, 4.28; N, 3.44. $C_{16}H_{17}Br_2NO$ requires C, 48.15; H, 4.29; N, 3.51). ^{1}H N.M.R. ($CDCl_3$) δ: 2.18, 6H, s, 2,6-CH_3; 2.47, 3H, s, 4-CH_3; 4.59, 4H, s, CH_2; 6.90, 1H, d, H3'; 6.95, 1H, t, H5'; 7.69, 1H, t, H4'; 8.11, 1H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 12.79, 2,6-CH_3; 14.92, 4-CH_3; 29.71, CH_2; 109.96, C3'; 117.84, C5'; 131.73, C2,6; 133.52, C3,5; 134.26, C4; 139.56, C4'; 147.75, C6'; 148.53, C1; 162.95, C2'.

1,3-Bis(bromomethyl)-4,6-dimethylbenzene, 500.

A mixture of 1,3-dimethylbenzene (3.19g, 30.0mmol), paraformaldehyde (1.85g, 60.0mmol) and hydrobromic acid (40% solution in acetic acid, 12ml) was heated in acetic acid (15ml) at 85°C for 24 hours. The resulting solution was poured into water (40ml) and the solid filtered and recrystallised from petroleum ether (3x50ml) to give 500 (2.72g, 31%), m.p. 109°C (lit. 111°C). ^{1}H N.M.R. ($CDCl_3$) δ: 2.37, 6H, s, CH_3; 4.48, 4H, s, CH_2; 7.02, 1H, s, H5; 7.25, 1H, s, H2. ^{13}C N.M.R. ($CDCl_3$) δ: 18.39, CH_3; 31.78, CH_2; 131.43, C5; 133.35, C2; 133.74, C4,6; 138.04, C1,3.

Preparation of Ligands.

General Procedure for Phase Transfer Catalysed (P.T.C.) Alkylations of Pyrazoles.

A mixture of the poly(bromomethyl)benzene, the pyrazole (1.1 equiv. per bromine), benzene (approx. 10ml per mmol of bromomethyl compound), 40% aqueous sodium hydroxide (approx. 2ml per mmol of bromomethyl compound) and 40% aqueous tetrabutylammonium hydroxide (1 drop per mmol of bromomethyl compound) was refluxed for 18-24 hours. The organic layer was then separated, dried (Na_2SO_4), and concentrated to give the crude product which was then purified by recrystallisation or column chromatography.

Preparation of the bis(2-pyridoxy)benzenes.

A mixture of the dihydroxybenzene (1 equiv.), 2-bromopyridine (2 equiv.) and potassium carbonate (2 equiv.) was heated, with stirring, at 210-220°C for 5 hours. The resulting tar was extracted several times with diethyl ether, the extracts combined and washed with aqueous sodium hydroxide (40%) then water. The solvent was then removed to give the crude product which was purified by recrystallisation or distillation. In this manner the following three compounds were prepared.

1,4-Bis(2-pyridoxy)benzene, 200.

Reaction of 1,4-dihydroxybenzene (0.57g, 5.2mmol), 2-bromopyridine (1.66, 10.5mmol) and potassium carbonate (1.45g, 10.5mmol) gave crude 200 (0.44g, 33%) as a solid, which was recrystallised from ethyl acetate, m.p. 158°C (Found: C, 71.47; H, 4.63; N, 10.29. $C_{16}H_{12}N_2O_2.¼H_2O$ requires C, 71.50; H, 4.69; N, 10.42). ^{1}H N.M.R. ($CDCl_3$) δ: 6.94, 2H, d, H3'; 7.00, 2H, t, H5'; 7.17, 4H, s, H2,3,5,6; 7.69, 2H, t, H4'; 8.21, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 111.38, C3'; 118.44, C5'; 122.32, C2,3,5,6; 139.41, C4'; 147.63, C6'; 150.58, C1,4; 163.73, C2'.

1,3-Bis(2-pyridoxy)benzene, 205.

Reaction of 1,3-dihydroxybenzene (1.15g, 10.4mmol), 2-bromopyridine (3.31g, 21.0mmol) and potassium carbonate (2.90g, 21.0mmol) gave crude 205 as a brown oil. Crystallisation of this oil from petroleum ether/ethyl acetate (2:1) yielded 205 (1.06g, 39%) as colourless crystals, m.p. 50-51°C (Found: C, 72.90; H, 4.76; N, 10.56.

$C_{16}H_{12}N_2O_2$ requires C, 72.72; H, 4.58; N, 10.60). ^{1}H N.M.R. ($CDCl_3$) δ: 6.93, 2H, d, H3'; 6.96, 1H, s, H2; 6.99, 2H, dd, H4,6; 7.00, 2H, t, H5'; 7.40, 1H, t, H5; 7.68, 2H, t, H4'; 8.21, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 111.48, C3'; 113.88, C2; 116.81, C4,6; 118.56, C5'; 129.92, C4; 139.26, C4'; 147.53, C6'; 154.98, C1,3; 163.07, C2'.

1,2-Bis(2-pyridoxy)benzene, 206.

Reaction of 1,2-dihydroxybenzene (1.15g, 10.4mmol), 2-bromopyridine (3.31g, 21.0mmol) and potassium carbonate (2.90g, 21.0mmol) gave crude 206 as a white solid. Recrystallisation from petroleum ether/ethyl acetate (2:1) yielded 206 (0.87g, 32%) as colourless crystals, m.p. 97-98°C (Found: C, 72.55; H, 4.69; N, 10.70. $C_{16}H_{12}N_2O_2$ requires C, 72.72; H, 4.58; N, 10.60). ^{1}H N.M.R. ($CDCl_3$) δ: 6.70, 2H, d, H3'; 6.90, 2H, t, H5'; 7.28, 4H, s, H3-6; 7.56, 2H, t, H4'; 8.10, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 110.73, C3'; 118.17, C5'; 123.60, C3,6; 125.73, C4,5; 138.96, C4'; 145.66, C1,2; 147.31, C6'; 163.06, C2'.

Preparation of 1,4-bis(2-pyridoxy)naphthalene, 204.

A mixture of 1,4-dihydroxynaphthalene (1.10g, 6.9mmol), 2-bromopyridine (2.17g, 13.7mmol) and potassium carbonate (1.89g, 13.7mmol) was refluxed in DMF (10ml) for 22 hours. Removal of solvent and subsequent washing of the residue with water, then methanol gave 204 (0.60g, 28%), m.p. >130°C (dec.) (Found: C, 76.04; H, 4.18; N, 8.60. $C_{20}H_{14}N_2O_2$ requires C, 76.42; H, 4.49; N, 8.91). ^{1}H N.M.R. ($CDCl_3$) δ: 6.99, 2H, d, H3'; 7.01, 2H, t, H5'; 7.25, 2H, s, H2,3; 7.48, 2H, d, H6,7; 7.71, 2H, t, H4'; 8.01, 2H, d, H5,8; 8.19, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 110.88, C3'; 117.12, C2,3; 118.46, C5'; 122.32, C6,7; 126.63, C5,8; 128.56, C4a,8a; 139.57, C4'; 146.93, C1,4; 147.81, C6'; 164.28, C2'.

Preparation of 1,4-bis(2-pyridoxymethyl)benzene, 213.

A mixture of 1,4-benzenedimethanol (0.57g, 4.1mmol), 2-bromopyridine (1.31g, 8.3mmol) and potassium hydroxide (1.86g, 33.2mmol) was refluxed in toluene (20ml) for 42 hours. The solvent was then removed and the residue divided between chloroform (15ml) and aqueous (30ml) layers. The organic layer was then separated, dried (Na_2SO_4) and concentrated to give crude 213. The remaining 2-bromopyridine was removed under vacuum at room temperature for 30 minutes. Covering the remaining residue in ice-cold

methanol gave a white precipitate which was filtered to give 213 (0.41g, 34%), m.p. 67-68°C (Found: C, 72.03; H, 5.55; N, 9.17. $C_{18}H_{16}N_2O_2.½H_2O$ requires C, 71.75; H, 5.69; N, 9.30). ^{1}H N.M.R. ($CDCl_3$) δ: 5.38, 4H, s, CH_2; 6.80, 2H, d, H3'; 6.87, 2H, t, H5'; 7.47, 4H, s, H2,3,5,6; 7.57, 2H, t, H4'; 8.17, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 67.11, CH_2; 111.19, C3'; 116.79, C5'; 127.96, C2,3,5,6; 136.87, C1,4; 138.48, C4'; 146.70, C6'; 163.45, C2'.

Preparation of 1,4-bis(2-pyridylmethoxy)benzene, 214.

A mixture of 1,4-dihydroxybenzene (2.05g, 18.6mmol), 2-picolylchloride hydrochloride (6.11g, 37.2mmol) and 40% aqueous tetrabutylammonium hydroxide (4 drops) was refluxed in benzene (40ml) and 40% aqueous sodium hydroxide (8ml) for 24 hours. The organic layer was then separated, dried (Na_2SO_4) and concentrated to give crude 214. Recrystallisation from petroleum ether/ethyl acetate (10:1) yielded 214 (2.63g, 48%), m.p. 106°C (Found: C, 73.55; H, 5.51; N, 9.46. $C_{18}H_{16}N_2O_2$. requires C, 73.96; H, 5.52; N, 9.58). ^{1}H N.M.R. ($CDCl_3$) δ: 5.16, 4H, s, CH_2; 6.92, 4H, s, H2,3,5,6; 7.23, 2H, t, H5'; 7.53, 2H, d, H3'; 7.72, 2H, t, H4'; 8.60, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 71.14, CH_2; 115.69, C2,3,5,6; 121.24, C3'; 122.54, C5'; 136.78, C4'; 149.16, C6'; 152.81, C1,4; 157.43, C2'.

Preparation of the (2-Pyridylsulfanylmethyl)benzenes.

The poly(bromomethyl)benzene was added to 2-mercaptopyridine (1 equiv. per bromine) and triethylamine (1.25 equiv. per bromine) stirred in ice-cooled acetonitrile (10ml). The reaction mixture was then stirred at room temperature for 24 hours. The mixture was then filtered and the product isolated from the solid collected by filtration, and/or by removal of the solvent from the filtrate, as described below. In this manner the following four compounds were prepared.

1,4-Bis(2-pyridylsulfanylmethyl)benzene, 221.

Reaction of 1,4-bis(bromomethyl)benzene (0.59g, 2.24mmol) with 2-mercaptopyridine (0.50g, 4.48mmol) and triethylamine (0.57g, 5.6mmol) gave a

semicrystalline yellow residue upon removal of the solvent. This was dissolved in chloroform (15ml) and washed with water (2x30ml). This was then dried (Na_2SO_4), and concentrated to give crude 221 as a white solid. Recrystallisation from petroleum ether gave 221 (0.29g, 40%). The solid isolated by filtration was washed with water (3x10ml) and recrystallised from petroleum ether to give 221 (0.11g, 15%). The two were then combined (0.40g, 55%), m.p. 76°C (Found: C, 66.26; H, 4.90; N, 8.71. $C_{18}H_{16}N_2S_2$ requires C, 66.63; H, 4.97; N, 8.63). ^{1}H N.M.R. ($CDCl_3$) δ: 4.41, 4H, s, CH_2; 6.98, 2H, t, H5'; 7.15, 2H, d, H3'; 7.33, 4H, s, H2,3,5,6; 7.46, 2H, t, H4'; 8.45, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 33.92, CH_2; 119.44, C3'; 121.92, C5'; 128.96, C2,3,5,6; 135.82, C4'; 136.71, C1,4; 149.23, C6'; 158.59, C2'.

1,3-Bis(2-pyridylsulfanylmethyl)benzene, 222.

Reaction of 1,3-bis(bromomethyl)benzene (0.59g, 2.24mmol) with 2-mercaptopyridine (0.50g, 4.48mmol) and triethylamine (0.57g, 5.6mmol) gave a semicrystalline yellow residue upon removal of the solvent. This was dissolved in chloroform (15ml) and washed with water (2x30ml). This was then dried (Na_2SO_4), and concentrated to give 222 as a yellow oil (0.61g, 84%) (Found: $M^{+\cdot}$, 324.0755. $C_{18}H_{16}N_2S_2$ requires $M^{+\cdot}$ 324.0755). ^{1}H N.M.R. ($CDCl_3$) δ: 4.40, 4H, s, CH_2; 6.98, 2H, t, H5'; 7.14, 2H, d, H3'; 7.22, 1H, t, H5; 7.28, 2H, d, H4,6; 7.46, 2H, t, H4'; 8.44, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 34.06, CH_2; 119.36, C3'; 121.74, C5'; 127.46, C4,6; 128.36, C5; 129.29, C2; 135.77, C4'; 137.81, C1,3; 149.04, C6'; 158.36, C2'.

1,2-Bis(2-pyridylsulfanylmethyl)benzene, 223.

Reaction of 1,2-bis(bromomethyl)benzene (0.59g, 2.24mmol) with 2-mercaptopyridine (0.50g, 4.48mmol) and triethylamine (0.57g, 5.6mmol) gave a semicrystalline yellow residue upon removal of the solvent. This was dissolved in chloroform (15ml) and washed with water (2x30ml). This was then dried (Na_2SO_4), and concentrated to give crude 223 as a yellow solid. Recrystallisation from petroleum ether gave 223 (0.61g, 84%), m.p. 82°C (Found: C, 66.42; H, 5.27; N, 8.61. $C_{18}H_{16}N_2S_2$ requires C, 66.63; H, 4.97; N, 8.63). ^{1}H N.M.R. ($CDCl_3$) δ: 4.61, 4H, s, CH_2; 6.96, 2H, t, H5'; 7.15, 2H, d, H3'; 7.19, 2H, dd, H4,5; 7.43, 2H, dd, H3,6; 7.45, 2H, t, H4'; 8.42, 2H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 31.71, CH_2; 119.41, C3'; 121.93, C5'; 127.53, C3,6; 130.46, C4,5; 135.80, C4'; 136.18, C1,2; 149.24, C6'; 158.70, C2'.

1,2,4,5-Tetrakis(2-pyridylsulfanylmethyl)benzene, 233.

Reaction of 1,2,4,5-tetra(bromomethyl)benzene (0.50g, 1.11mmol) with 2-mercaptopyridine (0.50g, 4.44mmol) and triethylamine (0.57g, 5.6mmol) gave a precipitate of 233 in the reaction mixture. This solid was isolated by filtration and washed with water (3x10ml) to give crude 233. Recrystallisation from acetonitrile gave 233 (0.52g, 82%), m.p. 114°C (Found: C, 62.84; H, 4.79; N, 9.98. $C_{18}H_{16}N_2S_2$. requires C, 63.12; H, 4.59; N, 9.81). ^{1}H N.M.R. ($CDCl_3$) δ: 4.52, 8H, s, CH_2; 6.95, 4H, t, H5'; 7.12, 4H, d, H3'; 7.44, 4H, t, H4'; 7.48, 2H, s, H3,6; 8.38, 4H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 31.38, CH_2; 119.40, C3'; 121.95, C5'; 132.75, C3,6; 135.41, C1,2,4,5; 135.79, C4'; 149.23, C6'; 158.62, C2'.

Preparation of the Bis(pyrazol-1-ylmethyl)benzenes.

A mixture of the bis(bromomethyl)benzene and 2.2 equiv. of pyrazole was reacted under P.T.C. conditions. In this manner the following two compounds were prepared.

1,3-Bis(pyrazol-1-ylmethyl)benzene, 300.

Reaction of 1,3-bis(bromomethyl)benzene (1.63g, 6.2mmol) with pyrazole (0.92g, 13.6mmol) gave 300 as a pale yellow solid (1.29g, 88%), which was suitable for subsequent reactions without further purification, m.p. 42-43°C (Found: $M^{+\cdot}$, 238.1217. $C_{14}H_{14}N_4$ requires $M^{+\cdot}$, 238.1218). ^{1}H N.M.R. ($CDCl_3$) δ: 5.25, 4H, s, CH_2; 6.25, 2H, t, H4'; 7.02, 1H, s, H2; 7.08, 2H, d, H4,6; 7.27, 1H, t, H5; 7.36, 2H, d, H5'; 7.53, 2H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 55.36, CH_2; 105.82, C4'; 126.40, C2; 126.90, C4,6; 129.07, C5; 129.15, C5'; 137.16, C1,3; 139.43, C3'.

1,2-Bis(pyrazol-1-ylmethyl)benzene, 301.

Reaction of 1,2-bis(bromomethyl)benzene (1.21g, 4.6mmol) with pyrazole (0.69g, 10.1mmol) gave 301 as a yellow oil (0.94g, 86%), which was suitable for subsequent reactions without further purification (Found: $M^{+\cdot}$, 238.1218. $C_{14}H_{14}N_4$ requires $M^{+\cdot}$, 238.1218). ^{1}H N.M.R. ($CDCl_3$) δ: 5.31, 4H, s, CH_2; 6.25, 2H, t, H4'; 7.07, 2H, dd, H4,5; 7.27, 2H, d, H5'; 7.29, 2H, dd, H3,6; 7.54, 2H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 52.86, CH_2; 105.90, C4'; 128.58, C3,6; 129.26, C4,5; 129.29, C5'; 134.58, C1,2; 139.40, C3'.

Preparation of 1-(2-pyridoxy)-4-(pyrazol-1-ylmethyl)benzene, 309.

A mixture of 1-(2-pyridoxy)-4-methylbenzene (1.05g, 5.7mmol), N-bromosuccinimide (1.01g, 5.7mmol) and a catalytic amount of benzoyl peroxide (60mg, 0.25mmol) was refluxed in carbon tetrachloride (15ml), using a 250W light source to irradiate the mixture for 4 hours. Upon cooling to room temperature the mixture was filtered and the filtrate concentrated to give an orange oil (1.05g). Without purification, this crude product (1.05g), pyrazole (0.18g, 2.6mmol) and tetrabutylammonium hydroxide (3 drops) were refluxed in benzene (15ml) and 40% aqueous sodium hydroxide (3ml) for 20 hours. The organic layer was then separated, dried (Na_2SO_4), and concentrated to give crude 309 as an orange oil. Column chromatography (silica, 200:1 $CHCl_3/CH_3OH$) gave 309 as a pale yellow oil (0.39g, 27%), (Found: $M^{+\cdot}$, 251.10579. $C_{15}H_{13}N_3O$ requires $M^{+\cdot}$, 251.10586). ^{1}H N.M.R. ($CDCl_3$) δ: 5.33, 2H, s, CH_2; 6.29, 1H, t, H4"; 6.91, 1H, d, H3'; 6.99, 1H, t, H5'; 7.12, 2H, d, H2,6; 7.25, 2H, d, H3,5; 7.42, 1H, d, H5"; 7.56, 1H, d, H3"; 7.69, 1H, t, H4'; 8.18, 1H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 55.15, CH_2; 105.82, C4"; 111.50, C3'; 118.47, C5'; 121.25, C2,6; 128.87, C3,5; 129.09, C5"; 132.69, C4; 139.34, C3", C4'; 147.46, C6'; 153.72, C1; 163.28, C2'.

Preparation of the Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzenes.

A mixture of the bis(bromomethyl)benzene and 2.2 equiv. of (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole was reacted under P.T.C. conditions. In this manner the following three compounds were prepared.

1,4-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene, 313.

Reaction of 1,4-bis(bromomethyl)benzene (0.50g, 1.9mmol) with (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole (0.73g, 4.2mmol) gave approximately a 3:1 mixture of 313 and its structural isomers as an orange oil. Column chromatography (silica, $CHCl_3$) gave 313 as a pale yellow semi-crystalline solid (0.42g, 49%) (Found: $M^{+\cdot}$, 454.3096. $C_{30}H_{38}N_4$ requires $M^{+\cdot}$, 454.3097). ^{1}H N.M.R. ($CDCl_3$) δ: 0.67, 6H, s, s-8-CH_3'; 0.94, 6H, s, a-8-CH_3'; 1.13, 2H, m, exo-H5'; 1.29, 6H, s, 7-CH_3'; 1.30, 2H, m, exo-H6'; 1.83, 2H, m, endo-H5'; 2.05, 2H, m, endo-H6'; 2.73, 2H, d, H4'; 5.22, 4H, s, CH_2; 6.87, 2H, s, H3'; 7.06, 4H, s, H2,3,5,6. ^{13}C N.M.R. ($CDCl_3$) δ: 10.62,

7-CH_3'; 19.04, a-8-CH_3'; 20.40, s-8-CH_3'; 27.66, C5'; 33.62, C6'; 47.13, C4'; 50.12, C8'; 54.61, CH_2; 60.47, C7'; 121.59, C3'; 127.13, C3a'; 127.19, C2,3,5,6; 137.23, C1,4; 166.05, C7a'.

1,3-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene, 314.

Reaction of 1,3-bis(bromomethyl)benzene (0.50g, 1.9mmol) with (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole (0.73g, 4.2mmol) gave approximately a 3:1 mixture of 314 and its structural isomers as an orange oil. Column chromatography (silica, $CHCl_3$) gave 314 as a pale yellow oil (0.35g, 40%), (Found: $M^{+\cdot}$, 454.3095. $C_{30}H_{38}N_4$ requires $M^{+\cdot}$, 454.3097). ^{1}H N.M.R. ($CDCl_3$) δ: 0.68, 6H, s, s-8-CH_3'; 0.94, 6H, s, a-8-CH_3'; 1.14, 2H, m, exo-H5'; 1.29, 6H, s, 7-CH_3'; 1.30, 2H, m, exo-H6'; 1.83, 2H, m, endo-H5'; 2.05, 2H, m, endo-H6'; 2.73, 2H, d, H4'; 5.20, 4H, s, CH_2; 6.85, 2H, s, H3'; 6.87, 1H, s, H2; 6.99, 2H, d, H3,6; 7.23, 1H, t, H5. ^{13}C N.M.R. ($CDCl_3$) δ: 10.59, 7-CH_3'; 19.01, a-8-CH_3'; 20.40, s-8-CH_3'; 27.64, C5'; 33.62, C6'; 47.10, C4'; 50.06, C8'; 54.76, CH_2; 60.40, C7'; 121.54, C3'; 125.61, C2; 126.02, C4,6; 127.05, C3a'; 128.74, C5; 138.31, C1,3; 166.10, C7a'.

1,2-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene, 315.

Reaction of 1,2-bis(bromomethyl)benzene (0.50g, 1.9mmol) with (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole (0.73g, 4.2mmol) gave approximately a 3:1 mixture of 315 and its structural isomers as an orange oil. Column chromatography (silica, $CHCl_3$) gave 315 as a pale yellow solid (0.34g, 39%), m.p. 151-152°C (Found: C, 79.11; H, 8.39; N, 12.50. $C_{30}H_{38}N_4$ requires C, 79.25; H, 8.42; N, 12.32). ^{1}H N.M.R. ($CDCl_3$) δ: 0.69, 6H, s, s-8-CH_3'; 0.94, 6H, s, a-8-CH_3'; 1.13, 2H, m, exo-H5'; 1.30, 6H, s, 7-CH_3'; 1.31, 2H, m, exo-H6'; 1.83, 2H, m, endo-H5'; 2.05, 2H, m, endo-H6'; 2.71, 2H, d, H4'; 5.24, 4H, s, CH_2; 6.72, 2H, s, H3'; 6.92, 2H, dd, H4,5; 7.23, 2H, dd, H3,6. ^{13}C N.M.R. ($CDCl_3$) δ: 10.72, 7-CH_3'; 19.14, a-8-CH_3'; 20.53, s-8-CH_3'; 27.77, C5'; 33.76, C6'; 47.20, C4'; 50.19, C8'; 52.41, CH_2; 60.53, C7'; 121.58, C3'; 127.28, C3a'; 128.05, C3,6; 128.36, C4,5; 135.61, C1,2; 166.12, C7a'.

Preparation of the Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzenes.

A mixture of the bis(bromomethyl)benzene and 2.2 equiv. of 3-(2'-pyridyl)pyrazole was reacted under P.T.C. conditions. In this manner the following three compounds were prepared.

1,4-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 325.

Reaction of 1,4-bis(bromomethyl)benzene (0.50g, 1.9mmol) with 3-(2'-pyridyl)pyrazole (0.61g, 4.2mmol) gave approximately a 2:1 mixture of 325 and its structural isomers as an orange solid. Column chromatography (silica, 99:1 $CHCl_3/CH_3OH$) gave 325 as a white solid (0.36g, 49%), m.p. 142°C (Found: C, 73.15; H, 5.14; N, 21.21. $C_{24}H_{20}N_6$ requires C, 73.45; H, 5.14; N, 21.41). ^{1}H N.M.R. ($CDCl_3$) δ: 5.38, 4H, s, CH_2; 6.90, 2H, d, H4'; 7.19, 2H, t, H5"; 7.23, 4H, s, H2,3,5,6; 7.41, 2H, d, H5'; 7.70, 2H, t, H4"; 7.93, 2H, d, H3"; 8.62, 2H, d, H6". ^{13}C N.M.R. ($CDCl_3$) δ: 55.85, CH_2; 104.93, C4'; 120.09, C3"; 122.35, C5"; 128.10, C2,3,5,6; 130.87, C5'; 136.37, C1,4; 136.51, C4"; 149.42, C6"; 151.84, C3'; 152.19, C2".

1,3-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 326.

Reaction of 1,3-bis(bromomethyl)benzene (0.60g, 2.3mmol) with 3-(2'-pyridyl)pyrazole (0.73g, 5.0mmol) gave approximately a 3:1 mixture of 326 and its structural isomers as an orange oil. Column chromatography (silica, 99:1 $CHCl_3/CH_3OH$) gave 326 as a white solid (0.53, 57%), m.p. 163-164°C (Found: $M^{+\cdot}$, 392.1751. $C_{24}H_{20}N_6$ requires $M^{+\cdot}$, 392.1749). ^{1}H N.M.R. ($CDCl_3$) δ: 5.37, 4H, s, CH_2; 6.90, 2H, d, H4'; 7.15, 1H, s, H2; 7.18, 2H, d, H4,6; 7.20, 2H, t, H5"; 7.32, 1H, t, H5; 7.41, 2H, d, H5'; 7.70, 2H, t, H4"; 7.92, 2H, d, H3"; 8.63, 2H, d, H6". ^{13}C N.M.R. ($CDCl_3$) δ: 55.95, CH_2; 104.93, C4'; 120.09, C3"; 122.34, C5"; 126.67, C2; 127.22, C4,6; 129.32, C5; 130.92, C5'; 136.50, C4"; 137.14, C1,3; 149.37, C6"; 151.81, C3'; 152.13, C2".

1,2-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 327.

Reaction of 1,2-bis(bromomethyl)benzene (0.60g, 2.3mmol) with 3-(2'-pyridyl)pyrazole (0.73g, 5.0mmol) gave approximately a 6:1 mixture of 327 and its structural isomers as a semicrystalline orange residue. Recrystallisation of this crude product from methanol gave 327 (0.40g, 45%), m.p. 163-164°C (Found: C, 73.21; H, 5.39; N, 21.32. $C_{24}H_{20}N_6$ requires C, 73.45; H, 5.14; N, 21.41). ^{1}H N.M.R. ($CDCl_3$) δ:

5.48, 4H, s, CH_2; 6.90, 2H, d, H4'; 7.17, 2H, dd, H3,6; 7.19, 2H, t, H5"; 7.32, 2H, dd, H4,5; 7.33, 2H, d, H5'; 7.70, 2H, t, H4"; 7.94, 2H, d, H3"; 8.62, 2H, d, H6". ^{13}C N.M.R. ($CDCl_3$) δ: 53.42, CH_2; 104.92, C4'; 120.11, C3"; 122.38, C5"; 128.92, C5'; 129.51, C3,6; 130.96, C4,5; 134.56, C1,2; 136.53, C4"; 149.36, C6"; 151.87, C3'; 152.11, C2".

Preparation of the 1,2,4,5-Tetrakis(pyrazolylmethyl)benzenes.

A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene and 4.4 equiv. of the pyrazole was reacted under P.T.C. conditions. In each case some product precipitated from the reaction mixture and was collected by filtration. Subsequent separation, drying and concentration of the organic layer furnished further crude product. These were recrystallised separately, but combined once pure. In this manner the following three compounds were prepared.

1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzene, 337.

Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (1.46g, 3.2mmol) with pyrazole (0.97g, 14.3mmol) and subsequent recrystallisation from benzene gave 337 (0.81g, 63%), m.p. 175°C (Found: $M^{+\cdot}$, 398.1969. C, 65.94; H, 5.65; N, 28.71. $C_{22}H_{22}N_8$ requires $M^{+\cdot}$, 398.1967. C, 66.31; H, 5.56; N, 28.12). ^1H N.M.R. ($CDCl_3$) δ: 5.25, 8H, s, CH_2; 6.25, 4H, t, H4'; 6.77, 2H, s, H3,6; 7.27, 4H, d, H5'; 7.52, 4H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 52.69, CH_2; 106.25, C4'; 129.53, C5'; 130.61, C3,6; 135.42, C1,2,4,5; 139.79, C3'.

1,2,4,5-Tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338.

Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (0.66g, 1.5mmol) with 3,5-dimethylpyrazole (0.62g, 6.5mmol) and subsequent recrystallisation from benzene gave 338) (0.34g, 45%), m.p. 240-241°C (Found: $M^{+\cdot}$, 510.3223. $C_{30}H_{38}N_8$ requires $M^{+\cdot}$, 510.3219. Found: C, 67.56; H, 7.48; N, 21.01. $C_{30}H_{38}N_8.H_2O$ requires C, 68.15; H, 7.63; N, 21.19). ^1H N.M.R. ($CDCl_3$) δ: 1.98, 12H, s, 5'-CH_3; 2.19, 12H, s, 3'-CH_3; 5.12, 8H, s, CH_2; 5.72, 2H, s, H3,6; 5.78, 4H, s, H4'. ^{13}C N.M.R. ($CDCl_3$) δ: 10.54, 5'-CH_3; 13.43, 3'-CH_3; 49.69, CH_2; 105.54, C4'; 125.70, C3,6; 134.28, C1,2,4,5; 139.48, C5'; 147.65, C3'.

1,2,4,5-Tetrakis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 339.

Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (0.42g, 0.9mmol) with 3-(2'-pyridyl)pyrazole (0.60g, 4.09mmol) and subsequent recrystallisation of the precipitate from ethanol gave 339 (0.31g, 47%), m.p. 230-231°C (Found: $M^{+\cdot}$, 706.3031. $C_{42}H_{34}N_{12}$ requires $M^{+\cdot}$, 706.3029.). ^{1}H N.M.R. ($CDCl_3$) δ: 5.42, 8H, s, CH_2; 6.83, 4H, d, H4'; 6.89, 2H, s, H3,6; 7.19, 4H, t, H5"; 7.31, 4H, d, H5'; 7.67, 4H, t, H4"; 7.86, 4H, d, H3"; 8.60, 4H, d, H6". ^{13}C N.M.R. ($CDCl_3$) δ: 52.91, CH_2; 105.07, C4'; 120.04, C3"; 122.36, C5"; 128.22, C5'; 131.04, C3,6; 135.25, C1,2,4,5; 136.45, C4"; 149.23, C6"; 151.84, C3'; 151.95, C2".

Preparation of 1,3,5-tris(pyrazolylmethyl)-2,4-dimethylbenzenes.

A mixture of 1,3,5-tris(bromomethyl)-2,4-dimethylbenzene, 407, and 3.3 equiv. of the pyrazole was reacted under P.T.C. conditions. In this manner the following two compounds were prepared.

1,3,5-Tris(pyrazol-1-ylmethyl)-2,4-dimethylbenzene, 405.

Reaction of 407 (1.00g, 2.6mmol) with pyrazole (0.58g, 8.6mmol) gave a crude product, which was recrystallised from petroleum ether to give 405 (0.57g, 63%), m.p. 79-80°C (Found: C, 69.09; H, 6.18; N, 24.03. $C_{20}H_{22}N_6$ requires C, 69.34; H, 6.40; N, 24.26). ^{1}H N.M.R. ($CDCl_3$) δ: 2.23, 6H, s, CH_3; 5.31, 4H, s, 1,5-CH_2; 5.40, 2H, s, 3-CH_2; 6.19, 1H, t, 3-H4'; 6.25, 2H, t, 1,5-H4'; 6.64, 1H, s, H6; 7.00, 1H, d, 3-H5'; 7.24, 2H, d, 1,5-H5'; 7.53, 3H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 15.03, CH_3; 49.99, 3-CH_2; 54.36, 1,5-CH_2; 105.43, 3-C4'; 105.89, 1,5-C4'; 127.93, 3-C5'; 129.01, 1,5-C5'; 130.16, C6; 133.38, C2,4; 133.45, C3; 137.02, C1,5; 139.37, 3-C3'; 139.51, 1,5-C3'.

1,3,5-Tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4-dimethylbenzene, 406.

Reaction of 407 (0.80g, 2.1mmol) with 3,5-dimethylpyrazole (0.66g, 6.9mmol) gave a crude product which precipitated out of the reaction mixture on cooling. This was filtered and recrystallised from benzene. Further product was isolated by treating the filtrate as for typical P.T.C. reactions. This was also recrystallised from benzene to give 406 (0.61g, 68%) m.p. 181-182°C (Found: C, 72.75; H, 8.03; N, 19.14. $C_{26}H_{34}N_6$ requires C, 72.52; H, 7.96; N, 19.52). ^{1}H N.M.R. ($CDCl_3$) δ: 1.98, 6H, s, 1,5-5'-CH_3;

2.01, 3H, s, 3-5'-CH_3; 2.17, 3H, s, 3-3'-CH_3; 2.20, 6H, s, 1,5-3'-CH_3; 2.22, 6H, s, 2,4-CH_3; 5.08, 4H, s, 1,5-CH_2; 5.24, 2H, s, 3-CH_2; 5.28, 1H, s, 3-H6; 5.76, 3H, s, H4'. ^{13}C N.M.R. ($CDCl_3$) δ: 10.80, 1,5-5'-CH_3; 11.26, 3-5'-CH_3; 13.47, 1,5-3'-CH_3; 13.55, 3-3'-CH_3; 14.92, 2,4-CH_3; 47.97, 3-CH_2; 50.86, 1,5-CH_2; 105.32, 1,5-C4'; 105.42, 3-C4'; 123.42, C6; 133.19, C3; 133.62, C2,4; 133.92, C1,5; 138.96, 3-C5'; 139.45, 1,5-C5'; 147.03, 3-C3'; 147.45, 1,5-C3'.

Preparation of 1,3,5-tris(pyrazolylmethyl)-2,4,6-triethylbenzenes.

A mixture of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene, 411, and 3.3 equiv. of the pyrazole was reacted under P.T.C. conditions. In this manner the following two compounds were prepared.

1,3,5-Tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 409.

Reaction of 411 (0.60g, 1.4mmol) with pyrazole (0.31g, 4.6mmol) gave a crude product, which was recrystallised from petroleum ether to give 409 (0.33g, 60%), m.p. 125-126°C (Found: C, 71.89; H, 7.73; N, 20.69. $C_{24}H_{30}N_6$ requires C, 71.61; H, 7.51; N, 20.88). ^1H N.M.R. ($CDCl_3$) δ: 0.96, 9H, t, CH_3; 2.70, 6H, m, 2,4,6-CH_2; 5.45, 6H, s, 1,3,5-CH_2; 6.20, 3H, t, H4'; 6.98, 3H, d, H5'; 7.55, 3H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 15.16, CH_3; 23.27, 2,4,6-CH_2; 49.55, 1,3,5-CH_2; 105.52, C4'; 127.75, C5'; 130.39, C2,4,6; 139.43, C3'; 145.99, C1,3,5.

1,3,5-Tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 410.

Reaction of 411 (0.80g, 1.8mmol) with 3,5-dimethylpyrazole (0.57g, 6.0mmol) gave a crude product, which was recrystallised from petroleum ether to give 410 (0.46g, 52%), m.p. 195-196°C (Found: C, 73.96; H, 8.59; N, 17.30. $C_{30}H_{42}N_6$ requires C, 74.03; H, 8.70; N, 17.27). ^1H N.M.R. ($CDCl_3$) δ: 0.86, 9H, t, 2,4,6-CH_3; 2.14, 9H, s, 5'-CH_3; 2.17, 9H, s, 3'-CH_3; 2.77, 6H, m, 2,4,6-CH_2; 5.17, 6H, s, 1,3,5-CH_2; 5.77, 3H, t, H4'. ^{13}C N.M.R. ($CDCl_3$) δ: 11.32, 5'-CH_3; 13.43, 3'-CH_3; 14.55, 2,4,6-CH_3; 23.67, 2,4,6-CH_2; 47.05, 1,3,5-CH_2; 105.42, C4'; 130.59, C2,4,6; 138.98, C5'; 144.92, C1,3,5; 147.09, C3'.

Preparation of hexakis(pyrazol-1-ylmethyl)benzene, 418.

A mixture of pyrazole (2.19g, 32.1mmol) and potassium (1.26g, 32.1mmol) in diglyme (50ml) was heated at 80C for 1 hour. To this was added hexakis(bromomethyl)benzene (3.10g, 4.9mmol) and the mixture was heated at 130°C for 72 hours. This was then filtered and the filtrate evaporated to dryness under vacuum. A precipitate of 418 (1.18g, 43%) formed in the remaining brown oil. A sample of this was recrystallised from diethyl ether/ethyl acetate (2:1) giving colourless blocks suitable for single crystal structure determination, m.p. 179°C (Found: C, 64.57; H, 5.54; N, 30.10. $C_{30}H_{30}N_{12}$ requires C, 64.50; H, 5.41; N, 30.09). ^{1}H N.M.R. ($CDCl_3$) δ: 5.61, 12H, s, CH_2; 6.14, 6H, t, H4'; 7.07, 6H, d, H5'; 7.46, 6H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 49.17, CH_2; 106.04, C4'; 129.31, C5'; 137.85, C1-6; 139.85, C3'.

Attempted preparation of 1,3,5-tris(2-pyridylmethyl)-2,4,6-trimethylbenzene, 422.

a) A mixture of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1.78g, 4.48mmol), 2-mercaptopyridine (1.49g, 13.4mmol) and triethylamine (1.69g, 16.8mmol), stirred in ice-cooled acetonitrile for 24 hours, gave a precipitate of the product in the reaction mixture. This solid was isolated by filtration and washed with water (3x10ml) to give the crude product. Recrystallisation from acetonitrile gave 420 (1.41g, 64%), m.p. 179°C (Found: C, 66.17; H, 5.57; N, 8.48. $C_{27}H_{27}N_3S_3$ requires C, 66.22; H, 5.56; N, 8.58). ^{1}H N.M.R. ($CDCl_3$) δ: 2.50, 9H, s, CH_3; 4.50, 6H, s, CH_2; 7.00, 3H, t, H5'; 7.19, 3H, d, H3'; 7.48, 3H, t, H4'; 8.48, 3H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 16.15, CH_3; 30.96, CH_2; 119.32 C3'; 121.92, C5'; 131.33, C1,3,5; 135.79, C4'; 136.81, C2,4,6; 149.48, C6'; 158.85, C2'.

b) To 422 (0.35g, 0.72mmol) dissolved in ice-cooled chloroform (10ml) was added meta-chloroperbenzoic acid (0.37g, 0.72mmol) dissolved in chloroform. The mixture was stirred at 0°C for two hours then filtered. The filtrate was then washed repeatedly with 40% aqueous sodium hydroxide, then with water, dried (Na_2SO_4), and concentrated to give crude 1,3,5-tris(2-pyridylsulfinylmethyl)-2,4,6-trimethylbenzene, 421, as a mixture of diastereoisomers (0.22g, 57%). ^{1}H N.M.R. ($CDCl_3$) δ: 2.40-2.43, 9H, CH_3; 4.42-4.56, 6H, CH_2; 7.40-7.44, 3H, H5'; 7.93-7.99, 6H, H3',4'; 8.66-8.69, 3H, H6'.

c) A THF (20ml) solution of phenylmagnesium bromide was prepared under a nitrogen atmosphere using bromobenzene (3.94g) and magnesium (0.61g). To this was added 421 (90mg, 0.17mmol) dissolved in THF (15ml), which was then stirred at room

temperature for 1 hour. Water (50ml) was then added and the solution neutralised by addition of hydrochloric acid (2M). This mixture was extracted with dichloromethane (3x25ml), the extracts dried (Na_2SO_4), and concentrated to give an orange oil containing 1,3,5-tris(2-pyridylmethyl)-2,4,6-trimethylbenzene, 422 (LRMS Found: $M^{+\cdot}$, 393. $C_{27}H_{27}N_3$ requires $M^{+\cdot}$, 393).

Preparation of the 3,5-bis(pyrazolylmethyl)-2,4,6-trimethyl-1-(2-pyridoxy)-benzenes.

A mixture of 3,5-bis(bromomethyl)-2,4,6-trimethyl-1-(2-pyridoxy)benzene, 424, and 2.2 equiv. of the pyrazole was reacted under P.T.C. conditions. In this manner the following two compounds were prepared.

3,5-Bis(pyrazol-1-ylmethyl)-2,4,6-trimethyl-1-(2-pyridoxy)benzene, 425.

Reaction of 424 (0.36g, 0.9mmol) with pyrazole (0.13g, 2.0mmol) gave a crude product, which was recrystallised from petroleum ether to give 425 (0.19g, 57%), m.p. 127°C (Found: C, 70.51; H, 6.05; N, 18.66. $C_{22}H_{23}N_5O$ requires C, 70.76; H, 6.21; N, 18.75). ^{1}H N.M.R. ($CDCl_3$) δ: 2.15, 6H, s, 2,6-CH_3; 2.27, 3H, s, 4-CH_3; 5.43, 4H, s, CH_2; 6.20, 2H, t, H4"; 6.94, 1H, d, H3'; 6.95, 1H, t, H5'; 7.09, 2H, d, H5"; 7.53, 2H, d, H3"; 7.70, 1H, t, H4'; 8.11, 1H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 13.24, 2,6-CH_3; 15.58, 4-CH_3; 50.42, CH_2; 105.33, C4"; 110.07, C3'; 117.86, C5'; 127.85, C5"; 131.36, C2,6; 132.52, C3,5; 135.55, C4; 139.22, C3"; 139.53, C4'; 147.67, C6'; 148.88, C1; 162.88, C2'.

3,5-Bis(3,5-dimethylpyrazol-1-ylmethyl)-2,4,6-trimethyl-1-(2-pyridoxy)benzene, 426.

Reaction of 424 (0.33g, 0.8mmol) with 3,5-dimethylpyrazole (0.17g, 1.8mmol) gave a crude product, which was recrystallised from petroleum ether/acetone (1:1) to give 426 (0.18g, 52%), m.p. 211-212°C (Found: C, 72.46; H, 7.41; N, 16.11. $C_{26}H_{31}N_5O$ requires C, 72.70; H, 7.27; N, 16.30). ^{1}H N.M.R. ($CDCl_3$) δ: 2.08, 6H, s, 2,6-CH_3; 2.09, 6H, s, 5"-CH_3; 2.15, 6H, s, 3"-CH_3; 2.17, 3H, s, 4-CH_3; 5.21, 4H, s, CH_2; 5.74, 2H, s, H4"; 6.88, 1H, d, H3'; 6.93, 1H, t, H5'; 7.66, 1H, t, H4'; 8.11, 1H, d, H6'. ^{13}C N.M.R. ($CDCl_3$) δ: 11.23, 5"-CH_3; 13.40, 3"-CH_3; 13.49, 2,6-CH_3; 15.99, 4-CH_3; 48.48, CH_2;

105.26, C4"; 109.87, C3'; 117.66, C5'; 131.32, C2,6; 132.04, C3,5; 135.27, C4; 139.01, C5"; 139.44, C4'; 146.95, C3"; 147.78, C6'; 148.49, C1; 163.25, C2'.

Preparation of the 1,3-bis(pyrazolylmethyl)-4,6-dimethylbenzenes.

A mixture of 1,3-bis(bromomethyl)-4,6-dimethylbenzene (107), the pyrazole (2.2 equiv.) and potassium carbonate (4 equiv.) was refluxed in dimethylformamide (5ml) for 24 hours, unless otherwise stated. The solvent was removed and the residue covered with water (15ml) and extracted with chloroform. The extracts were concentrated and the crude product purified by recrystallisation or column chromatography. In this manner the following four compounds were prepared.

1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene, 502.

Reaction of 500 (0.49g, 1.7mmol), pyrazole (0.25g, 3.7mmol) and potassium carbonate (0.93, 6.7mmol) gave a brown solid. Recrystallisation from petroleum ether gave 502 (0.29g, 66%) as a white solid, m.p. 86°C (Found: C, 72.34; H, 6.67; N, 20.90. $C_{16}H_{18}N_4$ requires C, 72.15; H, 6.81; N, 21.04). ^{1}H N.M.R. ($CDCl_3$) δ: 2.21, 6H, s, CH_3; 5.25, 4H, s, CH_2; 6.23, 2H, t, H4'; 6.75, 1H, s, H2; 7.03, 1H, s, H5; 7.23, 2H, d, H5'; 7.52, 2H, d, H3'. ^{13}C N.M.R. ($CDCl_3$) δ: 18.45, CH_3; 53.62, CH_2; 105.62, C4'; 128.81, C5'; 129.75, C2; 132.28, C4,6; 133.03, C5; 136.66, C1,3; 139.22, C3'.

1,3-Bis(3,5-dimethylpyrazol-1-ylmethyl)-4,6-dimethylbenzene, 503.

Reaction of 500 (0.52g, 1.8mmol), 3,5-dimethylpyrazole (0.37g, 3.9mmol) and potassium carbonate (0.98, 7.1mmol) gave a brown solid. Recrystallisation from petroleum ether gave 503 (0.30g, 52%) as a white solid, m.p. 115°C (Found: C, 74.41; H, 8.01; N, 17.42. $C_{20}H_{26}N_4$ requires C, 74.50; H, 8.13; N, 17.37). ^{1}H N.M.R. ($CDCl_3$) δ: 1.99, 6H, s, 5'-CH_3; 2.20, 6H, s, 3'-CH_3; 2.25, 6H, s, 4,6-CH_3; 5.04, 4H, s, CH_2; 5.43, 1H, s, H2; 5.76, 2H, s, H4'; 6.93, 1H, s, H5. ^{13}C N.M.R. ($CDCl_3$) δ: 10.45, 5'-CH_3; 13.13, 3'-CH_3; 18.07, 4,6-CH_3; 49.61, CH_2; 104.93, C4'; 123.22, C2; 131.67, C5; 133.04, C4,6; 133.14, C1,3; 139.01, C5'; 146.90, C3'.

1,3-bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]-4,6-dimethylbenzene, 504.

Reaction of 500 (0.50g, 1.7mmol), (4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole (0.67g, 3.8mmol) and potassium carbonate (0.95g, 6.8mmol) for 48 hours gave a mixture of 504 and its structural isomers as an orange oil. Column chromatography (silica, $CHCl_3$) gave 504 (0.15g, 17%) (Found: $M^{+\cdot}$, 482.3408. $C_{32}H_{42}N_4$ requires $M^{+\cdot}$, 482.3410). ^{1}H N.M.R. ($CDCl_3$) δ: 0.66, 6H, s, s-8-CH_3'; 0.93, 6H, s, a-8-CH_3'; 1.10, 2H, m, exo-H5'; 1.29, 6H, s, 7-CH_3'; 1.29, 2H, m, exo-H6'; 1.82, 2H, m, endo-H5'; 2.04, 2H, m, endo-H6'; 2.17, 6H, s, 4,6- CH_3; 2.69, 2H, d, H4'; 5.16, 4H, s, CH_2; 6.59, 1H, s, H2; 6.68, 2H, s, H3'; 6.97, 1H, s, H5. ^{13}C N.M.R. ($CDCl_3$) δ: 10.72, 7-CH_3'; 18.42, 4,6-CH_3; 19.15, a-8-CH_3'; 20.49, s-8-CH_3'; 27.84, C5'; 33.81, C6'; 47.25, C4'; 50.20, C8'; 53.28, CH_2; 60.54, C7'; 121.07, C3'; 126.95, C3a'; 129.29, C5; 132.77, C2; 133.22, C4,6; 136.19, C1,3; 165.81, C7a'.

1,3-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)-4,6-dimethylbenzene, 505.

Reaction of 500 (0.50g, 1.7mmol), 3-(2'-pyridyl)pyrazole (0.55g, 3.8mmol) and potassium carbonate (0.95, 6.8mmol) gave a brown oil. Column chromatography (silica, $CHCl_3$/CH_3OH 99:1) gave 505 (0.30g, 42%) as a white solid, m.p. 129-130°C (Found: $M^{+\cdot}$, 420.2064. $C_{26}H_{24}N_6$ requires $M^{+\cdot}$, 420.2063). ^{1}H N.M.R. ($CDCl_3$) δ: 2.26, 6H, s, CH_3; 5.32, 4H, s, CH_2; 6.83, 2H, t, H4'; 6.85, 1H, s, H2; 7.06, 1H, s, H5; 7.17, 2H, t, H5"; 7.23, 2H, d, H5'; 7.68, 2H, t, H4"; 7.91, 2H, d, H3"; 8.61, 2H, d, H6". ^{13}C N.M.R. ($CDCl_3$) δ: 18.57, CH_3; 54.01, CH_2; 104.55, C4'; 119.97, C3"; 122.22, C5"; 129.83, C2; 130.37, C5'; 132.09, C4,6; 133.08, C5; 136.42, C4"; 136.87, C1,3; 149.29, C6"; 151.51, C3'; 152.17, C2".

Preparation of Complexes.

General Procedure for the Preparation of Palladium Complexes.

The ligand, dissolved in hot methanol (5ml), was added to palladium chloride, 1, (0.5 equiv. per heterocycle) dissolved in hot aqueous hydrochloric acid (5ml, 2M). Orange/yellow precipitates formed within minutes unless otherwise stated.

General Procedure for the Preparation of Silver Complexes.

The ligand, dissolved in methanol or acetone (5ml) (at room temperature unless otherwise stated), was added to silver nitrate, 2, (0.5-0.6 equiv per heterocycle) dissolved in water or hot methanol. The time and conditions for precipitation of the product varied.

General Procedure for the Preparation of Copper Complexes.

The ligand, dissolved in methanol (5ml at room temperature unless otherwise stated), was added to copper chloride dihydrate, 3, (0.5-0.6 equiv per heterocycle) dissolved in methanol (5ml). Green/blue precipitates formed within minutes unless otherwise stated.

Complexes of 1,4-Bis(2-pyridoxy)benzene, 200.

With palladium chloride *viz* 201.

Reaction of 200 (46mg, 0.17mmol) with 1 (31mg, 0.17mmol) gave 201 as an orange precipitate (67mg, 88%), m.p. > 300°C (Found: C, 43.35; H, 2.80; N, 6.26; Cl, 15.87. $C_{16}H_{12}N_2O_2Cl_2Pd$ requires C, 43.52; H, 2.74; N, 6.34; Cl, 16.06). ^{1}H N.M.R.: Not sufficiently soluble in common N.M.R. solvents.

With silver nitrate *viz* 202.

Reaction of 200 (150mg, 0.56mmol) dissolved in acetone (10ml) with 2 (86mg, 0.56mmol) dissolved in water (5ml) gave crude 202 as a brown precipitate (105mg, 43%). Slow evaporation of an acetonitrile solution of the crude product gave brown crystals of 202 suitable for single crystal X-ray structure determination, m.p. 222-223°C

(Found: C, 42.74; H, 3.10; N, 9.58. $C_{32}H_{24}N_6O_{10}Ag_2.2H_2O$ requires C, 42.50; H, 3.12; N, 9.29).

With copper chloride dihydrate *viz* 203.

Reaction of 200 (70mg, 0.26mmol) dissolved in hot acetone (6ml) with 3 (54mg, 0.31mmol) gave 203 as a blue precipitate (98mg, 92%), m.p. > 265°C (dec.) (Found: C, 46.80; H, 3.34; N, 6.74; Cl, 17.80. $C_{16}H_{12}N_2O_2Cl_2Cu.½H_2O$ requires C, 47.13; H, 3.29; N, 6.87; Cl, 17.39).

Complexes of 1,3-Bis(2-pyridoxy)benzene, 205.

With palladium chloride *viz* 207.

Reaction of 205 (60mg, 0.23mmol) with 1 (40mg, 0.23mmol) gave crude 207 as an orange precipitate. This was subsequently recrystallised by vapour diffusion of acetone into a DMSO solution of the crude product to give 207 (82mg, 81%), m.p. > 235°C (dec.) (Found: C, 41.29; H, 3.41; N, 5.98; Cl, 14.72. $C_{16}H_{12}N_2O_2Cl_2Pd.H_2O.¼CH_3SOCH_3$ requires C, 41.36; H, 3.26; N, 5.85; Cl, 14.80). ^1H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 208.

Reaction of 205 (70mg, 0.26mmol), dissolved in methanol (8ml), with 2 (54mg, 0.31mmol) dissolved in water (5ml) gave, over a period of several days, 208 as crystals suitable for single crystal X-ray structure determination (96mg, 83%), m.p. 185-186°C (Found: C, 42.61; H, 3.29; N, 9.16. $C_{32}H_{24}N_6O_{10}Ag_2.2H_2O$ requires C, 42.50; H, 3.12; N, 9.29).

With copper chloride dihydrate *viz* 209.

Reaction of 205 (70mg, 0.26mmol) with 3 (54mg, 0.31mmol) gave 209 as a blue precipitate (87mg, 84%), m.p. > 205°C (dec.) (Found: C, 47.97; H, 3.10; N, 6.82; Cl, 17.76. $C_{16}H_{12}N_2O_2Cl_2Cu$ requires C, 48.20; H, 3.03; N, 7.03; Cl, 17.78).

Complexes of 1,2-Bis(2-pyridoxy)benzene, 206.

With palladium chloride *viz* 210.

Reaction of 206 (61mg, 0.23mmol) with 1 (41mg, 0.23mmol) gave 210 as orange crystals suitable for single crystal X-ray structure determination (79mg, 78%), m.p. > 260°C (dec.) (Found: C, 43.25; H, 2.65; N, 6.38; Cl, 16.00. $C_{16}H_{12}N_2O_2Cl_2Pd$ requires C, 43.52; H, 2.74; N, 6.34; Cl, 16.06). ^{1}H N.M.R. (CD_2Cl_2) δ: 7.12, 2H, t, H5'; 7.16, 2H, d, H3'; 7.32, 2H, dd, H4,5; 7.59, 2H, dd, H3,6; 7.84, 2H, t, H4'; 8.69, 2H, d, H6'.

With silver nitrate *viz* 211.

Reaction of 206 (70mg, 0.26mmol), dissolved in methanol (5ml), with 2 (54mg, 0.31mmol) dissolved in methanol (5ml) gave a colourless solution. This was concentrated to approximately 5ml. Subsequent vapour diffusion of diethyl ether into this solution gave crystals of 211 (101mg, 80%), m.p. > 130°C (Found: C, 39.76; H, 2.50; N, 9.21. $C_{64}H_{48}N_{13}O_{23}Ag_5.2H_2O$ requires C, 39.57; H, 2.70; N, 9.37).

With copper chloride dihydrate *viz* 212.

Reaction of 206 (70mg, 0.26mmol) with 3 (54mg, 0.31mmol) gave 212 as a blue precipitate (85mg, 82%), m.p. > 245°C (dec.) (Found: C, 47.58; H, 3.22; N, 7.11; Cl, 17.48. $C_{16}H_{12}N_2O_2Cl_2Cu.¼H_2O$ requires C, 47.66; H, 3.12; N, 6.94; Cl, 17.58).

Complexes of 1,4-Bis(2-pyridoxymethyl)benzene, 213.

With palladium chloride *viz* 215.

Reaction of 213 (60mg, 0.21mmol) with 1 (36mg, 0.21mmol) gave 215 as an orange precipitate, which was filtered and washed with hot ethanol (89mg, 87%), m.p. > 220°C (dec) (Found: C, 44.26; H, 3.59; N, 5.60; Cl, 14.62. $C_{18}H_{16}N_2O_2Cl_2Pd.H_2O$ requires C, 44.22; H, 3.72; N, 5.74; Cl, 14.54). ^{1}H N.M.R.: Not sufficiently soluble in common N.M.R. solvents.

With silver nitrate *viz* 216.

Reaction of 213 (50mg, 0.17mmol) dissolved in acetone (7ml), with 2 (29mg, 0.17mmol) dissolved in water (3ml) upon leaving to evaporate, gave colourless crystals of 216, suitable for single crystal X-ray structure determination (63mg, 79%), m.p. 187-

188°C (Found: C, 46.68; H, 3.39; N, 9.15. $C_{18}H_{16}N_3O_5Ag$ requires C, 46.78; H, 3.49; N, 9.09).

With copper chloride dihydrate *viz* 217.

Reaction of 213 (50mg, 0.17mmol) with 3 (29mg, 0.17mmol) gave 217 as a blue precipitate (62mg, 84%), m.p. 188-189°C (Found: C, 49.45; H, 3.89; N, 6.19; Cl, 16.53. $C_{18}H_{16}N_2O_2Cl_2Cu.½H_2O$ requires C, 49.61; H, 3.93; N, 6.42; Cl, 16.27).

Complexes of 1,4-Bis(2-pyridylmethoxy)benzene, 214.

With palladium chloride *viz* 218.

Reaction of 214 (45mg, 0.15mmol) with 1 (27mg, 0.15mmol) gave 218 as an orange precipitate (59mg, 82%), m.p. > 300°C. Vapour diffusion of acetone into a DMSO solution of 218 gave crystals suitable for single crystal X-ray structure determination (Found: C, 46.68; H, 3.63; N, 5.70; Cl, 14.40. $C_{36}H_{32}N_4O_4Cl_4Pd_2.CH_3COCH_3$ requires C, 46.97; H, 3.84; N, 5.62; Cl, 14.22). ^{1}H N.M.R. (DMSO) δ: 5.47, 8H, s, CH_2; 7.16, 8H, s, H2,3,5,6; 7.93, 4H, t, H5'; 8.06, 4H, d, H3'; 8.49, 4H, t, H4'; 8.92, 4H, d, H6'.

With silver nitrate *viz* 219.

Reaction of 214 (50mg, 0.17mmol), dissolved in methanol (10ml), with 2 (29mg, 0.17mmol) dissolved in water (10ml) gave colourless needles of 219 over 15-30 minutes, which were filtered and washed with methanol (65mg, 82%). Slow evaporation of an acetonitrile solution of 219 gave crystals suitable for single crystal X-ray structure determination, m.p. > 190°C (Found: C, 46.72; H, 3.53; N, 9.23. $C_{18}H_{16}N_3O_5Ag$ requires C, 46.78; H, 3.49; N, 9.09).

With copper chloride dihydrate *viz* 220.

Reaction of 214 (72mg, 0.25mmol) with 3 (42mg, 0.25mmol) gave 220 as a green precipitate (96mg, 89%), m.p. 187°C (Found: C, 49.90; H, 3.83; N, 6.40; Cl, 16.59. $C_{18}H_{16}N_2O_2Cl_2Cu.¼H_2O$ requires C, 50.13; H, 3.86; N, 6.49; Cl, 16.44).

Complexes of 1,4-Bis(2-pyridylsulfanylmethyl)benzene, 221.

With palladium chloride *viz* 224.

Reaction of 221 (60mg, 0.18mmol) with 1 (33mg, 0.18mmol) gave an orange precipitate, which was filtered and washed with hot ethanol to give 224 (86mg, 84%), m.p. > 165°C (dec.) (Found: C, 40.16; H, 3.84; N, 5.21. $C_{18}H_{16}N_2S_2Cl_2Pd.2H_2O$ requires C, 40.20; H, 3.74; N, 5.20). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 225.

Reaction of 221 (71mg, 0.22mmol), dissolved in hot methanol (12ml), with 2 (37mg, 0.22mmol) dissolved in water (3ml) gave 225 as a white precipitate (73mg, 68%), m.p. > 162°C (dec.) (Found: C, 43.60; H, 3.42; N, 8.37. $C_{18}H_{16}N_3O_3S_2Ag$ requires C, 43.73; H, 3.26; N, 8.50). Slow evaporation of an acetonitrile solution of 225 gave crystals suitable for single crystal X-ray structure determination.

With copper chloride dihydrate *viz* 226.

Reaction of 221 (70mg, 0.22mmol), dissolved in hot methanol (8ml), with 3 (37mg, 0.22mmol) dissolved in hot methanol (2ml) gave 226 as a green precipitate (92mg, 91%), m.p. 203-204°C (Found: C, 46.96; H, 3.70; N, 6.25. $C_{18}H_{16}N_2S_2Cl_2Cu$ requires C, 47.11; H, 3.51; N, 6.10).

Complexes of 1,3-Bis(2-pyridylsulfanylmethyl)benzene, 222.

With palladium chloride *viz* 227.

Reaction of 222 (60mg, 0.18mmol) with 1 (33mg, 0.18mmol) gave an orange precipitate which was filtered and washed with hot ethanol to give 227 (94mg, 92%), m.p. > 165°C (dec.) (Found: C, 39.89; H, 3.64; N, 5.32. $C_{18}H_{16}N_2S_2Cl_2Pd.2H_2O$ requires C, 40.20; H, 3.74; N, 5.20). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 228.

Reaction of 222 (79mg, 0.24mmol), dissolved in methanol (10ml), with 2 (41mg, 0.24mmol) dissolved in water (3ml) gave 228 as a white precipitate. Slow evaporation of an acetonitrile solution of 228 gave crystals suitable for single crystal X-ray structure determination (98mg, 83%), m.p. 151-152°C (Found: C, 43.64; H, 3.26; N, 8.57. $C_{18}H_{16}N_3O_3S_2Ag$ requires C, 43.73; H, 3.26; N, 8.50).

With copper chloride dihydrate *viz* 229.

Reaction of 222 (75mg, 0.23mmol) with 3 (39mg, 0.23mmol) gave a green solution and a yellow precipitate (6mg). This was filtered then diethyl ether was vapour diffused into the filtrate to give 229 as small green crystals (77mg, 73%), m.p. 178-179°C (Found: C, 46.82; H, 3.39; N, 6.14. $C_{18}H_{16}N_2S_2Cl_2Cu$ requires C, 47.11; H, 3.51; N, 6.10).

Complexes of 1,2-Bis(2-pyridylsulfanylmethyl)benzene, 223.

With palladium chloride *viz* 230.

Reaction of 223 (60mg, 0.18mmol) with 1 (33mg, 0.18mmol) gave an orange precipitate, which was filtered and washed with hot ethanol to give 230 (84mg, 88%), m.p. 174-175°C (Found: C, 41.15; H, 3.70; N, 5.36. $C_{18}H_{16}N_2S_2Cl_2Pd.1½H_2O$ requires C, 40.88; H, 3.62; N, 5.30). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 231.

Reaction of 223 (82mg, 0.25mmol), dissolved in hot methanol (10ml), with 2 (43mg, 0.25mmol) dissolved in hot methanol (5ml) gave a colourless solution. This was filtered then diethyl ether was vapour diffused into this solution to give 231 as a white solid (86mg, 71%). Slow evaporation of an acetonitrile solution of 231 gave crystals suitable for single crystal X-ray structure determination, m.p. 152-153°C (Found: C, 43.51; H, 3.33; N, 8.59. $C_{18}H_{16}N_3O_3S_2Ag$ requires C, 43.73; H, 3.26; N, 8.50).

With copper chloride dihydrate *viz* 232.

Reaction of 223 (73mg, 0.22mmol), dissolved in hot methanol (8ml), with 3 (38mg, 0.22mmol) dissolved in hot methanol (2ml) gave 232 as a green crystals suitable for

single crystal X-ray structure determination (90mg, 83%), m.p. 161-162°C (Found: C, 46.54; H, 3.83; N, 5.75. $C_{18}H_{16}N_2S_2Cl_2Cu.CH_3OH$ requires C, 46.48; H, 4.11; N, 5.71).

Complexes of 1,2,4,5-Tetrakis(2-pyridylsulfanylmethyl)benzene, 233.

With palladium chloride *viz* 234.

Reaction of 233 (61mg, 0.11mmol) with 1 (38mg, 0.22mmol) gave an orange precipitate which was filtered and washed with hot ethanol to give 234 (96mg, 91%), m.p. > 190°C (dec.) (Found: C, 37.21; H, 2.73; N, 5.65. $C_{30}H_{26}N_4S_4Cl_4Pd_2.2H_2O$ requires C, 37.48; H, 3.14; N, 5.83). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 235.

Reaction of 233 (70mg, 0.12mmol), dissolved in hot acetone (10ml), with 2 (42mg, 0.24mmol) dissolved in water (4ml) gave 235 as a white precipitate (98mg, 86%), m.p. 153-154°C. Slow evaporation of an acetonitrile solution of 235 gave crystals suitable for single crystal X-ray structure determination (Found: C, 38.24; H, 3.18; N, 8.94. $C_{30}H_{26}N_6O_6S_4Ag_2.2H_2O$ requires C, 38.07; H, 3.19; N, 8.88).

With copper chloride dihydrate *viz* 236.

Reaction of 233 (61mg, 0.11mmol), dissolved in hot acetone (8ml), with 3 (39mg, 0.23mmol) dissolved in hot acetone (6ml) gave 236c as a green/yellow precipitate (81mg, 88%), m.p. 164-165°C (Found: C, 42.69; H, 3.36; N, 6.75. $C_{30}H_{26}N_4S_4Cl_4Cu_2$ requires C, 42.91; H, 3.12; N, 6.67).

Complex of 1,4-Bis(pyrazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene, 302, with silver nitrate *viz* 303.

Reaction of 302 (95mg, 0.33mmol), dissolved in methanol (10ml), with 2 (57mg, 0.33mmol) dissolved in water (3ml) gave 303 (118mg, 77%). Slow evaporation of an acetonitrile solution of 303 gave crystals suitable for single crystal X-ray structure determination, m.p. > 180°C (dec.) (Found: C, 46.46; H, 4.77; N, 15.24. $C_{18}H_{22}N_5O_3Ag$ requires C, 46.56; H, 4.78; N, 15.08).

Complexes of 1,3-Bis(pyrazol-1-ylmethyl)benzene, 300.

With palladium chloride *viz* 304.

Reaction of 300 (55mg, 0.23mmol) with 1 (41mg, 0.23mmol) gave 304 (81mg, 85%). Vapour diffusion of methanol into a DMSO solution of 304 gave crystals, although they were not suitable for single crystal X-ray structure determination, m.p. > 250°C (dec.) (Found: C, 40.12; H, 3.43; N, 13.11; Cl, 17.11. $C_{14}H_{14}Cl_2N_4Pd.¼H_2O$ requires C, 40.02; H, 3.48; N, 13.34; Cl, 16.88). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 305.

Reaction of 300 (47mg, 0.20mmol), dissolved in methanol (10ml), and 2 (40mg, 0.24mmol) dissolved in water (10ml) gave crystals of 305 suitable for single crystal X-ray structure determination over a period of 1-2 days (42mg, 53%), m.p. 200-201°C (Found: C, 41.49; H, 3.28; N, 17.17. $C_{14}H_{14}N_5O_3Ag$ requires C, 41.20; H, 3.46; N, 17.16).

With copper chloride dihydrate *viz* 306.

Reaction of 300 (73mg, 0.31mmol) with 3 (63mg, 0.37mmol) gave a green precipitate over a period of 1-2 hours. Recrystallisation from 1:1 acetonitrile/ethanol gave 306 (77mg, 67%), m.p. 206-207°C (Found: C, 45.02; H, 3.48; N, 14.90; Cl, 19.10. $C_{14}H_{14}Cl_2N_4Cu$ requires C, 45.11; H, 3.79; N, 15.03; Cl, 19.02).

Complexes of 1,2-Bis(pyrazol-1-ylmethyl)benzene, 301.

With palladium chloride *viz* 307.

Reaction of 301 (55mg, 0.23mmol) with 1 (41mg, 0.23mmol) gave 307 (78mg, 82%). Vapour diffusion of methanol into a DMSO solution of 307 gave crystals, although they were not suitable for single crystal X-ray structure determination, m.p. > 250°C (dec.) (Found: C, 40.30; H, 3.13; N, 13.19; Cl, 16.67. $C_{14}H_{14}Cl_2N_4Pd$ requires C, 40.46; H, 3.40; N, 13.48; Cl, 17.06). ^{1}H N.M.R. (DMSO) δ: 5.78, 2H, d, CH_2; 6.51, 2H, t, H4'; 7.54, 2H, dd, H4,5; 7.69, 2H, d, CH_2; 7.97, 2H, dd, H3,6; 8.09, 2H, d, H5'; 8.42, 2H, d, H3'.

With silver nitrate *viz* 308.

Reaction of 301 (66mg, 0.28mmol), dissolved in methanol (2ml), and 2 (57mg, 0.34mmol) dissolved in hot methanol (8ml), and subsequent vapour diffusion of diethyl ether into the reaction mixture gave 308 as clusters of small crystals (78mg, 64%). Slow evaporation of an acetonitrile solution of these clusters gave crystals suitable for single crystal X-ray structure determination, m.p. 197-198°C (Found: C, 41.07; H, 3.39; N, 17.31. $C_{14}H_{14}N_5O_3Ag$ requires C, 41.20; H, 3.46; N, 17.16).

Complexes of (2-Pyridoxy)-4-(pyrazol-1-ylmethyl)benzene, 309.

With palladium chloride *viz* 310.

Reaction of 309 (33mg, 0.13mmol) with 1 (23mg, 0.13mmol) gave 310 as an orange precipitate which was filtered and washed with hot ethanol (42mg, 72%), m.p. > 235°C (dec) (Found: C, 40.31; H, 3.30; N, 9.23; Cl, 16.12. $C_{15}H_{13}N_3OCl_2Pd.H_2O$ requires C, 40.33; H, 3.38; N, 9.41; Cl, 15.88). ^{1}H N.M.R.: Not sufficiently soluble in common N.M.R. solvents.

With silver nitrate *viz* 311.

Reaction of 309 (70mg, 0.28mmol), dissolved in methanol (5ml), with 2 (47mg, 0.28mmol) dissolved in water (4ml) upon leaving to evaporate gave colourless crystals of 311 suitable for single crystal X-ray structure determination (92mg, 78%), m.p. 205-206°C (Found: C, 42.89; H, 3.27; N, 13.32. $C_{15}H_{13}N_4O_4Ag$ requires C, 42.78; H, 3.31; N, 13.30).

With copper chloride dihydrate *viz* 312.

Reaction of 309 (47mg, 0.19mmol) with 3 (38mg, 0.23mmol) gave 312 as a blue/green precipitate (62mg, 84%), m.p. >260°C (dec.) (Found: C, 46.34; H, 3.67; N, 10.70; Cl, 17.87. $C_{15}H_{13}N_3OCl_2Cu.¼H_2O$ requires C, 46.17; H, 3.49; N, 10.76; Cl, 18.16).

Complexes of 1,4-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene 313.

With palladium chloride *viz* 316.

Reaction of 313 (82mg, 0.18mmol) with 1 (32mg, 0.18mmol) gave only a small amount of precipitate upon cooling. Removal of methanol under reduced pressure gave further 316 (82mg, 72%). Vapour diffusion of diethyl ether into an acetonitrile solution of 316 gave crystals suitable for single crystal X-ray structure determination, m.p.>300°C (Found: C, 56.95; H, 6.20; N, 8.85; Cl, 11.06. $C_{60}H_{76}Cl_4N_8Pd_2$ requires C, 57.02; H, 6.06; N, 8.87; Cl, 11.22). ^{1}H N.M.R. (DMSO) δ: 0.68, 12H, s, s-8-CH_3'; 1.02, 12H, s, a-8-CH_3'; 1.10, 4H, m, exo-H5'; 1.59, 4H, m, exo-H6'; 1.91, 4H, m, endo-H5'; 2.03, 12H, s, 7-CH_3'; 2.12, 4H, m, endo-H6'; 2.82, 4H, d, H4'; 5.72, 8H, dd, CH_2; 7.25, 8H, s, ArH; 7.34, 4H, s, H3'.

With silver nitrate *viz* 317.

Reaction of 313 (81mg, 0.18mmol), dissolved in methanol (10ml), and 2 (36mg, 0.21mmol) dissolved in water (5ml) gave 317 over a period of days (68mg, 61%). Slow evaporation of an acetonitrile solution of 317 gave crystals suitable for single crystal X-ray structure determination, m.p. > 230°C (dec.) (Found: C, 57.62; H, 6.29; N, 11.07. $C_{30}H_{38}N_5O_3Ag$ requires C, 57.70; H, 6.13; N, 11.21).

With copper chloride dihydrate *viz* 318.

Reaction of 313 (60mg, 0.13mmol) with 3 (27mg, 0.16mmol) gave a green solution. This was concentrated to approximately 2ml. Subsequent vapour diffusion of diethyl ether into this solution gave 318 as a dark green solid (58mg, 75%), m.p. 233-234°C (Found: C, 59.89; H, 6.19; N, 9.05; Cl, 12.24. $C_{30}H_{38}Cl_2N_4Cu.½H_2O$ requires C, 60.24; H, 6.57; N, 9.36; Cl, 11.85).

Complexes of 1,3-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-yl) methyl]benzene, 314.

With palladium chloride *viz* 319.

Reaction of 314 (51mg, 0.11mmol) with 1 (20mg, 0.11mmol) gave some precipitate over half an hour. Removal of methanol under reduced pressure gave further

precipitation of 319 (62mg, 89%). The crude product was washed with dichloromethane leaving an orange solid, 319a (28mg, 40%), m.p. > 300°C (Found: C, 56.65; H, 5.99; N, 8.44; Cl, 11.59. $C_{30}H_{38}Cl_2N_4Pd$ requires C, 57.02; H, 6.06; N, 8.87; Cl, 11.22). ^1H N.M.R. : Insoluble or unstable in common N.M.R. solvents. The dichloromethane washings were concentrated to give 319b (29mg, 42%), m.p. > 260°C (Found: $M^{+\cdot}$, 1227.3337 $C_{60}H_{76}Cl_3N_8Pd_2$ requires $M^{+\cdot}$,1227.3330). ^1H N.M.R. ($CDCl_3$): signals of spectrum broad and not assigned.

With silver nitrate *viz* 320.

To a mixture of 314 (91mg, 0.20mmol), dissolved in methanol (10ml), and 2 (34mg, 0.20mmol) dissolved in water (3ml) was added excess sodium perchlorate solution, giving 320 as a white solid (93mg, 71%), m.p. >180°C (dec.) (Found: $M^{+\cdot}$, 561.2142. $C_{30}H_{38}N_4Ag$ requires $M^{+\cdot}$, 561.2147).

With copper chloride dihydrate *viz* 321.

Reaction of 314 (62mg, 0.14mmol) with 3 (28mg, 0.17mmol) gave a green solution. This was concentrated to approximately 5ml. Subsequent vapour diffusion of diethyl ether into this solution gave 321 as a green/grey powder (54mg, 66%), m.p. 214-215°C (Found: C, 60.88; H, 6.27; N, 9.57; Cl, 12.18. $C_{30}H_{38}Cl_2N_4Cu$ requires C, 61.18; H, 6.50; N, 9.51; Cl, 12.04).

Complexes of 1,2-Bis[((4S,7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2H-indazol-2-ylmethyl]benzene, 314.

With palladium chloride *viz* 322a and 322b.

Reaction of 314 (90mg, 0.20mmol) with 1 (35mg, 0.20mmol) gave only a small amount of precipitate over an hour. Removal of methanol under reduced pressure gave crude 322 (113mg, 89%). Column chromatography (silica, $CHCl_3$) gave 322a as an orange solid (69mg, 54%), m.p. >260°C (dec.) (Found: $M^{+\cdot}$, 597.1824; C, 56.71; H, 6.01; N, 8.64; Cl, 11.31. $C_{30}H_{38}Cl_2N_4Pd$ requires $M^{+\cdot}$, 597.1819; C, 57.02; H, 6.06; N, 8.87; Cl, 11.22). ^1H N.M.R. ($CDCl_3$) δ: 0.62, 3H, s, s-8'-CH_3; 0.68, 3H, s, s-8'-CH_3; 0.92, 3H, s, a-8'-CH_3; 0.94, 3H, s, a-8'- CH_3; 1.14, 2H, m, exo-H5'; 1.35, 1H, m, exo-H6'; 1.44, 1H, m, exo-H6'; 1.68, 3H, s, 7-CH_3'; 1.74, 3H, s, 7-CH_3'; 1.76, 1H, m, endo-H6'; 1.86, 1H, m, endo-H6'; 2.03, 2H, m, endo-H5'; 2.74, 1H, d, H4'; 2.76, 1H, d, H4';

5.18, 1H, d, CH_2; 5.19, 1H, d, CH_2; 6.97, 1H, d, CH_2; 7.04, 1H, d, CH_2; 7.24-7.33, 4H, H3,4,5,6; 7.37, 1H, s, H3'; 7.40, 1H, s, H3'. Further elution (99:1 $CHCl_3/CH_3OH$) gave 322b as an orange solid (29mg, 23%), m.p. >270°C (dec.) (Found: $M^{+\cdot}$, 1227.3338. $C_{60}H_{76}Cl_3N_8Pd_2$ requires $M^{+\cdot}$, 1227.3330). ^1H N.M.R. ($CDCl_3$): signals of spectrum broad and not assigned.

With silver nitrate *viz* 323.

To a mixture of 315 (50mg, 0.11mmol), dissolved in methanol (3ml), and 2 (22mg, 0.13mmol) dissolved in water (3ml) was added excess sodium perchlorate solution, which gave 323 as a white solid (47mg, 64%), m.p. > 170°C (dec.) (Found: $M^{+\cdot}$, 561.2142. $C_{30}H_{38}N_4Ag$ requires $M^{+\cdot}$, 561.2147).

With copper chloride dihydrate *viz* 324.

Reaction of 315 (61mg, 0.13mmol) with 3 (27mg, 0.16mmol) gave a deep green solution. This was concentrated to approximately 5ml. Subsequent vapour diffusion of diethyl ether into this solution gave crystals of 324 suitable for single crystal X-ray structure determination (55mg, 72%), m.p. 231-233°C (Found: C, 61.09; H, 6.58; N, 9.32; Cl, 12.23. $C_{30}H_{38}Cl_2N_4Cu$ requires C, 61.18; H, 6.50; N, 9.51; Cl, 12.04).

Complexes of 1,4-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 325.

With palladium chloride *viz* 328.

Reaction of 325 (60mg, 0.15mmol), dissolved in hot methanol, and 1 (54mg, 0.30mmol) gave 328 as an orange precipitate which was filtered and washed with hot ethanol (98mg, 87%), m.p. >300°C (Found: C, 38.54; H, 2.45; N, 11.09; Cl, 18.88. $C_{24}H_{20}Cl_4N_6Pd_2$ requires C, 38.59; H, 2.70; N, 11.25; Cl, 18.98). ^1H N.M.R. (DMSO) δ: 6.22, 4H, s, CH_2; 7.46, 2H, d, H4'; 7.47, 4H, s, H2,3,5,6; 7.73, 2H, s, H5"; 8.30, 2H, d, H3"; 8.34, 2H, t, H4"; 8.40, 2H, d, H5'; 9.06, 2H, d, H6".

With silver nitrate *viz* 329.

Reaction of 325 (71mg, 0.18mmol), dissolved in hot methanol (8ml), and 2 (73mg, 43mmol) dissolved in hot methanol (6ml) gave crystals of 329 over 15-30 minutes (91mg, 89%). Slow evaporation of an acetonitrile solution of (8b) gave crystals that

were suitable for single crystal X-ray structure determination, m.p. >300°C (Found: C, 50.76; H, 3.50; N, 17.35. $C_{24}H_{20}N_7O_3Ag.¼H_2O$ requires C, 50.86; H, 3.64; N, 17.29).

With copper chloride dihydrate *viz* 330.

Reaction of 325 (55mg, 0.14mmol) and 3 (57mg, 0.34mmol) gave 330, which was collected by filtration and washed with hot ethanol (90mg, 96%), m.p. > 280°C (dec.) (Found: C, 42.80; H, 3.06; N, 12.30; Cl, 21.04. $C_{24}H_{20}Cl_4N_6Cu_2.½H_2O$ requires C, 43.00; H, 3.16; N, 12.54; Cl, 21.15).

Complexes of 1,3-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 326.

With palladium chloride *viz* 331.

Reaction of 326 (63mg, 0.16mmol), dissolved in hot methanol, and 1 (57mg, 0.32mmol) gave 331 (97mg, 81%), m.p. >300°C (Found: C, 38.37; H, 2.78; N, 11.02; Cl, 18.90. $C_{24}H_{20}Cl_4N_6Pd_2$ requires C, 38.59; H, 2.70; N, 11.25; Cl, 18.98). ^{1}H N.M.R. (DMSO) δ: 6.21, 4H, s, CH_2; 7.29, 1H, s, H2; 7.38, 2H, d, H4,6; 7.45, 2H, d, H4'; 7.49, 1H, t, H5; 7.69, 2H, t, H5"; 8.25, 2H, d, H3"; 8.32, 2H, t, H4"; 8.37, 2H, d, H5'; 8.97, 2H, d, H6".

With silver nitrate *viz* 332.

Reaction of 326 (70mg, 0.18mmol), dissolved in hot methanol (8ml), and 2 (73mg, 43mmol) dissolved in hot methanol (6ml) gave 332 over a period of 1-2 hours (96mg, 95%), m.p. 265-266°C (Found: C, 50.64; H, 3.28; N, 17.19. $C_{24}H_{20}N_7O_3Ag.¼H_2O$ requires C, 50.86; H, 3.64; N, 17.29).

With copper chloride dihydrate *viz* 333.

Reaction of 326 (40mg, 0.10mmol) and 3 (41mg, 0.24mmol) gave 333 which was collected by filtration and washed with hot ethanol (58mg, 87%), m.p. > 280°C (dec.) (Found: C, 42.82; H, 3.33; N, 12.22; Cl, 21.04. $C_{24}H_{20}Cl_4N_6Cu_2.½H_2O$ requires C, 43.00; H, 3.16; N, 12.54; Cl, 21.15).

Complexes of 1,2-Bis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 327.

With palladium chloride *viz* 334.

Reaction of 327 (60mg, 0.15mmol), dissolved in hot methanol (8ml), and 1 (54mg, 0.30mmol) gave 334 (97mg, 87%). Vapour diffusion of methanol into a DMSO solution of 334 gave a microcrystalline solid, m.p. >300°C (Found: C, 38.52; H, 2.83; N, 11.11; Cl, 18.72. $C_{24}H_{20}Cl_4N_6Pd_2$ requires C, 38.59; H, 2.70; N, 11.25; Cl, 18.98). ^{1}H N.M.R. (DMSO) δ: 6.24, 4H, s, CH_2; 7.05, 2H, dd, H3,6; 7.49, 2H, dd, H4,5; 7.52, 2H, d, H4'; 7.74, 2H, t, H5"; 8.12, 2H, d, H5'; 8.36, 2H, t, H4"; 8.36, 2H, d, H3"; 9.07, 2H, d, H6".

With silver nitrate *viz* 335.

Reaction of 327 (70mg, 0.18mmol), dissolved in hot methanol (8ml), and 2 (73mg, 43mmol) dissolved in hot methanol (6ml) gave, over a period of 2-3 hours, crystals of 335 suitable for single crystal X-ray structure determination (75mg, 64%), m.p. > 200°C (dec.) (Found: C, 44.67; H, 3.14; N, 15.89. $C_{48}H_{40}N_{15}O_9Ag_3$ requires C, 44.54; H, 3.11; N, 16.23).

With copper chloride dihydrate *viz* 336.

Reaction of 327 (59mg, 0.15mmol), dissolved in hot methanol (10ml), and 3 (61mg, 0.36mmol) gave 336, which was collected by filtration and washed with hot methanol (89mg, 89%), m.p. > 280°C (dec.) (Found: C, 43.63; H, 3.03; N, 12.62; Cl, 21.24. $C_{24}H_{20}Cl_4N_6Cu_2$ requires C, 43.59; H, 3.05; N, 12.71; Cl, 21.44).

Complexes of 1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzene, 337.

With palladium chloride *viz* 340.

Reaction of 337 (45mg, 0.11mmol), dissolved in hot methanol, and 1 (40mg, 0.23mmol) gave 340 as an orange precipitate which was filtered and washed with hot ethanol (61mg, 68%), m.p. > 300°C (Found: C, 33.49; H, 3.33; N, 14.04; Cl, 18.23. $C_{22}H_{22}Cl_4N_8Pd_2$ requires C, 33.48; H, 3.32; N, 14.20; Cl, 17.97). ^{1}H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 341a and 341b.

Reaction of 337 (104mg, 0.26mmol), dissolved in hot methanol (15ml), and 2 (106mg, 0.63mmol) dissolved in water (5ml) gave a brown precipitate. This was subsequently recrystallised from acetonitrile to give 341a (92mg, 62%), m.p. 247-248°C (Found: C, 46.45; H, 3.93; N, 22.25. $C_{22}H_{22}N_9O_3Ag$ requires C, 46.49; H, 3.90; N, 22.18). Slow evaporation of an acetonitrile solution of 341a gave a crystal of 341b suitable for single crystal X-ray structure determination.

With copper chloride dihydrate *viz* 342a and 342b.

Reaction of 337 (47mg, 0.12mmol) and 3 (40mg, 0.23mmol) gave 342a as orange/brown crystals suitable for single crystal X-ray structure determination (30mg, 38%), m.p. > 250°C (dec.) (Found: C, 39.56; H, 3.40; N, 16.66; Cl, 21.01. $C_{22}H_{22}Cl_4N_8Cu_2$ requires C, 39.59; H, 3.32; N, 16.79; Cl, 21.25). Green/yellow crystals of 342b, suitable for single crystal X-ray structure determination, were also produced in this reaction (46mg, 53%), m.p. > 250°C (dec.) (Found: C, 39.32; H, 3.98; N, 15.36; Cl, 19.52. $C_{22}H_{22}Cl_4N_8Cu_2.2CH_3OH$ requires C, 39.41; H, 4.13; N, 15.32; Cl, 19.39).

Complexes of 1,2,4,5-Tetrakis(3-(2'-pyridyl)pyrazol-1-ylmethyl)benzene, 339.

With palladium chloride *viz* 343.

Reaction of 339 (40mg, 0.06mmol) with 1 (51mg, 0.29mmol) gave an orange precipitate, which was filtered and washed with hot ethanol to give 343 (71mg, 86%), m.p. > 300°C (Found: C, 35.33; H, 2.92; N, 11.85; Cl, 19.75. $C_{42}H_{34}N_{12}Cl_8Pd_4.CH_3OH$ requires C, 35.66; H, 2.64; N, 11.61; Cl, 19.59). ^{1}H N.M.R.: Not sufficiently soluble in common N.M.R. solvents.

With silver nitrate *viz* 344.

Reaction of 339 (71mg, 0.10mmol), dissolved in methanol (8ml), and 2 (75mg, 0.44mmol) dissolved in hot methanol (5ml) gave small crystals of 344 (68mg, 54%), m.p. > 300°C (Found: C, 43.73; H, 2.76; N, 17.75. $C_{84}H_{68}N_{29}O_{15}Ag_3.2H_2O$ requires C, 43.88; H, 3.16; N, 17.67).

With copper chloride dihydrate *viz* 345.

Reaction of 339 (40mg, 0.06mmol) with 3 (50mg, 0.29mmol) gave 345 as a green precipitate over 15-30 minutes (60mg, 80%), m.p. > 300°C (Found: C, 38.36; H, 3.47;

N, 12.71; Cl, 21.54. $C_{42}H_{34}N_{12}Cl_8Cu_4.4H_2O$ requires C, 38.31; H, 3.21; N, 12.77; Cl, 21.54).

Complexes of 1,3,5-Tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene, 400.

With palladium chloride *viz* 401.

Reaction of 400 (110mg, 0.31mmol) with 1 (81mg, 0.46mmol) gave an orange precipitate, which was filtered and washed with methanol to give 400 (189mg, 92%), m.p. > 300°C (Found: C, 38.65; H, 4.27; N, 12.41; Cl, 16.34. $C_{42}H_{48}N_{12}Cl_6Pd_3.CH_3OH.2½H_2O$ requires C, 38.83; H, 4.32; N, 12.64; Cl, 15.99). ^1H N.M.R.: Complex soluble only in DMSO, which gives a spectrum of the ligand and some sort of complex with peaks too broad and overlapped for assignment.

With silver nitrate *viz* 402.

Reaction of 400 (70mg, 0.19mmol), dissolved in methanol (10ml), and 2 (50mg, 0.29mmol) dissolved in water (10ml) gave 402 as colourless needles (86mg, 85%), m.p. > 260°C (dec.). Slow evaporation of an acetonitrile solution of 402 gave crystals suitable for single crystal X-ray structure determination (Found: C, 47.50; H, 4.17; N, 18.48. $C_{14}H_{14}N_5O_3Ag$ requires C, 47.56; H, 4.56; N, 18.49).

With copper chloride dihydrate *viz* 403.

Reaction of 400 (104mg, 0.28mmol) with 3 (49mg, 0.29mmol) gave a green precipitate, which was filtered and washed with methanol to give 403 (122mg, 79%), m.p. > 130°C (Found: C, 46.61; H, 5.32; N, 15.56; Cl, 13.42. $C_{21}H_{24}N_6Cl_2Cu.2½H_2O$ requires C, 46.71; H, 5.41; N, 15.56; Cl, 13.13).

With dichlorotetrakis(dimethylsulfoxide)ruthenium(II) *viz* 404.

A mixture of 400 (41mg, 0.11mmol) and 5 (50mg, 0.10mmol) was refluxed in ethanol/water (3:1, 10ml) for 12 hours. The solvent was then removed under reduced pressure to give the chloride salt of 404 (Found: $M^{+\cdot}$ 497.0801. $C_{21}H_{24}N_6ClRu$ requires $M^{+\cdot}$ 497.0795). This was dissolved in water and filtered. Ammonium hexafluorophosphate (51mg, 0.30mmol) was added to the filtrate to give a pale

yellow/green precipitate of the PF_6^- salt of 404 (34mg, 42%), m.p. > 250°C (dec.). UV/VIS (CH_3CN) λ/nm (ε/M^{-1} cm^{-1}) 222 (11200), 344 (625). ^1H N.M.R. (CD_3CN) δ: 2.19, 9H, s, CH_3; 5.48, 6H, s, CH_2; 6.70, 3H, t, H4'; 7.69, 3H, d, H5'; 8.12, 3H, d, H3'. ^{13}C N.M.R. (CD_3CN) δ: 13.0, CH_3; 51.6, CH_2; 100.6, C2,4,6; 109.2, C1,3,5; 109.6, C4'; 135.1, C5'; 140.7, C3'.

Alternatively, zinc chloride (28mg, 0.21mmol) and aqueous hydrochloric acid (several drops, 2M) were added to the above filtrate, which, over a period of weeks, gave yellow crystals of the $ZnCl_4^{2-}$ salt of 404 suitable for single crystal X-ray structure determination (Found: C, 35.60; H, 3.91; N, 11.83. $C_{21}H_{24}N_6RuZnCl_4.2H_2O$ requires C, 35.79; H, 4.00; N, 11.92.

Complex of 1,3,5-Tris(pyrazol-1-ylmethyl)-2,4-dimethylbenzene, 405, with dichlorotetrakis(dimethylsulfoxide)ruthenium(II) *viz* 408.

A mixture of 405 (60mg, 0.12mmol) and 5 (43mg, 0.12mmol) was refluxed in ethanol/water (3:1, 10ml) under an argon atmosphere for 9 hours. The solvent was then removed under reduced pressure to give the chloride salt of 408 (Found: $M^{+\cdot}$ 483.0642. $C_{20}H_{22}N_6ClRu$ requires $M^{+\cdot}$ 483.0638). This was dissolved in water and filtered. Ammonium hexafluorophosphate (102mg, 0.60mmol) was added to the filtrate to give a pale yellow/green precipitate of the PF_6 salt of 408 (10mg, 11%), m.p. > 240°C (dec.). ^1H N.M.R. (CD_3CN) δ: 2.51, 6H, s, CH_3; 5.58, 2H, d, 1,5-CH_2; 6.03, 2H, s, 3-CH_2; 6.12, 2H, d, 1,5-CH_2; 6.88, 3H, t, 1,3,5-H4'; 6.89, 1H, s, H6; 8.21, 2H, d, 1,5-H5' ; 8.24, 1H, d, 3-H5'; 8.49, 3H, d, 1,3,5-H3'.

Complexes of 1,3,5-Tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 409.

With palladium chloride *viz* 412.

Reaction of 409 (60mg, 0.15mmol), dissolved in hot methanol, and 1 (40mg, 0.23mmol) gave crude 412 as an orange precipitate which was filtered and washed with methanol. This was subsequently recrystallised by vapour diffussion of acetone into a DMSO solution of the precipitate to give pure 412 as crystals suitable for single crystal X-ray structure determination (94mg, 87%), m.p. > 295°C (dec.) (Found: C, 41.09; H, 4.92; N, 11.37; Cl, 14.93. $C_{96}H_{120}N_{24}Cl_{12}Pd_6.2CH_3SOCH_3.4H_2O$ requires C, 41.38; H,

4.86; N, 11.58; Cl, 14.66). ^{1}H N.M.R. (DMSO) δ: 1.23, 36H, t, 2,4,6-CH_3; 2.50, 24H, q, 2,4,6-CH_2; 6.50, 24H, s, 1,3,5-CH_2; 6.65, 12H, t, H4'; 7.93, 12H, d, H5'; 8.15, 12H, d, H3'.

With silver nitrate *viz* 413.

Reaction of 409 (60mg, 0.15mmol) dissolved in methanol (4ml) and 2 (50mg, 0.30mmol) dissolved in water (4ml) gave crystals of 413 suitable for single crystal X-ray structure determination (90mg, 81%), m.p. 244-245°C (Found: C, 39.12; H, 4.03; N, 15.28. $C_{24}H_{30}N_8O_6Ag_2$ requires C, 38.83; H, 4.07; N, 15.10).

With copper chloride dihydrate *viz* 414.

Reaction of 409 (50mg, 0.12mmol) and 3 (21mg, 0.12mmol) gave a green solution. This was filtered, then concentrated under reduced pressure to ~10ml. Diethyl ether was then vapour diffused into this solution to give 414 as a green precipitate (71mg, 96%), m.p. > 170°C (dec.) (Found: C, 46.30; H, 5.18; N, 13.26; Cl, 17.64. $C_{48}H_{60}N_{12}Cl_6Cu_3.1½\ H_2O$ requires C, 46.66; H, 5.14; N, 13.60; Cl, 17.22).

Complexes of 1,3,5-Tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4,6-triethylbenzene, 410.

With palladium chloride *viz* 415.

Reaction of 410 (60mg, 0.12mmol), dissolved in hot methanol, and 1 (33mg, 0.18mmol), upon leaving to evaporate, gave orange crystals of 415, although these were not suitable for single crystal X-ray structure determination (49mg, 59%), m.p. > 300°C (Found: C, 40.04; H, 4.94; N, 9.12; Cl, 22.85. $C_{30}H_{44}N_6Cl_6Pd_2$. ½CH_3OH. requires C, 39.38; H, 4.98; N, 9.03; Cl, 22.86). ^{1}H N.M.R. (DMSO) δ: 0.87, 9H, t, 2,4,6-CH_3; 2.09, 9H, s, 5'-CH_3; 2.39, 9H, s, 3'-CH_3; 2.84, 6H, m, 2,4,6- CH_2; 5.18, 6H, s, 1,3,5- CH_2; 5.91, 3H, t, H4'.

With silver nitrate *viz* 416.

To a mixture of 410 (60mg, 0.12mmol), dissolved in methanol (5ml), and 2 (31mg, 0.18mmol) dissolved in water (3ml) was added excess sodium perchlorate solution, giving 416 as a white solid (66mg, 66%) m.p. >220°C (dec.) (Found: C, 43.14; H, 5.47;

N, 9.95; Cl, 6.52. $(C_{30}H_{42}N_6)_2(AgClO_4)_3.4½H_2O$ requires C, 42.99; H, 5.59; N, 10.02; Cl, 6.34).

With copper chloride dihydrate *viz* 417.

Reaction of 410 (42mg, 0.09mmol) and 3 (22mg, 0.14mmol) gave a green solution. This was concentrated under reduced pressure to ~2ml. Diethyl ether was then vapour diffused into this solution to give crystals of 417 suitable for single crystal X-ray structure determination (39mg, 69%), m.p. > 155°C (dec.) (Found: C, 55.89; H, 7.21; N, 12.76; Cl, 10.68. $C_{30}H_{44}N_6OCl_2Cu.½CH_3OH$ requires C, 55.91; H, 7.08; N, 12.83; Cl, 10.82).

Complex of Hexakis(pyrazol-1-ylmethyl)benzene, 418, with dichlorotetrakis-(dimethylsulfoxide)ruthenium(II) *viz* 419.

A mixture of 418 (73mg, 0.13mmol) and 5 (139mg, 0.29mmol) were refluxed in ethanol/water (3:1, 10ml) for 24 hours, during which time 419 formed as a red/brown precipitate (67mg, 57%), m.p. > 300°C ($M^{+\cdot}$ found: 866.9889. $C_{30}H_{30}N_{12}Cl_3Ru_2$ requires $M^{+\cdot}$ 866.9869. Found: C, 39.57; H, 3.23; N, 17.71; Cl, 15.52. $C_{30}H_{30}N_{12}Cl_4Ru_2$ requires C, 39.92; H, 3.35; N, 18.62; Cl, 15.71).

Cyclopalladated Complexes of Poly(pyrazol-1-ylmethyl)benzenes.

Complex of 1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene, 502, *viz* 506.

A mixture of 502 (50mg, 0.19mmol) and palladium acetate (42mg, 0.19mmol) was refluxed in glacial acetic acid (5ml) for 16 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 2 days and filtered to give 506 (44mg, 56%), m.p. > 285°C (dec.) (Found: C, 45.87; H, 4.34; N, 13.26; Cl, 8.69. $C_{16}H_{17}N_4ClPd.½H_2O$ requires C, 46.17; H, 4.36; N, 13.46; Cl, 8.51). ^1H N.M.R. (DMSO) δ: 2.42, 6H, s, CH_3; 5.53, 4H, s, CH_2; 6.52, 2H, t, H4'; 6.81, 1H, s, H5; 7.92, 2H, d, H5'; 8.39, 2H, d, H3'. ^{13}C N.M.R. (DMSO) δ: 19.60, CH_3; 53.17, CH_2; 106.57, C4'; 129.05, C5; 132.48, C4,6; 132.77, C1,3; 133.02, C5'; 142.74, C3'; 143.97, C2. Recrystallisation of 506 from DMSO yielded crystals suitable for single crystal X-ray structure determination.

Complex of 1,3-Bis(3,5-dimethylpyrazol-1-ylmethyl)-4,6-dimethylbenzene, 503, *viz* 507.

A mixture of 503 (60mg, 0.19mmol) and palladium acetate (42mg, 0.19mmol) was refluxed in glacial acetic acid (5ml) for 6 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 2 days and filtered to give 507 (68mg, 79%), m.p. > 240°C (dec.) (Found: C, 52.08; H, 5.34; N, 12.04; Cl, 7.62. $C_{20}H_{25}N_4ClPd$ requires C, 51.85; H, 5.44; N, 12.09; Cl, 7.65). ^{1}H N.M.R. (DMSO) δ: 2.35, 6H, s, 4,6-CH_3; 2.47, 6H, s, 5'-CH_3; 2.54, 6H, s, 3'-CH_3; 5.40, 4H, s, CH_2; 6.06, 2H, t, H4'; 6.69, 1H, s, H5. ^{13}C N.M.R. (DMSO) δ: 11.35, 5'-CH_3; 14.85, 3'-CH_3; 18.79, 4,6-CH_3; 49.97, CH_2; 106.47, C4'; 127.89, C5; 131.90, C4,6; 133.27, C1,3; 140.69, C5'; 147.33, C2; 150.55, C3'. Vapour diffusion of acetone into a DMSO solution of 507 furnished crystals suitable for single crystal X-ray structure determination.

Complex of 1,3,5-Tris(pyrazol-1-ylmethyl)-2,4-dimethylbenzene, 405, *viz* 508.

A mixture of 405 (61mg, 0.18mmol) and palladium acetate (40mg, 0.18mmol) was refluxed in glacial acetic acid (5ml) for 21 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 2 days and filtered to give 508 (72mg, 74%), m.p. > 280°C (dec.) (Found: C, 44.43; H, 4.84; N, 15.32; Cl, 6.80. $C_{20}H_{21}N_6ClPd.3H_2O$ requires C, 44.38; H, 5.02; N, 15.52; Cl, 6.55). ^{1}H N.M.R. (DMSO) δ: 2.49, 6H, s, CH_3; 5.44, 2H, s, 3- CH_2; 5.64, 4H, s, 1,5-CH_2*; 6.27, 1H, t, 3-H4'; 6.52, 2H, t, 1,5-H4'; 7.47, 1H, d, 3-H5'; 7.60, 1H, d, 3-H3'; 7.90, 2H, d, 1,5-H5'; 8.38, 2H, d, 1,5-H3'. ^{13}C N.M.R. (CD_2Cl_2) δ: 16.09, 2,4-CH_3; 49.85, 3-CH_2; 53.64, 1,5-CH_2; 104.97, 3-C4'; 106.33, 1,5-C4'; 129.25, 3-C5'; 129.93, C3; 132.62, C2,4; 133.14, 1,5-C5'; 133.22, C1,5; 138.53, 3-C3'; 142.36, 1,5-C3'; 144.85, C6.

* At 23°C two broadened signals at 5.44 and 5.84 ppm.

Complex of 1,3,5-Tris(3,5-dimethylpyrazol-1-ylmethyl)-2,4-dimethylbenzene, 406, *viz* 509.

A mixture of 406 (60mg, 0.14mmol) and palladium acetate (31mg, 0.14mmol) was refluxed in glacial acetic acid (5ml) for 22 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 5 days and filtered to give crude 509. This was subsequently recrystallised by vapour diffussion of pentane into a dichloromethane

solution of the crude product to give 509 (62mg, 77%), m.p. > 300°C (Found: C, 54.94; H, 6.07; N, 14.70; Cl, 6.10. $C_{26}H_{33}N_6ClPd$ requires C, 54.65; H, 5.82; N, 14.71; Cl, 6.20). ^{1}H N.M.R. (DMSO) δ: 2.03, 3H, s, 3-5'-CH_3; 2.34, 6H, s, 2,4-CH_3; 2.37, 3H, s, 3-3'-CH_3; 2.47, 6H, s, 1,5-5'-CH_3; 2.54, 6H, s, 1,5-3'-CH_3; 5.07, 2H, s, 3- CH_2; 5.54, 4H, s, 1,5-CH_2*; 5.87, 1H, s, 3-H4'; 6.06, 2H, s, 1,5-H4'. ^{13}C N.M.R. (CD_2Cl_2) δ: 11.16, 3-5'-CH_3; 11.79, 1,5-5'-CH_3; 13.43, 3-3'-CH_3; 14.97, 2,4-CH_3; 15.79, 1,5-3' CH_3; 46.96, 3-CH_2; 50.97, 1,5-CH_2; 104.74, 3-C4'; 106.93, 1,5-C4'; 130.08, C3; 132.68, C2,4; 134.28, C1,5; 138.72, 3-C5'; 140.49, 1,5-C5'; 147.15, 3-C3'; 147.83, C6; 151.93, 1,5-C3'.

* At 23°C two pairs of geminally coupled doublets at 5.48 and 5.60 ppm.

Complexes of 1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzene, 337.

Singly palladated complex *viz* 511.

A mixture of 337 (309mg, 0.78mmol) and palladium acetate (87mg, 0.39mmol) was refluxed in glacial acetic acid (20ml) for 2 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 44 hours and filtered to give crude 511 as a white precipitate (172mg, 80%). This was used in this form for subsequent reactions although a sample was purified by vapour diffusion of acetone into a DMSO solution of the crude product, m.p. > 300°C (Found: C, 48.61; H, 3.72; N, 20.50; Cl, 6.93. $C_{22}H_{21}ClN_8Pd$ requires C, 48.99; H, 3.92; N, 20.78; Cl, 6.57). ^{1}H N.M.R. (DMSO) δ: 5.55, 4H, s, 3,5- CH_2; 5.71, 4H, s, 2,6-CH_2*; 6.34, 2H, t, 3,5-H4'; 6.51, 2H, t, 2,6-H4'; 6.94, 1H, s, H4; 7.54, 2H, d, 3,5-H5'; 7.82, 2H, d, 3,5-H3'; 7.90, 2H, d, 2,6-H5'; 8.17, 2H, d, 2,6-H3'. ^{13}C N.M.R. (DMSO) δ: 52.50, 2,4-CH_2; 52.86, 1,5-CH_2; 105.62, 2,4-C4'; 106.37, 1,5-C4'; 128.08, C3; 129.88, 2,4-C5'; 132.57, C2,4; 132.78, 1,5-C5'; 135.02, C1,5; 139.00, 2,4-C3'; 142.54, 1,5-C3'; 146.29, C6. Unreacted 337 was recovered by removing the acetone from the filtrate under reduced pressure and filtering the resulting precipitate (94mg).

* At 23°C two broad signals at 5.39 and 6.03 ppm.

Doubly palladated complex *viz* 510.

a) A mixture of 337 (54mg, 0.14mmol) and palladium acetate (61mg, 0.27mmol) was refluxed in glacial acetic acid (5ml) for 21 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 10 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 4 days and filtered to give crude 510

as a yellow/brown precipitate. Isolation of 510 from this product mixture was not achieved.

b) A mixture of 511 (66mg, 0.12mmol) and palladium acetate (27mg, 0.12mmol) was refluxed in glacial acetic acid (5ml) for 24 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 5 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 4 days and filtered to give 510 as a white precipitate (69mg, 85%), m.p. > 300°C (Found: C, 39.16; H, 3.12; N, 16.50; Cl, 10.18. $C_{22}H_{20}Cl_2N_8Pd_2$ requires C, 38.85; H, 2.96; N, 16.47; Cl, 10.42). ^{1}H N.M.R. (DMSO) δ: 5.78, 8H, s, CH_2*; 6.51, 4H, t, H4'; 7.93, 4H, d, H5'; 8.33, 4H, d, H3'. ^{13}C N.M.R. (DMSO) δ: 53.22, CH_2; 106.60, C4'; 132.13, C1,2,4,5; 132.39, C5'; 142.43, C3'; C3,6, not observed.

* At 23°C two broad signals at 5.47 and 6.15 ppm.

Complex of 1,2,4,5-Tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene, 338, *viz* 512.

A mixture of 338 (78mg, 0.15mmol) and palladium acetate (67mg, 0.30mmol) was refluxed in glacial acetic acid (5ml) for 28 hours. The solvent was then removed under vacuum. To the resulting residue was added excess lithium chloride (> 10 equiv.) and this was stirred in acetone/water (3:2, 5ml) for 4 days and filtered to give crude 512 as a yellow/brown precipitate. Vapour diffusion of methanol into a DMSO solution of the crude product yielded crystals of 512 suitable for single crystal X-ray structure determination (37mg, 27%), m.p. > 300°C (Found: C, 44.76; H, 5.01; N, 13.23; Cl, 8.45. $C_{30}H_{36}N_8Cl_2Pd_2.2CH_3OH$. requires C, 44.88; H, 5.18; N, 13.08; Cl, 8.28). ^{1}H N.M.R. (DMSO) δ: 2.51, 12H, s, 5'-CH_3; 2.55, 12H, s, 3'-CH_3; 5.54, 8H, s, CH_2*; 6.03, 4H, s, H4'. ^{13}C N.M.R. (DMSO) δ: 11.58, 5'-CH_3; 14.79, 3'-CH_3; 50.07, CH_2; 106.66, C4'; 131.81, C1,2,4,5; 141.24, C5'; 143.10, C3,6; 150.55, C3';

* At 23°C two pairs of geminally coupled doublets at 5.50 and 5.58 ppm.

Attempted Cycloruthenation Reactions of Poly(pyrazol-1-ylmethyl)benzenes.

Cycloruthenation of 1,3-Bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene, 502, *viz* 514 and 515.

A mixture of terpyridinetrichlororuthenium(III) (60mg, 0.14mmol) and silver tetrafluoroborate (85mg, 0.44mmol) was refluxed in acetone (15ml) for 2 hours. This mixture was then filtered and the solvent removed under reduced pressure. 502 (36mg,

0.14mmol) was added and this mixture refluxed in 1-butanol (10ml) for 19 hours then filtered. The residue was washed repeatedly with water.

a) The aqueous washings were concentrated, then subjected to ion exchange chromatography (sephadex, 50:50 NaCl(0.1M)/acetone). The first fraction collected was concentrated, redissolved in water and excess ammonium hexafluorophosphate added to give pure 514 (40mg, 33%), m.p. > 210°C (dec.) (Found: $M^{+\cdot}$, 746.1172. $C_{31}H_{29}N_7RuPF_6$ requires $M^{+\cdot}$, 746.1170). ^{1}H N.M.R. ($(CD_3)_2CO$) δ: 2.74, 6H, s, CH_3; 5.62, 2H, d, CH_2; 6.07, 2H, d, CH_2; 6.29, 2H, t, H4'; 6.51, 2H, d, H3'; 6.52, 1H, d, H6''''; 7.39, 1H, s, H2; 7.58, 1H, t, H5''''; 8.03, 1H, t, H5''; 8.19, 1H, t, H4''''; 8.31, 2H, d, H5'; 8.38, 1H, s, H5; 8.44, 1H, t, H4''; 8.63, 1H, t, H4'''; 8.78, 1H, d, H3''''; 8.97, 1H, d, H3''; 9.01, 1H, d, H5'''; 9.04, 1H, d, H3'''; 10.09, 1H, d, H6''.

b) To the aqueous washings was added excess ammonium hexafluorophosphate, which gave a mixture of 514 and another terpyridineruthenium complex not containing the pyrazolyl ligand. Upon subjecting this mixture to column chromatography (silica, acetone), an intense purple band developed in the column. This fraction was collected and the solvent removed under reduced pressure to give 515 (33mg, 33%), m.p. > 300°C (Found: $M^{+\cdot}$, 600.1447. $C_{31}H_{28}N_7Ru$ requires $M^{+\cdot}$, 600.1450). UV/VIS (CH_3CN) λ/nm (ε/M^{-1} cm^{-1}) 230 (31331), 280 (27003), 316 (26953), 324 (29568), 384 (5888), 526 (6531), 576 (6308), 658 (2666). ^{1}H N.M.R. ($(CD_3)_2CO$) δ: 2.64, 6H, s, CH_3; 5.56, 4H, s, CH_2; 6.01, 2H, t, H4'; 6.18, 2H, d, H3'; 6.93, 1H, s, H5; 7.48, 2H, t, H5''; 8.00, 2H, d, H5'; 8.08, 2H, t, H4''; 8.35, 1H, t, H4'''; 8.39, 2H, d, H6''; 8.73, 2H, d, H3''; 8.93, 2H, d, H3''', 5'''. Vapour diffusion of pentane into an acetone solution of 515 gave crystals suitable for single crystal X-ray structure analysis.

Attempted Cycloruthenation of 1,2,4,5-Tetrakis(pyrazol-1-ylmethyl)benzene, 337.

A mixture of terpyridinetrichlororuthenium(III) (101mg, 0.23mmol) and silver tetrafluoroborate (143mg, 0.73mmol) was refluxed in acetone (20ml) for 3 hours. This mixture was then filtered and the solvent removed under reduced pressure. 337 (35mg, 0.089mmol) was added and this mixture refluxed in 1-butanol (10ml) for 20 hours then filtered. The residue was washed repeatedly with water. To the aqueous washings was added excess ammonium hexafluorophosphate which gave a mixture of compounds as a brown precipitate. Isolation of the components of this mixture was not achieved.

Crystallography

Crystallography

Tables E1-E7 list crystal data and X-ray experimental details for the thirty two structures determined. While selected bond distances and angles were listed below the structures discussed, remaining distances and angles, as well as atom coordinates, anisotropic displacement parameters and hydrogen atom coordinates, are available in the University of Canterbury Chemistry Department.

Intensity data were collected with a Siemens P4s four-circle diffractometer by using monochromatized Mo $K\alpha$ radiation. Cell parameters were determined by least squares refinement, the setting angles of at least 18 accurately centred reflections ($2\theta > 20°$) being used. Throughout the data collections the intensities of three standard reflections were monitored at regular intervals and, in most cases, this indicated no significant crystal decomposition. The intensities were corrected for Lorentz polarisation and, where necessary, absorption effects.

The structures were solved by direct or Patterson methods using SHELXS 93/96[288] and refined, using SHELXL,[289] on F^2 using all data. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma 2(F_o^2) + aP^2 + bP]^{-1}$ where $P = [\max(F_o^2 + 2F_c^2)]/3$. Hydrogens were included in calculated positions and assigned isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. In all cases final Fourier syntheses showed no significant residual electron density in chemically sensible locations.

Table E1 Crystal Data and X-Ray Experimental Details for 202, 208, 210, 216 and 219

Compound	**202**	**208**	**210**	**216**	**219**
Formula	$C_{16}H_{14}AgN_3O_6$	$C_{16}H_{14}AgN_3O_6$	$C_{16}H_{12}Cl_2N_2O_2Pd$	$C_9H_8Ag_{0.5}N_{1.5}O_{2.5}$	$C_{18}H_{16}AgN_3O_5$
Formula Weight	452.17	452.17	441.58	231.11	462.21
a (Å)	11.111(1)	20.751(4)	8.512(1)	15.793(2)	12.235(1)
b (Å)	10.964(1)	9.311(1)	17.845(1)	12.699(1)	9.050(1)
c (Å)	13.128(1)	18.659(3)	11.172(1)	10.959(1)	15.820(2)
α (°)	90	90	90	90	90
β (°)	92.324(6)	113.21(1)	106.41(1)	128.283(8)	97.36(1)
γ (°)	90	90	90	90	90
V (Å^3)	1598.0(2)	3313.4(9)	1627.9(3)	1725.3(4)	1737.3(3)
Space Group	$P2_1/n$	C2/c	$P2_1/c$	C2/c	$P2_1/c$
Z	4	8	4	8	4
F(000)	904	1808	872	928	928
Temperature (K)	130(2)	158(2)	168(2)	188(2)	130(2)
Crystal Size (mm)	0.50 x 0.36 x 0.30	0.56 x 0.49 x 0.31	0.60 x 0.19 x 0.16	0.52 x 0.28 x 0.19	0.31 x 0.15 x 0.12
2θ range	4 - 52	4 - 55	4 - 50	4 - 50	4 - 50
Unique reflections	3145	3797	2874	1513	3057
GooF	0.942	1.074	0.940	1.068	0.766
R [I > 2σ(I)]	0.0257	0.0235	0.0213	0.0475	0.0281
wR2 (all data)	0.0631	0.0623	0.0523	0.1182	0.0441

Table E2 Crystal Data and X-Ray Experimental Details for 218, 225, 228, 231 and 232

Compound	**218**	**225**	**228**	**231**	**232**
Formula	$C_{19.5}H_{19}Cl_2N_2O_{2.5}Pd$	$C_{18}H_{16}AgN_3O_3S_2$	$C_{18}H_{16}AgN_3O_3S_2$	$C_{18}H_{16}AgN_3O_3S_2$	$C_{19}H_{20}Cl_2CuN_2OS_2$
Formula Weight	498.67	494.33	494.33	494.33	490.93
a (Å)	15.428(4)	7.803(2)	8.281(3)	8.556(1)	8.785(4)
b (Å)	7.921(2)	10.173(1)	10.011(3)	10.617(1)	11.075(5)
c (Å)	32.63(1)	13.206(2)	11.488(4)	19.827(2)	12.090(5)
α (°)	90	104.39(1)	106.16(2)	90	97.10(3)
β (°)	97.86(3)	103.84(2)	97.04(3)	97.25(1)	102.87(3)
γ (°)	90	104.66(1)	91.75(3)	90	112.28(3)
V ($Å^3$)	3950(2)	929.9(3)	905.8(5)	1786.7(3)	1032.5(8)
Space Group	C2/c	P-1	P-1	$P2_1/n$	P-1
Z	8	2	2	4	2
F(000)	2000	496	496	992	502
Temperature (K)	130(2)	168(2)	158(2)	169(2)	158(2)
Crystal Size (mm)	0.68 x 0.41 x 0.03	0.26 x 0.21 x 0.13	0.54 x 0.52 x 0.12	0.64 x 0.46 x 0.27	0.41 x 0.26 x 0.10
2θ range	4 - 48	4 - 55	4 - 50	4 - 50	4 - 50
Unique reflections	3083	4194	3152	3153	3271
GooF	0.807	0.903	0.966	1.027	0.738
R [$I > 2\sigma(I)$]	0.0622	0.0301	0.0795	0.0253	0.0585
wR2 (all data)	0.1874	0.0598	0.2145	0.0643	0.1070

Table E3 Crystal Data and X-Ray Experimental Details for 235, 303, 305, 308 and 311

Compound	**235**	**303**	**305**	**308**	**311**
Formula	$C_{15}H_{15}AgN_3O_4S_2$	$C_9H_{11}Ag_{0.5}N_{2.5}O_{1.5}$	$C_{28}H_{28}Ag_2N_{10}O_6$	$C_{14}H_{14}AgN_5O_3$	$C_{30}H_{26}Ag_2N_8O_8$
Formula Weight	473.29	232.14	816.34	408.17	836.35
a (Å)	9.360(1)	14.342(3)	16.918(2)	10.156(2)	17.039(5)
b (Å)	9.712(1)	10.239(2)	7.903(1)	16.784(1)	8.981(2)
c (Å)	10.042(1)	13.864(3)	22.728(2)	17.294(2)	20.276(5)
α (°)	92.42(1)	90	90	90	90
β (°)	100.10(1)	119.43(3)	90	90	95.30(2)
γ (°)	109.98(1)	90	90	90	90
V (Å^3)	839.5(2)	1773.2(6)	3038.8(6)	2947.9(7)	3090(1)
Space Group	P-1	C2/c	$Pna2_1$	Pbca	$P2_1/n$
Z	2	8	4	8	8
F(000)	474	944	1632	1632	1680
Temperature (K)	169(2)	137(2)	130(2)	137(2)	169(2)
Crystal Size (mm)	0.42 x 0.31 x 0.21	0.42 x 0.36 x 0.09	0.40 x 0.15 x 0.11	0.50 x 0.35 x 0.23	0.35 x 0.34 x 0.10
2θ range	4 - 50	4 - 54	4 - 50	4 - 50	4 - 50
Unique reflections	2944	1906	2719	2583	5432
GooF	0.876	1.085	0.750	0.877	0.750
R [I > 2σ(I)]	0.0320	0.0233	0.0319	0.0377	0.0673
wR2 (all data)	0.0658	0.0576	0.0485	0.0857	0.1653

Table E4 Crystal Data and X-Ray Experimental Details for 316, 317, 324, 335 and 341b

Compound	**316**	**317**	**324**	**335**	**341b**
Formula	$C_{30}H_{38}Cl_2N_4Pd$	$C_{30}H_{38}AgN_5O_3$	$C_{30}H_{38}Cl_2CuN_4$	$C_{24}H_{20}Ag_{1.5}N_{7.5}O_{4.5}$	$C_{34}H_{33}Ag_3N_{15}O_6$
Formula Weight	631.94	624.52	589.08	647.28	1071.32
a (Å)	15.178(3)	13.142(3)	15.784(2)	9.814(3)	10.943(1)
b (Å)	29.512(5)	7.128(3)	15.784(2)	9.937(2)	33.873(5)
c (Å)	13.829(4)	15.827(3)	23.806(3)	12.368(3)	10.416(2)
α (°)	90	90	90	78.82(2)	90
β (°)	90	102.12(1)	90	77.21(2)	102.54(1)
γ (°)	90	90	90	81.66(2)	90
V (Å^3)	6195(2)	1449.6(7)	5904(1)	1147.2(6)	3769(1)
Space Group	$P2_12_12$	$P2_1$	$P4_3$	P-1	$P2_1/c$
Z	8	2	8	2	4
F(000)	2608	648	2472	646	2124
Temperature (K)	173(2)	158(2)	168(2)	166(2)	168(2)
Crystal Size (mm)	0.78 x 0.62 x 0.14	0.89 x 0.36 x 0.12	0.53 x 0.26 x 0.24	0.35 x 0.17 x 0.16	0.42 x 0.31 x 0.15
2θ range	4 - 48	4 - 60	4 - 55	4 - 50	4 - 52
Unique reflections	5344	4536	6920	4039	7415
GooF	0.840	0.834	0.532	0.856	0.744
R [I > 2σ(I)]	0.0631	0.0478	0.0457	0.0420	0.0363
wR2 (all data)	0.1586	0.0964	0.0712	0.0915	0.0650

Table E5 Crystal Data and X-Ray Experimental Details for 342a, 342b, 402, 404 and 413 –

Compound	**342a**	**342b**	**402**	**404**	**413**
Formula	$C_{22}H_{22}Cl_4Cu_2N_8$	$C_{24}H_{30}Cl_4Cu_2N_8O_2$	$C_{21}H_{24}AgN_7O_3$	$C_{21}H_{30}Cl_4N_6O_3RuZn$	$C_{24}H_{30}Ag_2N_8O_6$
Formula Weight	667.36	731.44	530.34	722.75	742.30
a (Å)	8.333(1)	8.785(1)	14.158(5)	10.330(2)	10.060(1)
b (Å)	13.645(1)	12.934(1)	10.022(1)	11.557(3)	11.695(1)
c (Å)	11.548(1)	13.064(1)	15.346(4)	12.835(3)	11.886(1)
α (°)	90	90	90	114.86(2)	85.22(1)
β (°)	102.15(1)	94.65(1)	106.57(2)	102.61(2)	75.38(1)
γ (°)	90	90	90	93.59(2)	81.84(1)
V (Å^3)	1283.6(2)	1479.5(2)	2087.0(9)	1336.0(5)	1337.8(2)
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1	P-1
Z	2	2	4	2	2
F(000)	672	744	1080	728	744
Temperature (K)	168(2)	168(2)	173(2)	188(2)	168(2)
Crystal Size (mm)	0.34 x 0.13 x 0.09	0.39 x 0.22 x 0.13	0.42 x 0.21 x 0.09	0.40 x 0.29 x 0.06	0.57 x 0.23 x 0.18
2θ range	4 - 50	4 - 50	4 - 50	4 - 50	4 - 50
Unique reflections	2253	2601	3321	4078	4477
GooF	0.782	0.890	1.027	0.916	1.039
R [I > 2σ(I)]	0.0331	0.0289	0.0496	0.0611	0.0428
wR2 (all data)	0.0659	0.0666	0.1041	0.1560	0.1088

Table E6 Crystal Data and X-Ray Experimental Details for 412, 418, 419, 506 and 507

Compound	**412**	**418**	**419**	**506**	**507**
Formula	$C_{112}H_{184}Cl_{12}N_{24}O_{16}Pd_6S_8$	$C_{61}H_{92}Cl_4Cu_2N_{12}O_3$	$C_{30}H_{30}N_{12}$	$C_{18}H_{23}ClN_4OPdS$	$C_{20}H_{25}ClN_4Pd$
Formula Weight	3443.12	1310.35	558.66	485.31	463.29
a (Å)	19.648(6)	12.929(3)	9.867(1)	11.686(4)	12.636(9)
b (Å)	19.730(5)	15.178(3)	10.472(1)	7.925(2)	8.051(3)
c (Å)	24.995(5)	16.934(3)	14.500(2)	21.587(6)	19.21(1)
α (°)	97.94(1)	93.63(1)	69.03(1)	90	90
β (°)	108.88(1)	97.60(1)	82.31(1)	91.93(2)	90.44(7)
γ (°)	95.17(2)	90.69(1)	77.69(1)	90	90
V ($Å^3$)	8985(4)	3286(1)	1364.1(3)	1998(1)	1954(2)
Space Group	P-1	P-1	P-1	$P2_1/c$	$P2_1$
Z	2	2	2	4	4
F(000)	3520	1384	588	984	944
Temperature (K)	168(2)	168(2)	131(2)	168(2)	132(2)
Crystal Size (mm)	0.44 x 0.30 x 0.17	0.49 x 0.27 x 0.26	0.75 x 0.60 x 0.57	0.54 x 0.38 x 0.22	0.30 x 0.28 x 0.13
2θ range	4 - 44	4 - 45	4 - 50	4 - 55	4 - 45
Unique reflections	21966	8581	4656	4592	2770
GooF	0.697	0.716	0.931	0.839	1.072
R [$I > 2\sigma(I)$]	0.0692	0.0506	0.0395	0.0376	0.0697
wR2 (all data)	0.1849	0.1087	0.0972	0.0822	0.1688

Table E7 Crystal Data and X-Ray Experimental Details for 512 and 515

Compound	**512**	**515**
Formula	$C_{32}H_{44}Cl_2N_8O_2Pd_2$	$C_{31}H_{28}F_6N_7PRu$
Formula Weight	856.45	744.64
a (Å)	14.546(5)	18.581(4)
b (Å)	15.461(7)	14.233(3)
c (Å)	16.435(4)	23.088(5)
α (°)	90.69(3)	90
β (°)	99.17(2)	90
γ (°)	106.55(3)	90
V (Å^3)	3491(2)	6106(2)
Space Group	P-1	Pbca
Z	4	8
F(000)	1736	3008
Temperature (K)	132(2)	151(2)
Crystal Size (mm)	0.32 x 0.24 x 0.21	0.64 x 0.51 x 0.10
2θ range	4 - 50	4 - 50
Unique reflections	12210	5369
GooF	0.865	0.772
R [I > 2σ(I)]	0.0563	0.0399
wR2 (all data)	0.1359	0.0807

References

References

1 *Comprehensive Coordination Chemistry, Vol 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, 1987.

2 *Comprehensive Coordination Chemistry, Vol 6* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, 1987.

3 P. J. Steel, *Coord. Chem. Rev.*, 1990, **106**, 227.

4 E. C. Constable, and P. J. Steel, *Coord. Chem. Rev.*, 1989, **93**, 205.

5 A. Togni, and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497 and references therein.

6 M. Beley, J.-P. Collin, and J.-P. Sauvage, *Inorg. Chem.*, 1993, **32**, 4539 and references therein.

7 A. J. Amoroso, A. M. Cargill Thompson, J. P. Maher, J. A. McCleverty, and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 4828 and references therein.

8 B. J. Coe, D. A. Friesen, D. W. Thompson, and T. J. Meyer, *Inorg. Chem.*, 1996, **35**, 4575.

9 S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115.

10 M. D. Ward, *Chem. Soc. Rev.*, 1995, 187.

11 G. A. Doyle, D. M. Goodgame, S. P. Hill, S. Menzer, A. Sinden, and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 2850.

12 A. Bilyk, M. M. Harding, P. Turner, and T. W. Hambley, *J. Chem. Soc. Dalton Trans.*, 1994, 2783 and references therein.

13 E. C. Constable, *Chem. Ind. (London)*, 1994, **56**, 12.

14 D. M. Goodgame, S. Menzer, A. M. Smith, and D. J. Williams, *J. Chem. Soc. Chem. Commun.*, 1995, 1975 and references therein.

15 S. Achar, and R. J. Puddephatt, *J. Chem. Soc. Chem. Commun.*, 1994, 1895.

16 L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *Inorg. Chem.*, 1995, **34**, 5698 and references therein.

17 E. C. Constable, S. A. Elder, J. Healy, M. D. Ward, and D. A. Tocher, *J. Am. Chem. Soc.*, 1990, **112**, 4590.

18 *Comprehensive Supramolecular Chemistry, Vol 9* (Ed.:J.-M. Lehn), Pergamon, Oxford, 1996.

19 C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1079.

20 D. S. Lawrence, T. Jiang, and T. Levett, *Chem. Rev.*, 1995, **95**, 2229.

21 J.-M. Lehn, *Supramolecular Chemistry*, 1995, VCH, Weinhem, 1995.

22 A. D. Hamilton in *Comprehensive Supramolecular Chemistry, Vol 9* (Ed.:J.-M. Lehn), Pergamon, Oxford, 1996, Chapter 18.

23 M. Fujita, and K. Ogura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1471.

24 E. C. Constable, *Pure. Appl. Chem.*, 1996, **68**, 253.

25 H. Murner, A. von Zelewsky, and H. Stoeckli-Evans, *Inorg. Chem.*, 1996, **35**,

26 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.

27 S. Ruttimann, G. Bernardinelli, and A. F. Williams, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 392.

28 B. Konig, *Chem. Ber.*, 1995, **128**, 1141 and references therein.

29 D. Philp, and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.

30 E. C. Constable, and D. Smith, *Chem. Brit.*, 1995, **31**, 33 and references therein.

31 W. L. Jorgensen, and D. L. Severance, *J. Am. Chem. Soc.*, 1990, **112**, 4768.

32 C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1584.

33 V. E. Williams, R. P. Lemieux, and G. R. Thatcher, *J. Org. Chem.*, 1996, **61**, 1927.

34 F. Cozzi, and J. S. Siegel, *Pure. Appl. Chem.*, 1995, **67**,

35 F. Blau, *Chem. Ber.*, 1888, **21**, 1077.

36 J. Reedijk in *Comprehensive Coordination Chemistry, Vol 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, 1987, p. 73 and references therein.

37 E. C. Constable, *Adv. Inorg. Chem.*, 1989, **34**, 1 and references therein.

38 G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A.-M. Manotti-Lanfredi, and A. Tiripicchio, *J. Chem. Soc. Dalton. Trans*, 1981, 2280.

39 E. Spodine, J. Manzur, S. Garcia-Blanco, M. T. Garland, J. P. Fackler, R. J. Staples, and B. Trzcinska-Bancroft, *Inorg. Chim. Acta*, 1993, **203**, 73.

40 N. Ray, and B. Hathaway, *J. Chem. Soc. Dalton Trans.*, 1980, 1105.

41 E. A. Griffith, H.-Y. Li, and E. L. Amma, *Inorg. Chim. Acta*, 1988, **148**, 203.

42 G. Tresoldi, E. Rotondo, P. Piraino, M. Lanfranchi, and A. Tiripicchio, *Inorg. Chim. Acta*, 1992, **194**, 233.

43 M. T. Garland, D. Grandjean, E. Spodine, and J. Manzur, *Acta Cryst., Sect. C*, 1987, **43**, 643.

44 G. R. Newkome, V. K. Gupta, H. C. Taylor, and F. R. Fronczek, *Organometallics*, 1984, **3**, 1549.

45 G. De Munno, G. Bruno, E. Rotondo, G. Giordano, S. Le Schiavo, P. Piraino, and G. Tresoldi, *Inorg. Chim. Acta*, 1993, **208**, 67.

46 G. A. Bowmaker, P. C. Healy, D. L. Kepert, J. P. Kildea, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton. Trans*, 1989, 1639.

47 R. A. Howie, and G. P. McQuillan, *J. Chem. Soc. Dalton Trans.*, 1986, 759.

48 S. O. Sommerer, B. L. Westcott, and K. A. Abboud, *Acta Cryst., Sect. C*, 1994, **50**, 48.

49 A. T. Marcelis, H.-J. Korte, B. Krebs, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 4059.

50 W. Kleibohmer, B. Krebs, A. T. Marcelis, J. Reedijk, and J. L. Van der Veer, *Inorg. Chim. Acta*, 1983, **75**, 45.

51 G. R. Newkome, G. E. Kiefer, Y. A. Frere, M. Onishi, V. K. Gupta, and F. R. Fronczek, *Organometallics*, 1986, **5**, 348.

52 K. Ida, H. Sakiyama, H. Okawa, M. Matsumoto, Y. Aratake, I. Murase, and S. Kida, *Polyhedron*, 1992, **11**, 65.

53 A. T. Baker, J. K. Crass, G. B. Kok, J. D. Orbell, and E. Yuriev, *Inorg. Chim. Acta*, 1993, **214**, 169.

54 M. M. Kadooka, L. G. Warner, and K. Seff, *Inorg. Chem.*, 1976, **15**, 812.

55 M. M. Kadooka, L. G. Warner, and K. Seff, *J. Am. Chem. Soc.*, 1976, **98**, 7569.

56 A. MacFarlane, J. R. Lusty, J. J. Fiol, A. Terron, E. Molins, C. Miracitlles, and V. Moreno, *Z. Naturforsch., Teil. B*, 1994, **49**, 844.

57 M. M. Kadooka, E. Hilti, L. G. Warner, and K. Seff, *Inorg. Chem.*, 1976, **15**, 1186.

58 E. Spodine, A. M. Atria, V. Calvo, J. Manzur, M. T. Garland, D. Grandjean, and O. Pena, *Bull. Soc. Chil. Quim.*, 1991, **36**, 209.

59 M. Fujita, J. Yazaki, and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.

60 M. Fujita, J. Yazaki, and K. Ogura, *Chem. Lett.*, 1991, 1031.

61 M. Fujita, and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249.

62 V. W.-W. Yam, V. C.-Y. Lau, and K.-K. Cheung, *J. Chem. Soc. Chem. Commun.*, 1995, 259.

63 M. Fujita, Y. J. Kwon, M. Miyazawa, and K. Ogura, *J. Chem. Soc. Chem. Commun.*, 1994, 1977.

64 M. Fujita, S. Nagao, M. Iida, K. Ogata, and K. Ogura, *J. Am. Chem. Soc.*, 1993, **115**, 1574.

65 M. Fujita, S. Nagao, and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649.

66 M. Fujita, F. Ibukuro, K. Yamaguchi, and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 4175.

67 J. Vicente, M.-T. Chicote, and C. Rubio, *Chem. Ber.*, 1996, **129**, 327 and references therein.

68 K. Umakoshi, I. Kinoshita, Y. Fukui-Yasuba, K. Matsumoto, S. Ooi, H. Nakai, and M. Shiro, *J. Chem. Soc. Dalton Trans.*, 1989, 815.

69 K. Umakoshi, I. Kinoshita, and S. Ooi, *Inorg. Chim. Acta*, 1987, **127**, L41.

70 E. Block, G. Ofori-Okai, H. Kang, J. Wu, and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 4784.

71 P. Mura, B. G. Olby, and S. D. Robinson, *Inorg. Chim. Acta*, 1985, **98**, L21.

72 A. Castineiras, W. Hiller, J. Strahle, J. Bravo, J. S. Casas, M. Gayoso, and J. Sordo, *J. Chem. Soc. Dalton Trans.*, 1986, 1945.

73 R. Uson, A. Laguna, M. Laguna, J. Jimenez, M. P. Gomez, A. Sainz, and P. G. Jones, *J. Chem. Soc. Dalton Trans.*, 1990, 3457.

74 S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Hountas, and A. Terzis, *Inorg. Chim. Acta*, 1991, **184**, 161.

75 P. Karagiannidis, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas, and A. Terzis, *Inorg. Chim. Acta*, 1989, **156**, 265.

76 P. Karagiannidis, P. Aslanidis, S. Kokkou, and C. J. Cheer, *Inorg. Chim. Acta*, 1990, **171**, 247.

77 A. J. Deeming, M. N. Meah, P. A. Bates, and M. B. Hursthouse, *Inorg. Chim. Acta*, 1988, **142**, 37.

78 R. R. Renshaw, and R. C. Conn, *J. Am. Chem. Soc.*, 1937, **59**, 297.

79 G. Smith, A. N. Reddy, K. A. Byriel, and C. H. Kennard, *Polyhedron*, 1994, **13**, 2425 and references therein.

80 M. Hedrich, and H. Hartl, *Acta Cryst., Sect. C*, 1983, **39**, 1649.

81 S. Menchetti, G. Rossi, and V. Tazzoli, *Read. Ist. Lomb. Acc. Sci. Lett. A*, 1970, **104**, 309.

82 L. M. Engelhardt, C. Pakawatchai, A. H. White, and P. C. Healy, *J. Chem. Soc. Dalton Trans.*, 1985, 117.

83 S. Gotsis, and A. H. White, *Aust. J. Chem.*, 1987, **40**, 1603.

84 X. Zhaoxiong, L. Wei, L. Haifeng, and Z. Lansun, *Xiamen Dax. Xuebao, Zir. Kex.*, 1992, **31**, 261.

85 S. P. Neo, Z. -. Zhou, T. C. Mak, and T. S. Hor, *Inorg. Chem.*, 1995, **34**, 520.

86 T. Susuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa, and M. Ochi, *Inorg. Chem.*, 1995, **34**, 530.

87 F. Caruso, M. Camalli, H. Rimml, and L. M. Venanzi, *Inorg. Chem.*, 1995, **34**, 673.

88 S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455.

89 S. K. Mandal, L. K. Thompson, M. J. Newlands, E. J. Gabe, and F. L. Lee, *J. Chem. Soc. Chem. Commun.*, 1989, 744.

90 S. K. Mandal, L. K. Thompson, M. J. Newlands, E. J. Gabe, and F. L. Lee, *Inorg. Chem.*, 1990, **29**, 3556.

91 S. S. Tandon, L. K. Thompson, J. N. Bridson, and J. C. Dewar, *Can. J. Chem.*, 1992, **70**, 2771.

92 G. Hogarth, and T. Norman, *J. Chem. Soc. Dalton Trans.*, 1996, 1077.

93 T. Dahl, *Acta Chem. Scand.*, 1994, **48**, 95.

94 A. S. Shetty, S. Zhang, and J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 1019 and references therein.

95 G. D. Smith, and R. L. Jaffe, *J. Phys. Chem.*, 1996, **100**, 9624 and references therein.

96 K. Tani, M. Yabuta, S. Nakamura, and T. Yamagata, *J. Chem. Soc. Dalton Trans.*, 1993, 2781.

97 H. M. Buch, and C. Kruger, *Acta Cryst., Sect. C*, 1984, **40**, 28.

98 G. R. Newkome, F. R. Fronczek, V. K. Gupta, W. E. Puckett, D. C. Pantaleo, and G. E. Kiefer, *J. Am. Chem. Soc.*, 1982, **104**, 1782.

99 W. L. Darby, R. J. Butcher, and L. M. Vallarino, *Inorg. Chim. Acta*, 1992, **194**, 113.

100 A. J. Canty, N. J. Minchin, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1992, **45**, 423.

101 G. B. Caygill, R. M. Hartshorn, and P. J. Steel, *J. Organomet. Chem.*, 1990, **382**, 455 and references therein.

102 J. S. Duggan, E. J. Grabowski, and W. K. Russ, *Synthesis*, 1980, 573.

103 J. Vicente, M.-T. Chicote, M.-C. Lagunas, P. G. Jones, and E. Bembenek, *Organometallics*, 1994, **13**, 1243.

104 J. H. Acquaye, and M. F. Richardson, *Inorg. Chim. Acta*, 1992, **201**, 101.

105 B. Viossat, N. Dung, and F. Robert, *Acta Cryst., Sect. C*, 1993, **49**, 84.

106 M. A. Makhyoun, N. A. Al-Salem, and M. S. El-Ezaby, *Inorg. Chim. Acta*, 1986, **123**, 117.

107 M. W. Mulqi, F. S. Stephens, and R. S. Vagg, *Inorg. Chim. Acta*, 1982, **63**, 197.

108 M. C. Ranninger, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Cryst., Sect. C*, 1985, **41**, 21.

109 G. Vasapollo, C. F. Nobile, M. Latronico, M. Lanfranchi, and M. A. Pellinghelli, *J. Organomet. Chem.*, 1987, **336**, 429.

110 N. Furukawa, F. Takahashi, T. Kawai, K. Kishimoto, S. Ogawa, and S. Oae, *Phosphorus Sulphur*, 1983, **16**, 167.

111 L. Haifeng, L. Wei, Z. Peng, H. Mingsheng, and Z. L. Sun, *Xiamen Dax. Xuebao, Zir. Kex.*, 1992, **31**, 57.

112 C.-F. Lee, and S.-M. Peng, *J. Chin. Chem. Soc. (Taipei)*, 1991, **38**, 559.

113 J. P. Fackler, C. A. Lopez, R. J. Staples, S. Wang, R. E. Winpenny, and R. P. Latimer, *J. Chem. Soc. Chem. Commun.*, 1992, 146.

114 N. C. Baenziger, and A. W. Struss, *Inorg. Chem.*, 1976, **15**, 1807.

115 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.

116 P. J. Steel, and E. C. Constable, *J. Chem. Soc. Dalton. Trans*, 1990, 1389 and references therein.

117 P. K. Byers, A. J. Canty, and R. T. Honeyman, *Adv. Organomet. Chem.*, 1992, **34**, 1 and references therein.

118 M. A. Cinellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli, and B. Bovio, *J. Organomet. Chem.*, 1989, **372**, 311 and references therein.

119 F. Bonati, and B. Bovio, *J. Cryst. Spectrosc. Res.*, 1990, **20**, 233 and references therein.

120 K.-B. Shiu, S.-T. Lin, C.-C. Chou, S.-M. Peng, M.-C. Cheng, S.-L. Wang, and F.-L. Liao, *J. Organomet. Chem.*, 1994, **469**, 169.

121 K.-B. Shiu, C.-J. Chang, S.-L. Wang, and F.-L. Liao, *J. Organomet. Chem.*, 1991, **407**, 225.

122 K.-B. Shiu, K.-S. Liou, S.-L. Wang, and S.-C. Wei, *Organometallics*, 1990, **9**, 669.

123 K.-B. Shiu, S.-T. Lin, D.-W. Fung, T.-J. Chan, S.-M. Peng, M.-C. Cheng, and J. L. Chou, *Inorg. Chem.*, 1995, **34**, 854.

124 A. Cingolani, A. Lorenzotti, G. Gioia Lobbin, D. Leonesi, F. Bonati, and B. Bovio, *Inorg. Chim. Acta*, 1987, **132**, 167.

125 R. M. Claramunt, P. Domiano, J. Elguero, and J. L. Lavandera, *Bull. Soc. Chim. Fr.*, 1989, 472.

126 C.-T. Chen, W.-K. Chang, S.-C. Sheu, G.-H. Lee, T.-I. Ho, Y.-C. Lin, and Y. Wang, *J. Chem. Soc. Dalton Trans.*, 1991, 1569.

127 F. Paap, A. Erdoumez, W. L. Driessen, and J. Reedijk, *Acta Cryst., Sect. C*, 1986, **42**, 783.

128 F. Paap, W. L. Driessen, J. Reedijk, M. Dartmann, and B Krebs, *Inorg. Chim. Acta*, 1986, **121**, 185.

129 B. Adhikary, and C. R. Lucas, *Inorg. Chem.*, 1994, **33**, 1376.

130 Y. C. Pennings, W. L. Driessen, and J. Reedijk, *Polyhedron*, 1988, **7**, 2583 and references therein.

131 K.-B. Shiu, J. L. Chou, Y. Wang, and G.-H. Lee, *J. Chem. Soc. Dalton Trans.*, 1990, 1989.

132 W. L. Driessen, W. G. Weismeijer, M. Schipper-Zablotskaja, R. A. de Graaff, and J. Reedijk, *Inorg. Chim. Acta*, 1989, **162**, 233.

133 T. N. Sorrell, and D. L. Jameson, *J. Am. Chem. Soc.*, 1982, **104**, 2053.

134 W.-K. Chang, G.-H. Lee, Y. Wang, T.-I. Ho, Y. O. Sun, and Y.-C. Lin, *Inorg. Chim. Acta*, 1994, **223**, 139 and references therein.

135 A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1990, **389**, 277.

136 K. H. Sugiyarto, D. C. Craig, A. D. Rae, and H. A. Goodwin, *Aust. J. Chem.*, 1994, **47**, 869.

137 A. A. Watson, D. A. House, and P. J. Steel, *Inorg. Chim. Acta*, 1987, **130**, 167.

138 S. Mahapatra, R. J. Butcher, and R. Mukherjee, *J. Chem. Soc. Dalton Trans.*, 1993, 3723.

139 A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1990, **396**, 105.

140 A. M. Masood, and D. J. Hodgson, *Inorg. Chem.*, 1994, **33**, 3038.

141 T. G. Traylor, P. S. Traylor, and B. Y. Liu, *Inorg. Chem.*, 1991, **30**, 4874.

142 M. Di Vaira, F. Mani, and P. Stoppioni, *J. Chem. Soc. Dalton Trans.*, 1992, 1127 and references therein.

143 F. B. Hulsberger, W. L. Driessen, J. Reedijk, and G. C. Verschoor, *Inorg. Chem.*, 1984, **23**, 3588.

144 W. Clegg, P. J. Cooper, J. C. Lockhart, and D. J. Rushton, *Acta Cryst., Sect. C*, 1994, **50**, 383 and references therein.

145 T. N. Sorrell, V. A. Vankai, and M. L. Garrity, *Inorg. Chem.*, 1991, **30**, 207.

146 J. Elguero in *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, and C. W. Rees), *Vol. 5* (Ed.: K. T. Potts), Pergamon, Oxford, 1984, p. 167.

147 H. Brunner, *Synthesis*, 1988, 645 and references therein.

148 K. Tomioka, *Synthesis*, 1990, 541 and references therein.

149 M. C. Lopez, N. Jagerovic, and P. Ballesteros, *Tetrahedron: Asymmetry*, 1994, **5**, 1887.

150 S. A. Popov, A. Y. Denisov, Y. V. Gatilov, I. Y. Bagryanskaya, and A. V. Tkachev, *Tetrahedron: Asymmetry*, 1994, **5**, 479.

151 D. D. Lecloux, and W. B. Tolman, *J. Am. Chem. Soc.*, 1993, **115**, 1153.

152 D. D. Lecloux, C. J. Tokar, M. Osawa, R. P. Houser, M. C. Keyes, and W. B. Tolman, *Organometallics*, 1994, **13**, 2855.

153 C. Kashima, I. Fukuchi, K. Takahashi, and A. Hosomi, *Tetrahedron Lett.*, 1993, **34**, 8305.

154 A. A. Watson, D. A. House, and P. J. Steel, *Aust. J. Chem.*, 1995, **48**, 1549.

155 M. Bovens, A. Togni, and L. M. Venanzi, *J. Organomet. Chem.*, 1993, **451**, C28.

156 H. Brunner, V. P. Singh, T. Boeck, S. Altmann, T. Scheck, and B. Wrackmeyer, *J. Organomet. Chem.*, 1993, **443**, C16.

157 C. J. Tokar, P. B. Kettler, and W. B. Tolman, *Organometallics*, 1992, **11**, 2737.

158 W.-H. Fung, W.-C. Cheng, W.-Y. Yu, C.-M. Che, and T. C. W. Mak, *J. Chem. Soc. Chem. Commun.*, 1995, 2007.

159 A. J. Amoroso, A. M. Cargill Thompson, J. C. Jeffrey, P. L. Jones, J. A. McCleverty, and M. D. Ward, *J. Chem. Soc. Chem. Commun.*, 1994, 2751.

160 A. J. Amoroso, J. C. Jeffrey, P. L. Jones, J. A. McCleverty, L. Rees, A. L. Rheingold, Y. Sun, J. Takats, S. Trofimenko, M. D. Ward, and G. P. Yap, *J. Chem. Soc. Chem. Commun.*, 1995, 1881.

161 A. J. Amoroso, J. C. Jeffrey, P. L. Jones, J. A. McCleverty, E. Psillakis, and M. D. Ward, *J. Chem. Soc. Chem. Commun.*, 1995, 1175.

162 A. J. Amoroso, J. C. Jeffrey, P. L. Jones, J. A. McCleverty, P. Thornton, and M. D. Ward, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1443.

163 W. Wenner, *J. Org. Chem.*, 1952, **17**, 523.

164 J. T. Stapler, and J. Bornstein, *J. Heterocycl. Chem.*, 1973, **10**, 983.

165 A. J. Downard, G. E. Honey, and P. J. Steel, *Inorg. Chem.*, 1991, **30**, 3733 and references therein.

166 C. M. Hartshorn, B.Sc. Hons research project, University of Canterbury, 1993.

167 H. Schmidbaur, A. Mair, G. Muller, L. Lachmann, and S. Gamper, *Z. Naturforsch., Teil. B*, 1991, **46**, 912.

168 A. J. Canty, and G. van Koten, *Acc. Chem. Res.*, 1995, **28**, 406 and references therein.

169 T. Kawamoto, I. Nagasawa, H. Kuma, and Y. Kushi, *Inorg. Chem.*, 1996, **35**, 2427.

170 R. P. Francisco, Y. P. Mascarenhas, and J. R. Lechat, *Acta Cryst., Sect. B.*, 1979, **35**, 177.

171 W. G. Haanstra, W. L. Driessen, M. Van Roon, A. L. Stoffels, and J. Reedijk, *J. Chem. Soc. Dalton Trans.*, 1992, 481.

172 J. M. Salas, M. P. Sanchez, E. Colacio, and R. Faure, *J. Cryst. Spectrosc. Res.*, 1990, **20**, 133.

173 A. A. Watson, Ph.D. Thesis, University of Canterbury, 1987.

174 T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa, and M. Ochi, *Inorg. Chem.*, 1995, **34**, 530.

175 C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1079.

176 V. M. Agre, N. P. Kozlova, V. K. Trunov, V. M. Oziomko, and E. J. Zaitseva, *Koord. Khim.*, 1980, **6**, 948.

177 A. A. Watson, D. A. House, and P. J. Steel, *J. Organomet. Chem.*, 1986, **311**, 387.

178 H. B. Kagan in *Comprehensive Organometallic Chemistry Vol. 8* (Eds.: G. Wilkinson, F. G. A. Stone, and E. W. Abel), Pergamon, Oxford, 1982, p. 463.

179 H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 897 and references therein.

180 R. P. Francisco, J. R. Lechat, A. C. Massabni, C. B. Melios, and M. Molina, *J. Coord. Chem*, 1980, **10**, 149.

181 A. A. Watson, D. A. House, and P. J. Steel, *Polyhedron*, 1989, **8**, 1345.

182 E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Organometallics*, 1989, **8**, 1067.

183 M. J. Freeman, A. G. Orpen, and I. D. Salter, *J. Chem. Soc. Dalton Trans.*, 1987, 379.

184 C. E. Briant, R. G. Smith, and D. M. Mingos, *J. Chem. Soc. Chem. Commun.*, 1984, 586.

185 E. Hartmann, and J. Strahle, *Z. Naturforsch., Teil. B*, 1988, **43**, 525.

186 X.-M. Chen, and T. C. W. Mak, *J. Chem. Soc. Dalton Trans.*, 1991, 3253.

187 C.-M. Che, H.-K. Yip, D. Li, S.-M. Peng, G.-H. Lee, Y.-M. Wang, and S.-T. Liu, *J. Chem. Soc. Chem. Commun.*, 1991, 1615 and references therein.

188 S.-M. Peng, D.-S. Liau, *Inorg. Chim. Acta*, 1986, **113**, L11.

189 S. Nishikiori, and T. Iwamoto, *Chem. Lett.*, 1994, 1199.

190 D. Cromer, A. C. Larson, and R. B. Roof, *Acta Cryst.*, 1965, **19**, 192.

191 B. Oswald, A. K. Powell, F. Rashwan, J. Heinze, and H. Vahrenkamp, *Chem. Ber.*, 1990, **123**, 243.

192 A. Shaver in *Comprehensive Coordination Chemistry, Vol 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, 1987, p. 245.

193 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.

194 G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291.

195 N. Kitajima, and W. B. Tolman, *Prog. Inorg. Chem.*, 1995, **43**, 419.

196 P. K. Byers, A. J. Canty, and R. T. Honeyman, *Adv. Organomet. Chem.*, 1992, **34**, 1.

197 T. Astley, J. M. Gulbis, M. A. Hitchman, and E. R. Tiekink, *J. Chem. Soc. Dalton Trans.*, 1993, 509 and references therein.

198 C. Janiak, *J. Chem. Soc. Chem. Commun.*, 1994, 545 and references therein.

199 T. N. Sorrell, W. E. Allen, and P. S. White, *Inorg. Chem.*, 1995, **34**, 952.

200 D. C. Reger, J. E. Collins, A. L. Rheingold, and L. M. Liable-Sands, *Organometallics*, 1996, **15**, 2029 and references therein.

201 M. Di Vaira, F. Mani, and P. Stoppioni, *J. Chem. Soc. Dalton Trans.*, 1994, 3739 and references therein.

202 W.-K. Chang, S.-C. Sheu, G.-H. Lee, T.-I. Ho, and Y.-C. Lin, *J. Chem. Soc. Dalton. Trans.*, 1993, 687.

203 R. N. Henrie, and W. H. Yeager, *Heterocycles*, 1993, **35**, 415.

204 K. R. Thomas, V. Chandrasekhar, S. R. Scott, R. Hallford, and A. W. Cordes, *J. Chem. Soc. Dalton. Trans.*, 1993, 2589 and references therein.

205 K. Shelly, D. C. Finster, Y. J. Lee, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, 1985, **107**, 5955 and references therein.

206 T. C. W. Mak, W. C. Ho, and N. Z. Huang, *J. Organomet. Chem.*, 1983, **251**, 413.

207 Z. Shirin, R. Mukherjee, J. F. Richardson, and R. M. Buchanan, *J. Chem. Soc. Dalton. Trans.*, 1994, 465.

208 D. Carmona, J. Ferrer, L. A. Ora, M. C. Apreda, C. Foces-Foces, F. H. Cano, J. Elguero, and M. L. Jimeno, *J. Chem. Soc. Dalton. Trans.*, 1990, 1463.

209 S. Bhambri, and D. A. Tocher, *Polyhedron*, 1996, **15**, 2763.

210 M. Stebler-Rothlisberger, and A. Ludi, *Polyhedron*, 1986, **5**, 1217.

211 R. J. Restivo, G. Ferguson, D. J. O'Sullivan, and F. J. Lalor, *Inorg. Chem.*, 1975, **14**, 3046.

212 G. C. Martin, G. J. Palenik, and J. M. Boncella, *Inorg. Chem.*, 1990, **29**, 1463.

213 W. Luginbuhl, P. Zbinden, P. A. Pittet, T. Armbruster, H.-B. Burgi, A. E. Merbach, and A. Ludi, *Inorg. Chem.*, 1991, **30**, 2350.

214 M. A. Bennett, M. I. Bruce, and T. W. Matheson in *Comprehensive Organometallic Chemistry, Vol. 4* (Eds.: G. Wilkinson, F. G. A. Stone, and E. W. Abel), Pergamon, Oxford, 1982, p. 691.

215 M. A. Bennett in *Comprehensive Organometallic Chemistry II, Vol. 7* (Eds.: E. W. Abel, F. G. A. Stone, and G. Wilkinson), Pergamon, Oxford, 1995, p. 549.

216 Z. Shirin, A. Pramanik, P. Ghosh, and R. Mukherjee, *Inorg. Chem.*, 1996, **35**, 3431.

217 A. W. van der Made, and R. H. van der Made, *J. Org. Chem.*, 1993, **58**, 1262.

218 C. Walsdorff, W. Saak, and S. Pohl, *J. Chem. Res (S).*, 1996, 282.

219 M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, and K. Ogura, *Nature (London)*, 1995, **378**, 469.

220 R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Muther, and A. X. Trautwein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1621.

221 T. Beissel, R. E. Powers, and K. N. Raymond, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1084.

222 F. Vogtle, J. Gross, C. Seel, and M. Nieger, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1069.

223 J. Gross, G. Harder, F. Vogtle, H. Stephan, and K. Gloe, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 481.

224 J. Cioslouski, and Q. Lin, *J. Am. Chem. Soc.*, 1995, **117**, 2553.

225 P. J. Fagan, J. C. Calabrese, and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408.

226 P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 134.

227 R. W. Turner, and E. L. Amma, *J. Am. Chem. Soc.*, 1966, **88**, 1877.

228 G. B. Ansell, M. A. Modrick, and J. S. Bradley, *Acta Cryst., Sect C.*, 1984, **40**, 365.

229 A. W. Duff, K. Jonas, R. Goddard, H.-J. Kraus, and C. Kruger, *J. Am. Chem. Soc.*, 1983, **105**, 5479.

230 H. Schumann, J. Winterfeld, L. Esser, and G. Kociok-Kohn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1208.

231 T. Arliguie, M. Lance, M. Nierlich, J. Vigner, and M. Ephritikhine, *J. Chem. Soc. Chem. Commun.*, 1994, 847.

232 M. J. Zaworotko, K. C. Strurge, L. Nunez, and R. D. Rogers, *Organometallics*, 1991, **10**, 1806 and references therein.

233 A. A. Freer, D. D. MacNicol, P. R. Mallinson, and I. Vallance, *Tetrahedron Lett.*, 1992, **33**, 261.

234 T. D. Stack, and R. H. Holm, *J. Am. Chem. Soc.*, 1988, **110**, 2484 and references therein.

235 M. Yasuda, G. Kuwamura, T. Nakazono, K. Shima, Y. Inoue, N. Yamasaki, and A. Tai, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 505.

236 S. Oae, T. Kawai, N. Furukawa, and F. Iwasaki, *J. Chem. Soc. Perkin Trans. II*, 1987, 405.

237 C. J. Moulton, and B. L. Shaw, *J. Chem. Soc. Dalton Trans.*, 1976, 1020.

238 H. C. Abbenhuis, N. Feiken, D. M. Grove, J. T. Jastrzebski, H. Kooijman, P. van der Sluis, W. J. Smeets, A. L. Spek, and G. van Koten, *J. Am. Chem. Soc.*, 1992, **114**, 9773.

239 A. Jouaiti, M. Geoffroy, and J.-P. Collin, *Inorg. Chim. Acta*, 1996, **245**, 69 and references therein.

240 M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73.

241 N. Lucena, J. Casabo, L. Escriche, G. Sanchez-Castello, F. Teixidor, R. Kivekas, and R. Sillanpaa, *Polyhedron*, 1996, **15**, 3009.

242 S. Chakladar, P. Paul, K. Venkatsubramanian, and K. Nag, *J. Chem. Soc. Dalton Trans.*, 1991, 2669.

243 K. Selvakumar, and S. Vancheesan, *Polyhedron*, 1996, **15**, 2535.

244 A. C. Cope, and R. W. Siekmann, *J. Am. Chem. Soc.*, 1965, **87**, 3272.

245 A. D. Ryabov, *Synthesis*, 1985, 233.

246 J. M. Vila, M. Gayoso, M. Lopez Torres, J. J. Fernandez, A. Fernandez, J. M. Ortigueira, N. A. Bailey, and H. Adams, *J. Organomet. Chem.*, 1996, **511**, 129.

247 M. T. Alonso, O. Juanes, J. de Mendoza, and C. J. Rodriguez-Ubis, *J. Organomet. Chem.*, 1994, **484**, 19.

248 S. Chakladar, P. Paul, A. K. Mukherjee, S. K. Dutta, K. K. Nanda, D. Podder, and K. Nag, *J. Chem. Soc. Dalton Trans.*, 1992, 3119.

249 S. Chakladar, P. Paul, and K. Nag, *Polyhedron*, 1991, **10**, 1513 and references therein.

250 K. Hiraki, Y. Fuchita, and K. Takechi, *Inorg. Chem.*, 1981, **20**, 4316.

251 S. Tollari, G. Palmisano, F. Demartin, M. Grassi, S. Magnaghi, and S. Cenini, *J. Organomet. Chem.*, 1995, **488**, 79.

252 A. J. Canty, N. J. Minchin, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton Trans.*, 1987, 1477.

253 L. F. Krylova, and N. V. Dulepova, *Zh. Neorg. Khim.*, 1994, **39**, 2022.

254 J. Barro, J. Granell, D. Sainz, J. Sales, M. Font-Bardia, and X. Solans, *J. Organomet. Chem.*, 1993, **456**, 147.

255 K. Hiraki, M. Nakashima, T. Uchiyama, and Y. Fuchita, *J. Organomet. Chem.*, 1992, **428**, 249.

256 J. Albert, R. M. Ceder, M. Gomez, J. Granell, and J. Sales, *Organometallics*, 1992, **11**, 1536.

257 Y. Fuchita, K. Yoshinaga, H. Kusaba, M. Mori, K. Hiraki, and K. Takehara, *Inorg. Chim. Acta*, 1995, **239**, 125.

258 G. Garcia-Herbosa, A. Munoz, D. Miguel, and S. Garcia-Granda, *Organometallics*, 1994, **13**, 1775.

259 P. L. Alsters, P. F. Engel, M. P. Hogerheide, M. Copijn, A. L. Spek, and G. van Koten, *Organometallics*, 1993, **12**, 1831.

260 E. C. Constable, S. J. Dunne, D. G. Rees, and C. X. Schmitt, *Chem. Commun.*, 1996, 1169.

261 P. Espinet, G. Garcia, F. J. Herrero, Y. Jeannin, and M. Philoche-Levisalles, *Inorg. Chem.*, 1989, **28**, 4207.

262 A. Jouaiti, M. Geoffroy, and G. Bernardinelli, *Tetrahedron Lett.*, 1993, **34**, 3413.

263 G. B. Caygill, and P. J. Steel, *J. Organomet. Chem.*, 1990, **395**, 359 and references therein.

264 T. Izumi, and A. Kasahara, *Bull. Yamagata Univ., Eng.*, 1979, **15**, 213.

265 S. J. Loeb, and G. K. Shimizu, *J. Chem. Soc. Chem. Commun.*, 1993, 1395.

266 S. Trofimenko, *J. Am. Chem. Soc.*, 1971, **93**, 1808.

267 I. G. Phillips, and P. J. Steel, *J. Organomet. Chem.*, 1991, **410**, 247.

268 G. van Koten, *Pure. Appl. Chem.*, 1989, **61**, 1681 and references therein.

269 W. L. Steffen, and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.

270 G. M. Intille, C. E. Pfluger, and W. A. Baker, *Cryst. Struc. Commun.*, 1973, **2**, 217.

271 V. G. Albano, C. Castellari, M. E. Cucciolito, A. Panunzi, and A. Vitagliano, *Organometallics*, 1990, **9**, 1269.

272 R. Arack, and K. Zetterberg, *Organometallics*, 1987, **6**, 1230.

273 J. A. Davies, A. A. Pinkerton, R. Syed, and V. Vilmer, *J. Chem. Soc. Chem. Commun.*, 1988, 47.

274 D. Perreault, M. Drouin, A. Michel, and P. D. Harvey, *Inorg. Chem.*, 1992, **31**, 2740.

275 J.-P. Collin, M. Beley, J.-P. Sauvage, and Barigelletti. F., *Inorg. Chim. Acta*, 1991, **186**, 91.

276 E. C. Constable, and M. J. Hannon, *Inorg. Chim. Acta*, 1993, **211**, 101.

277 M. D. Ward, *J. Chem. Soc. Dalton Trans.*, 1994, 3095.

278 D. A. Bardwell, J. C. Jeffrey, E. Schatz, E. E. Tilley, and M. D. Ward, *J. Chem. Soc. Dalton Trans.*, 1995, 825.

279 R. H. Crabtree, E. M. Holt, M. Lavin, and S. M. Morehouse, *Inorg. Chem.*, 1985, **24**, 1986.

280 M. Brookhart, and M. L. Green, *J. Organomet. Chem.*, 1983, **250**, 395.

281 H. Nagao, T. Mizukawa, and K. Tanaka, *Inorg. Chem.*, 1994, **33**, 3415.

282 A. Gerli, J. Reedijk, M. T. Lakin, and A. L. Spek, *Inorg. Chem.*, 1995, **34**, 1836.

283 S. C. Rasmussen, S. E. Ronco, D. A. Mlsna, M. A. Billadeau, W. T. Pennington, J. W. Kolis, and J. D. Petersen, *Inorg. Chem.*, 1995, **34**, 821.

284 H. J. Backer, *Rec. Trav. Chim.*, 1935, **54**, 745.

285 H. C. Brown, and B. C. Subba Rao, *J. Am. Chem. Soc.*, 1956, **78**, 2582.

286 I. P. Evans, A. Spencer, and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 1973, 204.

287 B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 1404.

288 G. M. Sheldrick, *Acta Cryst., Sect A*, 1990, **46**, 467.

289 G. M. Sheldrick, SHELXL, University of Gottingen.