Synthesis and reactions of Ruthenium Complexes with *Tris*(2-pyridyl)methanol and related ligands

A thesis presented to the University of London
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the degree of Doctor of Philosophy.

By

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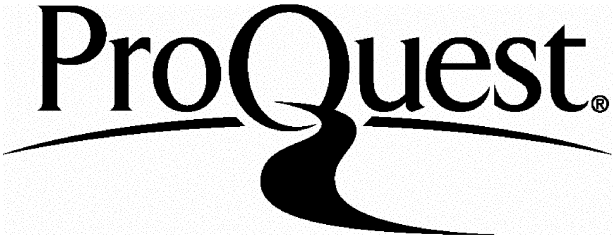

For my family

Abstract

This thesis describes the synthesis and reactions of a variety of (η^6-arene)ruthenium(II) complexes with *tris*(2-pyridyl)methanol and related ligands. By way of an introduction to this chemistry, Chapter **1** reviews the most relevant of earlier studies, mainly concerning i) *tris*(2-pyridyl) compounds and derived metal complexes, and ii) (η^6-arene)ruthenium(II) complexes and their reactions with nucleophiles.

Chapter **2** describes how modifications of literature procedures led to the preparations of methyl-substituted analogs of *tris*(2-pyridyl)methanol, and their chloromethane, ethoxymethane and methane derivatives. The crystal structure of (3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol is described.

Chapter **3** reports the reactions of *tris*(2-pyridyl)methanol and methyl-substituted analogs with $[(\eta^6\text{-arene})RuCl_2]_2$ dimers (arene = benzene, *para*-cymene). Mono and dicationic [(η^6-arene)Ru(*tris*(pyridyl)methanol)] complexes were synthesised depending on whether or not the tripodal ligand had become deprotonated, however in all cases the ligand adopted the tridentate N,N',O-coordination mode. In addition, two heterometallic complexes of *tris*(2-pyridyl)methanol were prepared. The crystal structures of the compounds $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$, $[\{(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$ and $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$ are presented.

Chapter **4** presents the syntheses of (η^6-arene)Ru(II) complexes of the chloromethane, ethoxymethane and methane derivatives of *tris*(2-

pyridyl)methanol and its closely related analogs. Mono and dicationic complexes were prepared depending on whether a bidentate or tridentate coordination mode had been adopted by the tripodal ligand. The compound $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(C_5H_4N)_3CH\}][PF_6]_2$ was crystallographically characterised.

Chapter **5** describes the reactions of dicationic (η^6-arene)Ru(II) complexes, containing either *tris*(2-pyridyl)ethoxymethane or *tris*(2-pyridyl)methane as ancillary ligands, with nucleophiles. In all cases monocationic (η^5-cyclohexadienyl)Ru(II) products were exclusively formed. In some cases, depending upon the reaction conditions employed, either of two isomeric forms of a given cyclohexadienyl product could be obtained - a kinetic or a thermodynamic isomer. The crystal structures of the compounds $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ and $[(\eta^5\text{-}C_6H_6CN)Ru(PMe_2Ph)\text{-}\{(C_5H_4N)_3COEt\}]PF_6$ are described.

Table of Contents

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I know that without the love and support of my dear family none of this would have been possible, and so it is to them that I extend my final thanks.

Abbreviations

NMR	nuclear magnetic resonance
IR	infrared
MS	mass spectroscopy
Me	methyl
Et	ethyl
^{i}Pr	*iso*propyl
Ph	phenyl
py	pyridyl
Ar	η^6-arene
***para*-cymene**	1-methyl-4-*iso*propylbenzene
PR_3	tertiary phosphine
PEt_3	triethylphosphine
PMe_2Ph	dimethylphenylphosphine
$PMePh_2$	diphenylmethylphosphine
THF	tetrahydrofuran

NMR spectroscopy:

s	singlet	**br**	broad
d	doublet	**sept**	septet
t	triplet	**d,d**	doublet of doublets
q	quartet	**d,t**	doublet of triplets
m	multiplet	**d,q**	doublet of quartets
d,d,d	doublet of doublet of doublets		

IR spectroscopy:

w	weak	**s**	strong
m	medium	**br**	broad

Chapter 1

Introduction

Foreword

Almost fifty years ago, the discovery of ferrocene's 'sandwich like' structure sparked an explosion in the already expanding field of organometallic chemistry. Innumerable studies over the intervening decades have led to the development of applications of this chemistry to areas as diverse as the stabilisation of highly reactive species *via* metal coordination (e.g. carbyne or cyclobutadiene), and the development of industrial catalysts (in such processes as propylene and acetic acid production), to name but a few.

This thesis describes some chemistry which makes up one small facet of the vast organometallic field. The work which has been pursued over the last three years concerns π-arene complexes of ruthenium(II) in which the ancillary ligand is *tris*(2-pyridyl)methanol or a closely related species. The ultimate goals of this project have been to investigate both the influence of methyl-substituted pyridyl rings and bridgehead atom substituents on the coordination modes adopted by the tripodal ligands in a number of (η^6-arene)Ru(II) complexes, and the reactions of some of these complexes with nucleophiles.

1.1 Heterocyclic nitrogen donor ligands

A good understanding of metal-ligand interactions is essential if one is to successfully predict a complex's properties and subsequent uses. Contrary to the main-group, the chemistry of transition metal complexes is generally ligand dominated. Heterocyclic nitrogen-donor ligands have been extensively

investigated with respect to transition metal ion complexation. Pyrazole is a well known ligand, possessing two ring nitrogens (see Figure 1.1), however pyridine is perhaps the best known example of a heterocyclic nitrogen-donor and has particular relevance to our studies in that it has been incorporated into numerous ruthenium(II) complexes.[1-7] Pyridine is a Lewis base and the ring, with few exceptions, coordinates in a sigma fashion through the nitrogen's lone pair, as opposed to bonding utilising the π-electron system.

Pyrazole Pyridine

Figure 1.1 Examples of heterocyclic nitrogen donor ligands

Ruthenium complexes of polypyridyl ligands (such as 2,2'-bipyridyl and 1,10-phenanthroline, Figure 1.2) have received considerable attention over the past two decades mainly due to their use as 'photosensitisers' in processes such as water or carbon dioxide reduction. The *tris*(2,2'-bipyridine)ruthenium(II) cation is the archetypal example of such species.[1,3,4,8-16]

2,2'-bipyridine 1,10-phenanthroline

Figure 1.2 Some polypyridyl ligands

Unlike the ligands shown in Figure 1.2, in which the rings are directly linked to one another, *tris*(1-pyrazolyl)methane (Figure 1.3) represents a type of

polycyclic ligand in which a central or 'bridgehead' atom links together neighbouring rings, pyrazoles in this case.

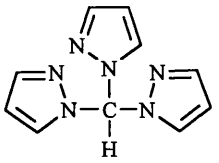
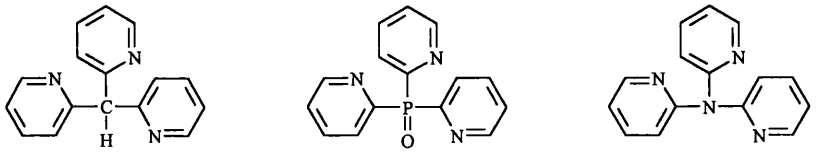


Figure 1.3 *Tris*(1-pyrazolyl)methane, a polycyclic pyrazolyl ligand

1.2 An introduction to *tris*(2-pyridyl) ligands

Previously our group has worked extensively on the synthesis of (arene)ruthenium complexes with *tris*(pyrazolyl) ancillary ligands.[17-20] This thesis however is concerned with the study of the analogous chemistry of complexes containing *tris*(2-pyridyl) ligands. A wide range of these are known with a variety of bridgehead atoms linking the rings (Figure 1.4).



tris(2-pyridyl)methane *tris*(2-pyridyl)phosphine oxide *tris*(2-pyridyl)amine

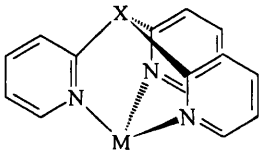
Figure 1.4 Some *tris*(2-pyridyl) ligands with differing bridgehead atoms

It has been noted previously[21] that pyridine-containing ligands are better σ-donors and π-acids than the analogous pyrazole-containing ligands, and that unlike *tris*(pyrazolyl)borate which is anionic, *tris*(2-pyridyl) ligands are generally neutral. One would therefore expect the analogous complexes of *tris*(pyrazolyl)

and *tris*(pyridyl) ligands to possess differing properties (such as redox potentials and solubility).[22]

1.3 The coordination chemistry of *tris*(2-pyridyl) ligands

Surprisingly, relatively little coordination chemistry of *tris*(2-pyridyl) ligands with transition metals has been reviewed.[22-24] However from published work it is clear that generally these ligands will coordinate in a tridentate manner *via* the three pyridyl nitrogen atoms (Figure 1.5).



X= CH, N, COH etc

Figure 1.5 Tridentate coordination of *tris*(2-pyridyl)X ligands to metal M

In our work we have focused solely on *tris*(2-pyridyl) ligands with a bridgehead carbon atom (*vide infra*), and the typical coordination chemistry of *tris*(2-pyridyl)methane, along with some of the other main ligand types (namely *tris*(2-pyridyl)amine and *tris*(2-pyridyl)phosphine), will be described here.

Many transition metal complexes of *tris*(2-pyridyl)methane,[25-38] *tris*(2-pyridyl)amine[27-29,33,39-47] and *tris*(2-pyridyl)phosphine[28,29,31,34,39,48-52] have been synthesised in which the ligand adopts the N,N',N" tridentate mode of coordination. Some ruthenium(II) complexes displaying this feature are described below.

The *bis*(ligand)Ru(II) complexes of these three ligands were synthesised by reacting $[Ru(DMF)_6]^{2+}$ (DMF = N,N-dimethyl formamide) with an excess of the appropriate ligand in propan-1-ol. As the X-ray structures of the three cations (Figure 1.6) show, tripodal N,N',N'' coordination to the ruthenium metal ion has occurred in each case. An increase in the bridgehead atom to pyridyl carbon bond length leads to increasing distortions from ideal D_{3d} symmetry, the [Ru(*tris*(2-pyridyl)phosphine)$_2$]$^{2+}$ cation being the least symmetric of the three examples.[28]

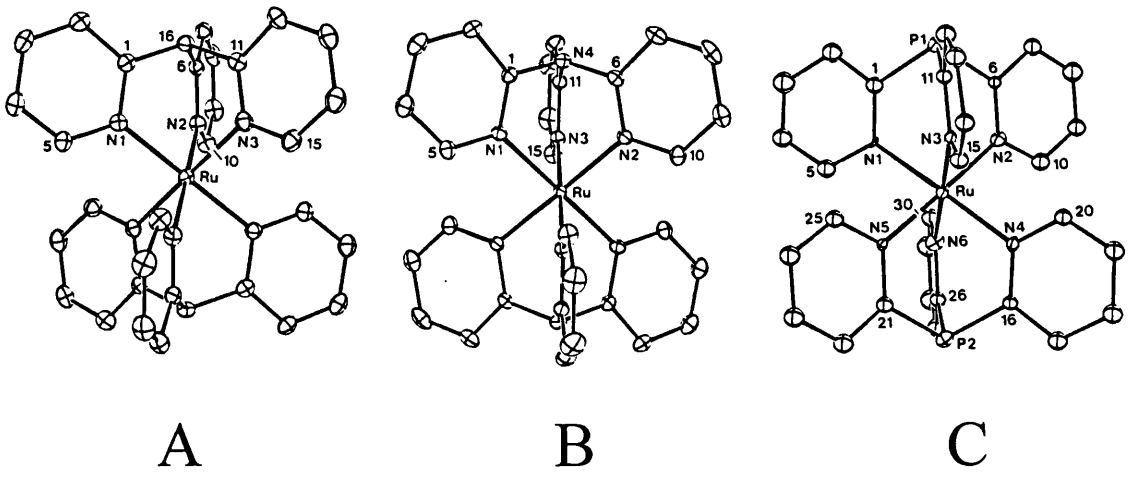


Figure 1.6 Ru(II) complex cations of the ligands *tris*(2-pyridyl)methane, **A**; *tris*(2-pyridyl)amine, **B**; *tris*(2-pyridyl)phosphine, **C**. [28]

The half-sandwich complex $[RuCl_2(PPh_3)$(*tris*(2-pyridyl)phosphine)] was prepared by the reaction of $RuCl_2(PPh_3)_3$ with *tris*(2-pyridyl)phosphine in benzene, and was shown to possess the N,N',N'' bound ligand by X-ray crystallography. This compound is readily oxidised *in situ* by oxygen to give a *tris*(2-pyridyl)phosphine oxide (Figure 1.4) complex $[RuCl_2(PPh_3)$(*tris*(2-pyridyl)phosphine oxide)].[48]

The presence of three potentially coordinating pyridyl nitrogens does not force the *tris*(2-pyridyl) ligands to adopt N,N',N'' tridentate coordination. For instance, a number of transition metal complexes incorporating N,N' bidentately coordinated *tris*(2-pyridyl) ligands (of the types previously mentioned) have been synthesised,[26,33,43,45-47,53-59] some examples of which will now be discussed.

The gold complex $[AuMe_2(tris(2\text{-pyridyl})methane)]NO_3.2H_2O$ was synthesised by treatment of $[AuMe_2]NO_{3(aq)}$ with *tris*(2-pyridyl)methane, and was found to possess a bidentately coordinated ligand on the square planar Au(I) ion (Figure 1.7).[54]

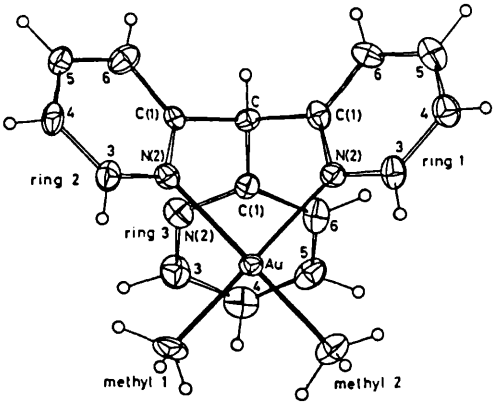


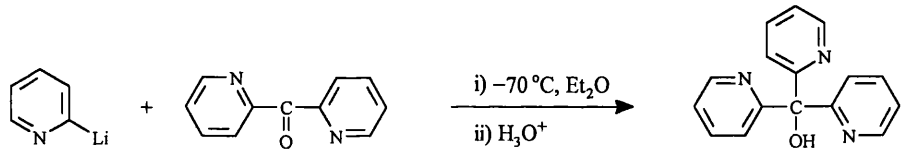
Figure 1.7 Structure of the cation in $[AuMe_2\{(C_5H_4N)_3CH\}]NO_3.2H_2O$ [54]

Complexes of the general formula $[Re(CO)_3Cl(tris(2\text{-pyridyl})X)]$ (X= methane, amine or phosphine) were prepared by reacting $[Re(CO)_5Cl]$ with the appropriate ligand under mild conditions. Subsequent investigations reveal the ligands to be coordinated in the N,N' mode. In contrast, repeating the reaction under visible light irradiation leads to tridentate coordination of the ligands, in the case of *tris*(2-pyridyl)methane and *tris*(2-pyridyl)amine, *via* loss of one

additional CO ligand.[33]

1.4 Preparation of carbon bridged *tris*(2-pyridyl) ligands

Tris(2-pyridyl)methanol, synthesised by Wibaut and co-workers[60] in 1951, was the first example of a series of *tris*(2-pyridyl) ligands with a bridgehead carbon atom. The compound was prepared by reacting 2-lithiopyridine (formed by treatment of 2-bromopyridine with butyllithium) with *bis*(2-pyridyl)ketone (synthesised from 2-lithiopyridine and 2-cyanopyridine) at –70 °C. Quenching of the reaction mixture and subsequent work-up gave a good yield of the white crystalline compound (see Scheme 1.1).



Scheme 1.1 The synthesis of *tris*(2-pyridyl)methanol

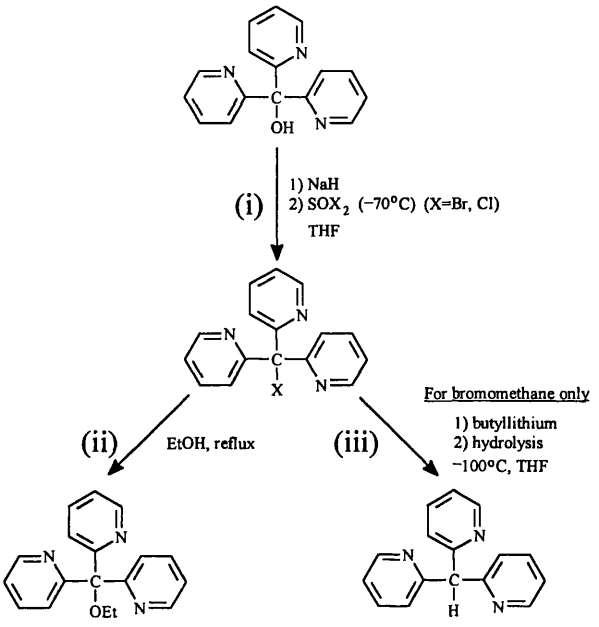
Tris(2-pyridyl)methanol has considerable synthetic versatility and the halomethane, alkoxymethane and methane derivatives are all readily prepared from this precursor,[25] as described below in conjunction with Scheme 1.2:

(i) Reacting *tris*(2-pyridyl)methanol with sodium hydride forms the sodium methoxide, which upon subsequent treatment, at –70 °C, with thionyl halide (bromide or chloride) gives the halomethane.

(ii) Refluxing the halomethane in ethanol forms the ethoxy derivative.

(iii) Treatment of *tris*(2-pyridyl)bromomethane with butyllithium at –100 °C gives the lithio derivative, which upon subsequent hydrolysis forms the

methane. (Prior to this, *tris*(2-pyridyl)methane was first synthesised, in 1956, as a by-product in the reaction of picolyllithium with 2-bromopyridine).[61]



Scheme 1.2 The preparation of *tris*(2-pyridyl)methanol derivatives

The coordination chemistry associated with this group of ligands is generally quite similar. However by modifying the substituents on the carbon bridgehead atom, properties such as a derived complex's overall charge or the mode of coordination which the ligand adopts may be changed. For instance, both the hydroxy and ethoxy derivatives offer additional coordination modes through the oxygen atom (which in the case of the former may become deprotonated), as discussed later.

1.5 Tris(2-pyridyl) ligands substituted at pyridine

A second approach to the functionalisation of this class of ligands involves the derivatisation of the pyridyl rings and it has been shown that this can

dramatically modify the ligand's coordination chemistry (Chapter 3).

The versatility of the general synthetic method described above is further highlighted in the stepwise synthesis of a multitude of substituted derivatives (e.g. (6-methyl-2-pyridyl)*bis*(2-pyridyl)methanol, **A**; (5-methyl-2-pyridyl)*bis*(2-pyridyl) methanol, **B**; and (3-methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol, **C**, Figure 1.8). Each of these ligands has been prepared in

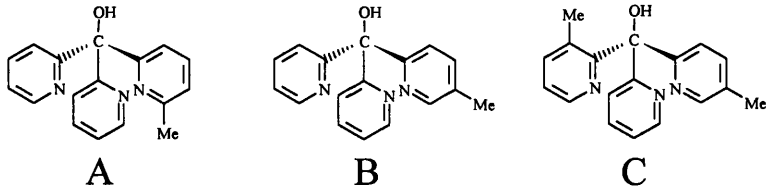


Figure 1.8 Methyl-substituted *tris*(2-pyridyl)methanol ligands

the course of this work (Chapter 2, sub-section 2.2.3), by utilising the appropriately methyl-substituted lithiopyridines or *bis*(2-pyridyl)ketones following the general procedure described in Scheme 1.1.

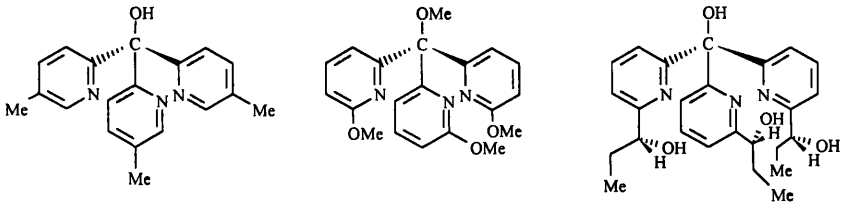
In a similar vein, although relatively rare, symmetrically *tris*-substituted derivatives of *tris*(2-pyridyl)methanol have been prepared,[62-64] and some examples are shown in Figure 1.9. The preparation of these ligands demonstrates the ease of derivatisation of the '*tris*(2-pyridyl)methane core'. They have been utilised in a number of interesting applications, for example:

i) Metal complexes of ligand **A**, and of closely related analogs, are currently being used in studies concerned with carbonic anhydrase mimics.[62]

ii) Copper complexes of the methoxy-substituted *tris*(2-pyridyl)methoxy-

methane ligand **B** were recently synthesised and utilised in a study concerned with the modelling of metalloenzymes.[63]

iii) Ligand **C** has been incorporated into a rhodium complex, which is currently under investigation as a catalyst for hydrosilylation reactions.[64]



A B C

Figure 1.9 Symmetrically tri-substituted *tris*(2-pyridyl) ligands

1.6 The coordination chemistry of *tris*(2-pyridyl)methanol

The N,N',N'' coordination mode (depicted in Figure 1.5) has been adopted by *tris*(2-pyridyl)methanol in a number of complexes.[65-73] The complex $[Rh\{(C_5H_4N)_3COH\}Cl_3]$[69] was synthesised by reacting *tris*(2-pyridyl)methanol with $[Rh(cyclooctadiene)Cl]_2$ in refluxing chloroform, and characterised crystallographically.[71] The X-ray structure of the rhodium compound (Figure 1.10) shows tridentate coordination of the *tris*(2-pyridyl)methanol ligand through the three pyridyl nitrogen atoms. These occupy three facial sites on a slightly distorted octahedron, with chloride ions occupying the remaining sites. The three Rh-N distances are indistinguishable (mean 2.037(7) Å) as are the three Rh-Cl distances (mean 2.355(6) Å).

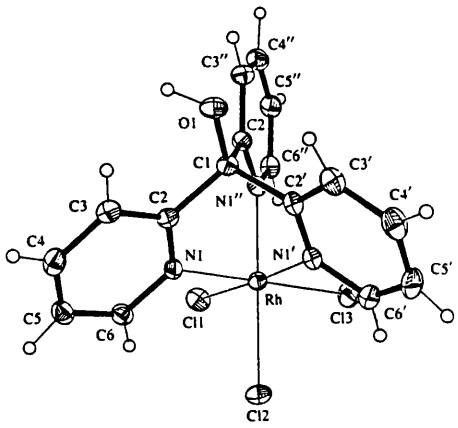
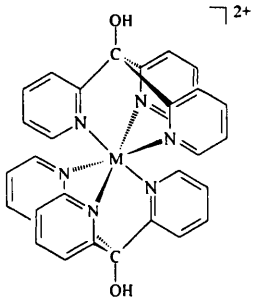


Fig 1.10 The structure of $[Rh\{(C_5H_4N)_3COH\}Cl_3]$ [71]

A number of symmetrical *bis*(ligand)M(II) (M = Mn, Cu, Zn) perchlorate complexes of *tris*(2-pyridyl)methanol have been prepared, in which the N,N',N'' coordination mode is displayed by both ligands[70] (Figure 1.11). These were the first examples of transition metal complexes possessing two



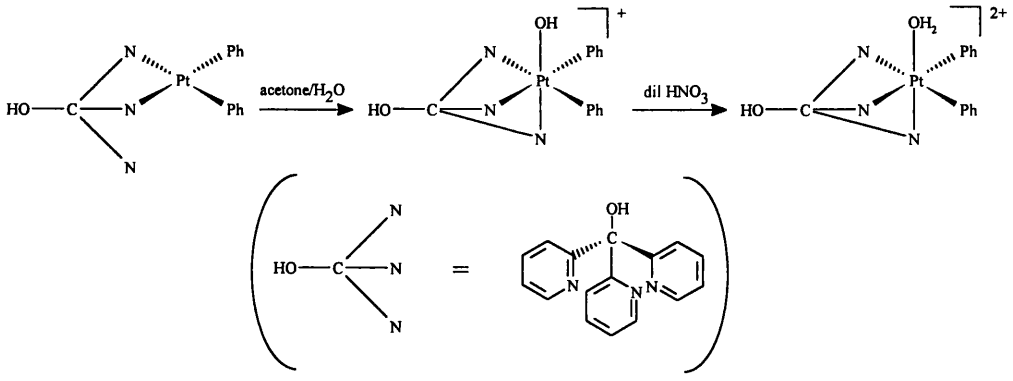
M = Mn, Cu or Zn

Figure 1.11 The octahedral *bis*[*tris*(2-pyridyl)methanol]M(II) complex cation displaying overall N_6 coordination

tris(2-pyridyl)methanol ligands. ^1H NMR and IR spectroscopy proved invaluable in the assignment of the ligands' coordination mode. For instance, a comparison of the Zn(II) complex's IR spectrum with that of the free ligand reveals a shift in the position of the ring-breathing mode and pyridyl band, from

991 and 1585 cm^{-1} respectively in the free ligand to 1016 and 1596 cm^{-1} in the complex, consistent with pyridyl coordination.[74] Furthermore, the ^1H NMR spectrum of the complex shows four pyridyl signals of equal integral, reflecting the equivalence of all six pyridyl rings.

Tris(2-pyridyl)methanol by analogy with the previously described *tris*(2-pyridyl) ligands (Section 1.3) has been known to coordinate in an N,N' bidentate manner in a number of heavier late transition metal complexes.[54,66] For example the square planar complex $[PtPh_2\{(C_5H_4N)_3COH\}]$ was obtained by treating $[PtPh_2(SEt_2)]_2$ with *tris*(2-pyridyl)methanol in benzene, and shown to incorporate a bidentately coordinated *tris*(2-pyridyl)methanol ligand.[66] Interestingly, as depicted in Scheme 1.3, this compound can be oxidised by water to form the octahedral monocation $[Pt(OH)Ph_2\{(C_5H_4N)_3COH\}]^+$,



Scheme 1.3 Platinum *tris*(2-pyridyl)methanol complexes

which now possesses an N,N',N'' tridentate ligand as well as an additional hydroxyl group. Subsequent protonation with dilute nitric acid gives the dicationic species $[Pt(H_2O)Ph_2\{(C_5H_4N)_3COH\}]^{2+}$.

Tris(2-pyridyl)methanol is a particularly interesting ligand in that it has the ability to offer an additional mode of coordination through the oxygen atom of the alcohol, i.e. to bond in an asymmetric N,N',O mode (Figure 1.12). In this mode the ligand can be either in the form of a neutral alcohol or of the anionic alkoxide.

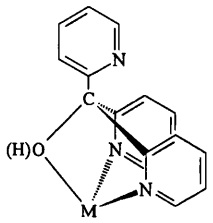


Figure 1.12 N,N',O coordination to a metal

A number of transition metal complexes have been prepared in which *tris*(2-pyridyl)methanol adopts this N,N',O tridentate coordination mode.[27,67,70,72,75] For example Boggess *et. al.*[70] isolated a Co(III) complex of the formula $[Co\{(C_5H_4N)_3COH\}\{(C_5H_4N)_3CO\}][ClO_4]_2$, by the reaction of Co(II) perchlorate with *tris*(2-pyridyl)methanol. Subsequent investigation[72] revealed this complex to be of the form $[Co\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3CO\}]^{2+}$, which contains one deprotonated ligand bound through two pyridyl nitrogen atoms and the alkoxide oxygen atom, as well as a neutral N,N',N'' coordinated ligand, Figure 1.13.

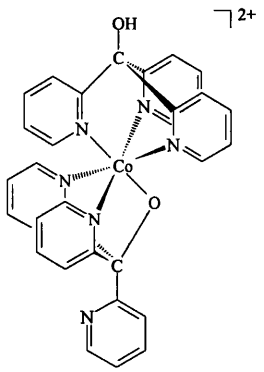


Figure 1.13 The asymmetric bis[*tris*(2-pyridyl)methanol]Co(III) cation

The various coordination modes of *tris*(2-pyridyl)methanol have been elegantly demonstrated in studies on the chemistry of iron(II).[67] Three different *bis*-ligand derivatives were prepared and identified by titration studies as well as by both electronic and ^{13}C NMR spectroscopy. These include one complex with both ligands bound to Fe(II) in an N,N',N'' manner, a second complex with one ligand bound N,N',N'' and the other N,N',O, and a third form closely related to the second by loss of a proton from the hydroxyl group of the N,N',O bound ligand. Figure 1.14 shows the $^{13}C-\{^1H\}$ NMR spectrum of the symmetric complex, with the expected six resonances being observed, five in the

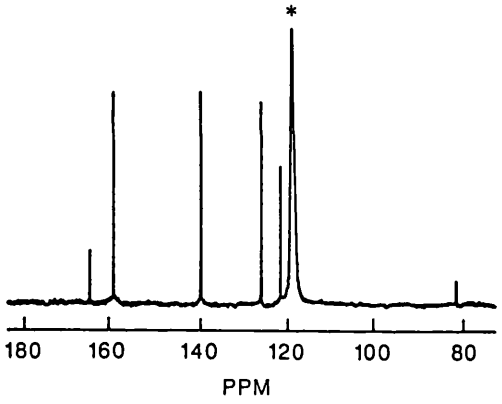


Figure 1.14 $^{13}C-\{^1H\}$ NMR spectrum of the symmetric complex $[Fe\{(C_5H_4N)_3COH\}_2][ClO_4]_2$ (The * refers to the carbon of the -CN of the solvent, CD_3CN) [67]

aromatic region corresponding to the five non-equivalent carbons of the six equivalent rings, and the aliphatic bridgehead carbon resonance occuring at 81.3ppm. When the symmetric complex is dissolved in a water-ethanol solvent system, the UV-visible spectrum is consistent with the unaltered symmetric isomer. However, when the complex is formed by reacting iron(II)chloride with *tris*(2-pyridyl)methanol in the same solvent system, the spectrum is pH-(Figure 1.15) and, to a lesser extent, time-dependent. Two species were identified in

solution, one is present at pH 3.0 and the other at pH 10.2, with spectra

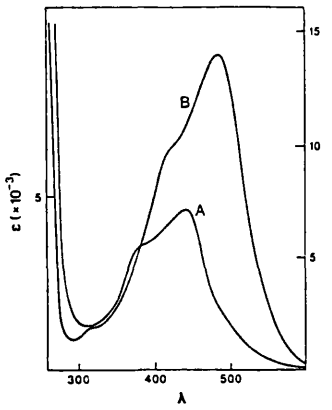


Figure 1.15 UV- visible spectrum of *tris*(2-pyridyl)methanol : Fe(II) (2:1 molar ratio) The left scale refers to curve A, pH 3.0, whereas the right scale refers to curve B, pH 10.2 [67]

differing from that of the symmetric isomer. It was postulated that the species observed at lower pH is the neutral asymmetric form, whereas the species present at higher pH is the analogous deprotonated isomer.

1.7 Ruthenium(II) complexes of *tris*(2-pyridyl)methanol

The versatility of the *tris*(2-pyridyl)methanol ligand, in that the oxygen atom is found in either the form of a neutral alcohol or an anionic alkoxide, is further demonstrated in the two forms of a cationic *bis*[*tris*(2-pyridyl)methanol] ruthenium(II) complex prepared by the reaction of $[Ru(H)(OH_2)_2(CH_3OH)(PPh_3)_2]BF_4$ with *tris*(2-pyridyl)methanol. An orange species, $[Ru\{(C_5H_4N)_3COH\}\{(C_5H_4N)_3CO\}]^+$, **A**, with an overall N_5O coordination, and its protonated analog, a yellow species, $[Ru\{(C_5H_4N)_3COH\}_2]^{2+}$, **B**, have both been isolated and crystallographically characterised (Figure 1.16).[75] ^{13}C NMR studies of both complexes are

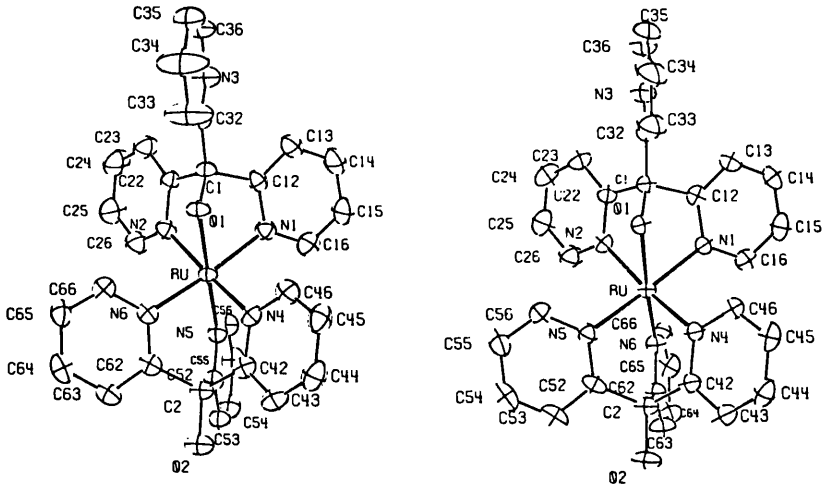


Figure 1.16 Molecular structures of *bis*[*tris*(2-pyridyl)methanol]ruthenium(II) cations [75]

consistent with the asymmetric modes of coordination for the ligands. Since ruthenium(II) is noted for having an affinity for nitrogen donor ligands such as pyridine[76] its preference for N_5O, as opposed to N_6, coordination is rather surprising. Steric effects due to the ligands can be neglected on the grounds that N_6 coordination readily occurs in the analogous *bis*(ligand)ruthenium(II) complexes of $(C_5H_4N)_3X$ ligands (X= N, CH, P).[28] Hence the observation of the N_5O mode could be due to kinetic control in the synthesis, although this remains unproven.

The cationic species $[Ru(NH_3)_3\{(C_5H_4N)_3COH\}]^{2+}$ was synthesised by the reaction of $[Ru(NH_3)_3(OH_2)_3]^{2+}$ with *tris*(2-pyridyl)methanol.[27] In this compound the ligand was also shown to display the N,N',O coordination mode (Figure 1.17). The geometry about the Ru(II) ion is that of a distorted octahedron, with the tripodal ligand donor atoms occupying three facial sites. It was postulated that the distortion of the coordination sphere is a consequence of the *tris*(2-pyridyl)methanol ligand's N,N',O mode of coordination, since the bridgehead

carbon atom-oxygen atom bond length, 1.439(6) Å, is considerably shorter than the two bridgehead carbon atom-nitrogen donor atom distances, 2.382 and 2.388 Å, thus hindering the occupation of octahedral facial positions by

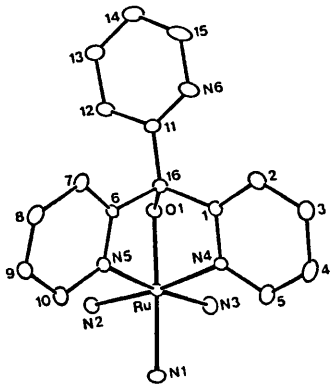


Figure 1.17 Structure of the cation in $[Ru(NH_3)_3\{(C_5H_4N)_3COH\}]Br_2.H_2O$ [27]

the donor atoms. An even greater distortion from ideal geometry was observed for the complex cation $[Ru\{(C_5H_4N)_3COH\}_2]^{2+}$ (Figure 1.16, **B**),[75] in that the N-Ru-O bond angles of the N,N',O bound ligand, 76.2(2) and 77.2(1) °, are smaller than the equivalent bond angles, 79.2(2) and 79.6(2) °, of $[Ru(NH_3)_3\{(C_5H_4N)_3COH\}]^{2+}$ (Figure 1.17). The symmetrically coordinated N-donor ligands of both these complexes have N-Ru-N bond angles closer to 90 °. Similarly the $[Ru\{(C_5H_4N)_3CH\}_2]^{2+}$ cation (Figure 1.6, **A**),[28] with its overall N_6 coordination, has a more regular octahedral geometry than either of the previously described complexes.

The studies carried out so far clearly demonstrate that the coordination mode of the *tris*(2-pyridyl)methanol ligand is difficult to predict in advance, and is greatly influenced by the method of synthesis, pH of the reaction medium, and the steric and electronic properties of the metal centre. Hence in our work we

should be alert to the possibility that *tris*(2-pyridyl)methanol may exhibit coordination modes other than the N_3 form which is our primary target.

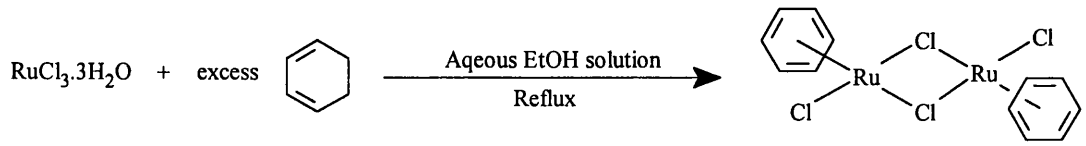
1.8 An introduction to (η^6-arene)ruthenium(II) complexes

During the course of our studies a range of (arene)ruthenium complexes of some *tris*(2-pyridyl) ligands were synthesised and characterised. To put this work in perspective a brief description of the related chemistry of some previously reported (arene)ruthenium complexes is given below.

The role that (arene)ruthenium complexes play in organometallic chemistry continues to increase and as a consequence they have been the subject of several detailed reviews.[1,2,4,77-81] It was E. O. Fischer and co-workers who first devised a general route for the preparation of (η^6-arene)Ru(II) complexes. They achieved the synthesis of a variety of symmetrical *bis*(η^6-arene)Ru(II) complexes *via* the reaction of $RuCl_3$ with excess arene (using an $AlCl_3$/Al powder catalyst). Unfortunately this method is restricted to arenes that are inert toward $AlCl_3$, ruling out numerous alkylated arenes and those with substituents possessing lone pairs.[82-84]

In an extension to an earlier, less successful study,[85] the reaction of cyclohexa-1,3-diene with ethanolic ruthenium(III)trichloride hydrate was reported, by Zelonka and Baird,[86] to give a dark red, diamagnetic material. With the assistance of infrared studies[87,88] this compound was identified as a dimer of formula $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, in which two chloride ions bridge across

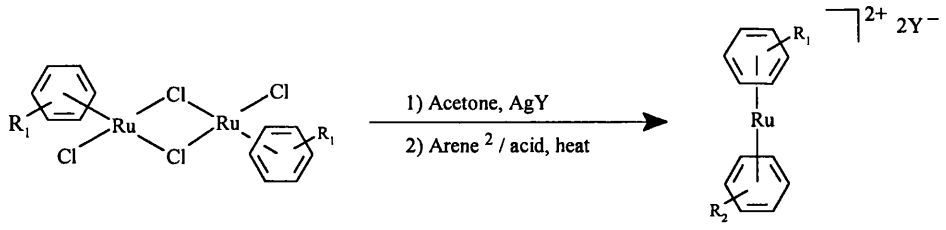
two ruthenium atoms (Scheme 1.4).



Scheme 1.4 Synthesis of the chloro-bridged ruthenium-benzene dimer

The use of appropriately substituted cyclohexadienes in the procedure shown in Scheme 1.4 results in the formation of analogous dimers containing arenes such as mesitylene and *para*-cymene.[5,89] The *para*-cymene ligand in the dimer $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ can be readily exchanged with a number of other substituted arenes (such as hexamethylbenzene or 1,3,5-triethylbenzene) by heating the dimer with an excess of the arene in the absence of solvent.[90-93] In addition, in some cases the chloride ligands can be readily substituted with bromide, iodide or thiocyanate ligands by reaction of the dimer with the respective sodium salt.[5,86]

Generally the $[(\eta^6\text{-arene})RuX_2]_2$ dimers (arene = benzene, *para*-cymene, etc; X = Br, Cl, etc.) are complexes of high synthetic versatility and are the source of the "$(\eta^6$-arene)Ru(II)" moiety in a number of (arene)ruthenium complex syntheses. For instance, Bennett and Matheson[94] reported a straightforward route to a large number of symmetric and asymmetric *bis*(arene)Ru(II) complexes of general formula $[(\eta^6\text{-arene}^1)Ru(\eta^6\text{-arene}^2)]Y_2$ ($arene^1$ = benzene, hexamethylbenzene, mesitylene; $arene^2$ = benzene, hexamethylbenzene, mesitylene, etc; Y = BF_4, PF_6), by the reaction of $[(\eta^6\text{-arene}^1)RuCl_2]_2$ in acetone with AgY, an acid (CF_3CO_2H or HY), and $arene^2$ (Scheme 1.5). It



Scheme 1.5 Synthesis of a symmetric or asymmetric $[(\eta^6\text{-arene}^1)Ru(\eta^6\text{-arene}^2)]Y_2$ complex

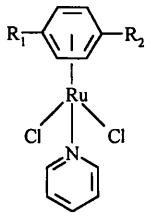
has previously been shown[95] that the cationic *tris*(acetone) complex $[(\eta^6\text{-arene}^1)Ru(OCMe_2)_3]^{2+}$ (formed *in situ via* step 1, Scheme 1.5) undergoes further reactions dependent on the nature of the counteranion. For example in the presence of BF_4^-, it forms the diacetone alcohol complex $[(\eta^6\text{-arene}^1)Ru(OCMe_2)(Me_2C(OH)CH_2COMe)][BF_4]_2$ *via* an aldol condensation reaction. However in the presence of PF_6^-, it reacts to give the tri-μ-difluorophosphato complex $[(\eta^6\text{-arene}^1)_2Ru_2(\mu\text{-}O_2PF_2)_3]PF_6$. In any case, both these complexes undergo an acid catalysed arene^2 exchange reaction forming the *bis*(arene) product (step 2). Several modifications to the original procedure have since been reported.[96,97]

1.9 (Arene)ruthenium(II) complexes with N-donor ligands

Most of the new chemistry described in this thesis is of compounds in which the arene present on the ruthenium is either benzene or *para*-cymene. The dimers $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ thus provided the "$(\eta^6\text{-}C_6H_6)Ru(II)$" and "$(\eta^6\text{-}MeC_6H_4{}^iPr)Ru(II)$" moieties found in the compounds described, *via* halide bridge cleavage reactions analogous to those described below (unless otherwise stated, the term "dimer" refers to both the benzene

and *para*-cymene containing binuclear compounds).

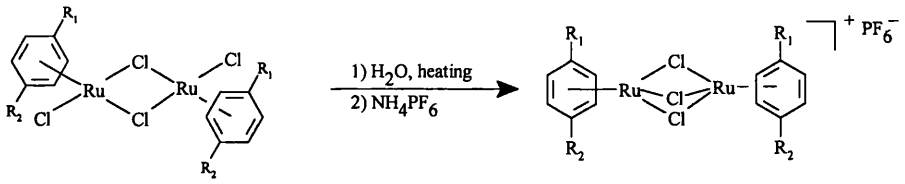
The dimer was found to undergo chloride bridge cleavage upon treatment with pyridine, forming the monomeric complex $[(\eta^6\text{-arene})RuCl_2(C_5H_5N)]$ (Figure 1.18).[5]



R_1 and R_2 = H or R_1 = Me and R_2 = ^{i}Pr

Figure 1.18 $[(\eta^6\text{-arene})RuCl_2(C_5H_5N)]$ (arene = benzene or para-cymene)

In the same study the synthesis of a novel binuclear tri-μ-chloro-bridged complex $[(\eta^6\text{-arene})_2Ru_2Cl_3]PF_6$ (Scheme 1.6) was achieved by reacting the



R_1 and R_2 = H or R_1 = Me and R_2 = ^{i}Pr

Scheme 1.6 Synthesis of the triply chloro-bridged complex $[(\eta^6\text{-arene})_2Ru_2Cl_3]PF_6$ (arene = benzene or *para*-cymene)

dimer with hot water and subsequently precipitating out the orange product by addition of NH_4PF_6.[5] It was later found that considerably greater yields of the triply chloro-bridged complex could be achieved by reacting the dimer with an excess of NH_4PF_6 in methanol.[6,98,99]

Refluxing the complex $[(\eta^6\text{-}C_6H_6)_2Ru_2Cl_3]PF_6$ with pyridine, in ethanol, led to the formation of the monomeric complex $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_5N)_2]PF_6$ in which two monodentate pyridine ligands are present on the metal (Figure 1.19).[6]

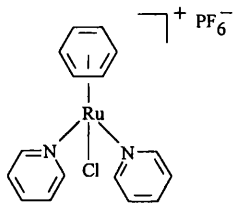


Figure 1.19 The structure of $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_5N)_2]PF_6$

Interestingly protonation of an equimolar mixture of $[(\eta^6\text{-}C_6H_6)RuCl_2(C_5H_5N)]$ and $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_5N)_2]PF_6$ with HBF_4 in methanol provides an almost quantitative synthetic route to the complex $[(\eta^6\text{-}C_6H_6)_2Ru_2Cl_3]BF_4$.[100]

The reaction of the dimer with hydrazine hydrate in methanol gives the dicationic species $[(\eta^6\text{-arene})Ru(N_2H_4)_3]^{2+}$, which was isolated as its tetraphenylborate salt. The polar nature of the solvent facilitates chloride loss. Subsequent treatment of this complex with pyridine, in acetone, gives $[(\eta^6\text{-arene})Ru(C_5H_5N)_3][BPh_4]_2$ in which all three hydrazine ligands are replaced by pyridine.[7]

The reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with an excess of 2,2'-bipyridyl (bipy) in methanol gives the monocationic complex $[(\eta^6\text{-}C_6H_6)RuCl(bipy)]^+$ which was precipitated out as its hexafluorophosphate salt by addition of NH_4PF_6. Unsurprisingly, the compound possesses a bidentately coordinated 2,2'-

bipyridyl ligand (Figure 1.20). A similar chemistry is known for the ligand 1,10-phenanthroline.[8,9]

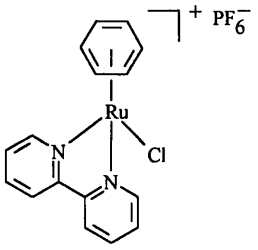


Figure 1.20 The structure of $[(\eta^6\text{-}C_6H_6)RuCl(bipy)]PF_6$

To the best of our knowledge, at the time of writing this thesis, no (η^6-arene)Ru(II) complexes of *tris*(2-pyridyl) ligands have been reported, other than our own. However, a variety of bi- and tri-dentate, pyridine containing ligands of the types shown in Figure 1.21 have been synthesised[101-104] and

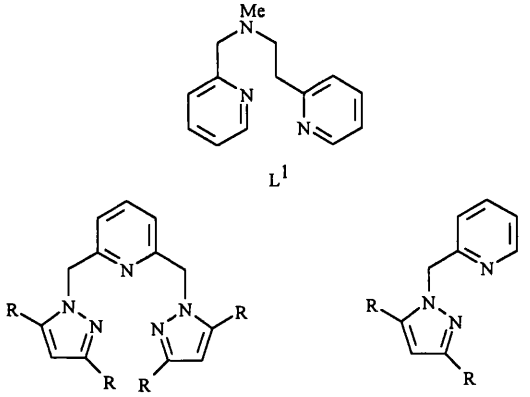


Figure 1.21 Pyridine containing ligands known to coordinate to "$(\eta^6\text{-}C_6H_6)Ru(II)$"

incorporated into "$(\eta^6\text{-}C_6H_6)Ru(II)$" complexes with piano stool geometries.[105] The general synthetic methods used were closely similar to those described above. The ^1H NMR spectra of all five complexes were recorded and assigned

with the assistance of previously recorded NMR data.[101-104,106-111] Each spectrum revealed the presence of the benzene ligand, which always appeared as a sharp singlet. It was apparent that only the ligand L^1 coordinated in a tridentate manner, to give the complex $[(\eta^6\text{-}C_6H_6)RuL^1][PF_6]_2$, while all the other ligands, L^2-L^5, coordinated in a bidentate fashion to give the complexes $[(\eta^6\text{-}C_6H_6)Ru(L^{2\text{-}5})Cl]PF_6$. Bidentate coordination, involving one pyridyl and one pyrazolyl ring, in the complexes of L^2 and L^3 was confirmed by the appearance of two sets of pyrazolyl ring protons/methyl group resonances in their ^1H NMR spectra, an observation consistent with one coordinated and one non-coordinated pyrazolyl group. The structure of the complex containing L^1 was further confirmed by X-ray crystallography, Figure 1.22.

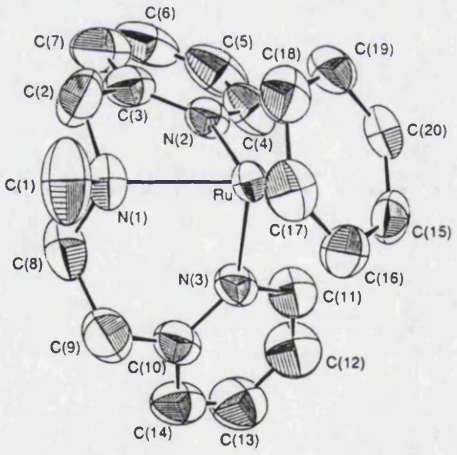


Figure 1.22 Structure of the cation in $[(\eta^6\text{-}C_6H_6)RuL^1][PF_6]_2$ [105]

The monoanionic ligands hydro*tris*(1-pyrazolyl)borate ($HB\{Pz\}_3^-$) and *tetrakis*(1-pyrazolyl)borate ($B\{Pz\}_4^-$) were synthesised in 1967 as their alkali metal salts, from alkali metal borohydrides and pyrazole,[112] and are amongst the most studied pyrazole-derived ligands. The complex $[(\eta^6\text{-}C_6H_6)Ru(B\{Pz\}_4)]PF_6$ was prepared by reacting $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with $KB(Pz)_4$

in refluxing acetonitrile, followed by treatment with NH_4PF_6, and crystallographically characterised.[107,113] The X-ray structure (Figure 1.23) reveals tridentate N,N',N" coordination of the ligand, with the fourth pyrazolyl

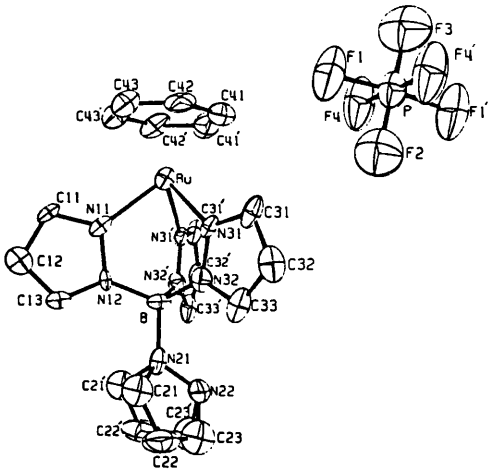


Figure 1.23 The structure of $[(\eta^6\text{-}C_6H_6)Ru(B\{Pz\}_4)]PF_6$ [107]

ring remaining uncoordinated. The Ru(II) coordination geometry is that of a distorted octahedron, with a mean N-Ru-N angle of 84.3(0.5) ° due to the ligand's bite.

Previously in our group, the complexes $[(\eta^6\text{-}C_6H_6)Ru(HB\{Pz\}_3)]PF_6$ and $[(\eta^6\text{-}C_6H_6)Ru(HB\{3,5\text{-}Me_2Pz\}_3)]PF_6$ were synthesised from the sodium salts of the appropriate ligand and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$.[17] In the ^1H NMR spectrum of each complex, there are four well-defined resonances consistent with tridentate coordination of the hydro*tris*(pyrazolyl)borate ligand.[114,115] In the former complex these correspond to three non-equivalent pyrazolyl protons of the three equivalent rings, as well as the benzene singlet, whilst in the latter complex two higher field resonances are consistent with the two methyl environments. In both ^1H NMR spectra the boron bound proton occurs as a

broad resonance.

The dicationic complexes $[(\eta^6\text{-arene})Ru(HC\{Pz\}_3)][PF_6]_2$ (arene = benzene, *para*-cymene) were prepared by reaction of the neutral *tris*(1-pyrazolyl)methane ligand (Figure 1.3) with the appropriate dimer,[17] and represent the archetypal complexes from which our studies have evolved. The N,N',N'' tridentate coordination mode was confirmed in these complexes by ^1H NMR spectroscopy and the complex $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru(HC\{Pz\}_3)][PF_6]_2$ was further characterised crystallographically (Figure 1.24). The three N-Ru-N

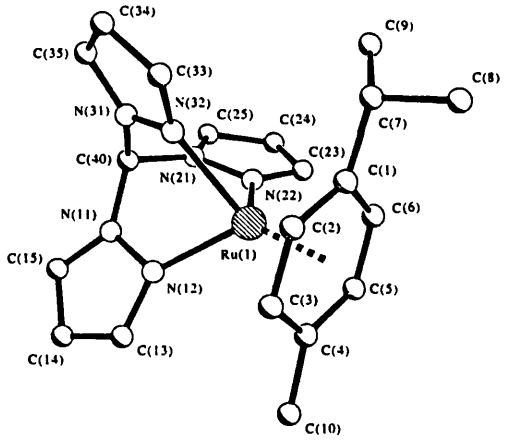


Figure 1.24 Structure of the cation in $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru(HC\{Pz\}_3)][PF_6]_2$ [17]

bond angles deviate from 90 °, consistent with distortion from ideal octahedral geometry of the Ru(II) coordination sphere. Furthermore two of the Ru-N bond lengths are noticeably shorter than the third. This is believed to be a consequence of interligand interaction, since the ^{i}propyl group of the *para*-cymene ligand is rotated such that one of the methyl substituents lies closer to the ancillary ligand.

1.10 Reactions of nucleophiles with (η^6-arene)Ru(II) complexes

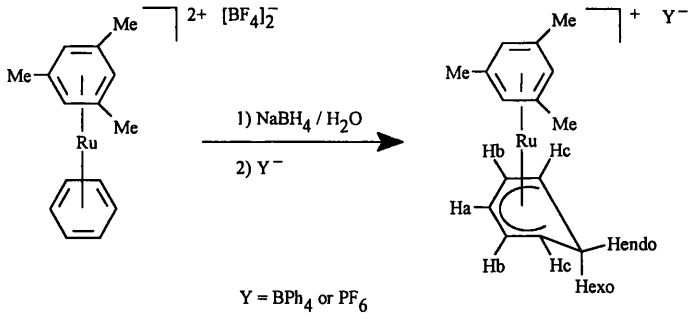
During the work leading up to this thesis the reactions of a variety of dicationic [(η^6-arene)Ru(*tris*(2-pyridyl) ligand)]$^{2+}$ complexes with nucleophiles (H^-, D^-, CN^-, OH^-) were investigated (Chapter 5). Only single addition to give cyclohexadienyl products was observed. Some related chemistry of analogous (η^6-arene)Ru(II) complexes will now be described, with emphasis on reactions of the same group of nucleophiles leading to cyclohexadienyl products. It should be noted however that cyclohexadienyl products derived from a variety of other nucleophiles, such as tertiary phosphines (e.g. PMe_3, PMe_2Ph)[116,117] and carbon-donors (e.g. $CH(CO_2Me)_2^-$, Ph^-),[118] are also quite common, as are reactions leading to diene containing products.

Nucleophilic addition reactions to arenes that have been electrophilically activated by coordination to a metal provide a feasible route to achieving arene functionalisation. *Bis*(arene)Fe(II) complexes are expected to be *ca.* 30 times more electrophilic than their ruthenium analogues and thus react more readily with nucleophiles.[119] However the use of *bis*(arene)Ru(II) complexes has advantages in that asymmetric *bis*(arene)Ru(II) complexes are readily available.[94,96,97] In addition the use of ruthenium complexes alleviates the problem of electron transfer reactions that frequently lead to decomposition in the case of iron complexes.[120-122]

The first example of an (η^5-cyclohexadienyl)ruthenium complex was prepared by Jones and co-workers in 1962[123] (after it was recognised that the η^5-

cyclohexadienyl ligand, in $[(\eta^5\text{-}C_6H_7)Mn(CO)_3]$ and related compounds, was stabilised by bonding to the metal[124]) by the reaction of $[(\eta^6\text{-}C_6H_6)_2Ru][ClO_4]_2$ with lithium aluminium hydride. A mixture of the two neutral compounds $[(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}1,3\text{-}C_6H_8)]$ and $[(\eta^5\text{-}C_6H_7)_2Ru]$ were formed and characterised by IR and ^1H NMR spectroscopy. Numerous stable η^5-cyclohexadienyl complexes derived from the '$(\eta^6$-arene)Ru' fragment have since been reported.[8,9,18,19,96,116-118,125-130]

In a study concerned with asymmetric *bis*(arene)Ru(II) complexes, the reaction of the dication $[(\eta^6\text{-}C_6H_6)Ru(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)]^{2+}$ with sodium borohydride in water yielded the monocationic species $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)]^+$, Scheme 1.7.[96] The ^1H NMR spectrum of $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)]PF_6$

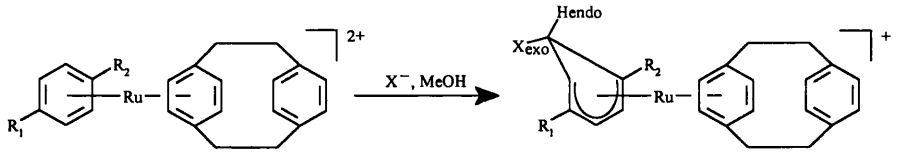


Scheme 1.7 Synthesis of the complex $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)]Y$

confirmed the suggested cationic structure in that, as well as the mesitylene signals, the following cyclohexadienyl signals were observed and assigned (in conjunction with the labelling shown in Scheme 1.7): H_a: triplet, δ 6.02; H_b: doublet of doublets, δ 5.07; H_c: doublet of doublets, δ 3.18; H_{exo}: doublet of triplets, δ 2.62; H_{endo}: doublet (J = 15 Hz), δ 2.22. Typical of the reactions of

asymmetric *bis*(arene)Ru(II) complexes with the hydride ion, the attack preferentially occurred at the less alkylated arene.

Treatment of the complexes $[(\eta^6\text{-arene})Ru(\eta^6\text{-[2.2]}\textit{para}\text{cyclophane})][BF_4]_2$ (arene = benzene, *para*-cymene) with nucleophiles (H^-, CN^- or D^-) in methanol exclusively give the monocationic products $[(\eta^5\text{-cyclohexadienyl})\text{-}Ru(\eta^6\text{-[2.2]}\textit{para}\text{cyclophane})]^+$, Scheme 1.8.[127,128] However repeating the



X = H, CN or D; R_1 and R_2 = H or R_1 = CH_3 and R_2 = ^{i}Pr or R_1 = ^{i}Pr and R_2 = CH_3

Scheme 1.8 Single nucleophilic addition to $[(\eta^6\text{-arene})Ru(\eta^6\text{-}C_{16}H_{16})]^{2+}$ (arene = benzene, *para*-cymene)

reaction in THF, with the hydride sources sodium *bis*(methoxyethoxy)-aluminium hydride (Red-Al) (arene = benzene)[131] or $NaBH_4$ (arene = *para*-cymene)[129] was found to give the dienes $[(\eta^4\text{-diene})Ru(\eta^6\text{-}$[2.2]*para*cyclophane)] as products. Figure 1.25 shows the ^{1}H NMR spectrum of $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}C_{16}H_{16})]BF_4$ along with the cyclohexadienyl ring assignments. In marked contrast to $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-1,3,5-}C_6Me_3H_3)]PF_6$ (*vide supra*)[96] the H_{endo} and H_{exo} resonance assignments for $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}C_{16}H_{16})]BF_4$ occur at δ 2.32 (multiplet) and 2.06 (doublet (J = 13.5 Hz)) respectively. The widely spaced doublet is a consequence of no vicinal coupling being observed between the H_{exo} and H_c protons due to the dihedral

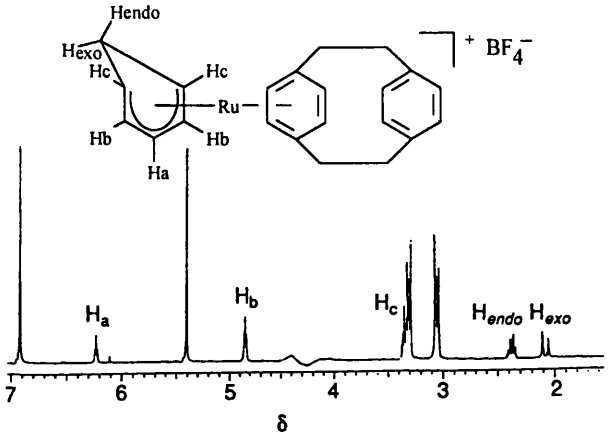


Figure 1.25 ^{1}H NMR spectrum of $[(\eta^5\text{-}C_6H_7)Ru(\eta^6\text{-}C_{16}H_{16})]BF_4$ [128]

angle between these protons being close to 90 °. The IR spectrum of this complex possesses two strong bands at 2926 and 2813 cm^{-1}, attributed to $\nu(CH_{endo})$ and $\nu(CH_{exo})$ respectively.[124,131] When the deuteride analog is prepared and the ^{1}H NMR spectrum examined it becomes apparent that the doublet due to H_{exo} is missing, while all other resonances are essentially unchanged. Likewise the IR band at 2813 cm^{-1} now occurs at 2113 cm^{-1} due to the deuterium isotope shift.[124,132] Hence in accordance with the Davies-Green-Mingos rules[133] it was concluded that *exo* addition of a single nucleophile had occured at the less alkylated arene. It should be noted that the ^{1}H NMR spectrum of the complex derived from the analogous *para*-cymene containing precursor demonstrated that two isomers of $[(\eta^5\text{-}MeC_6H_5{}^{i}Pr)Ru(\eta^6\text{-}C_{16}H_{16})]BF_4$ were formed, of the types shown in Figure 1.26.

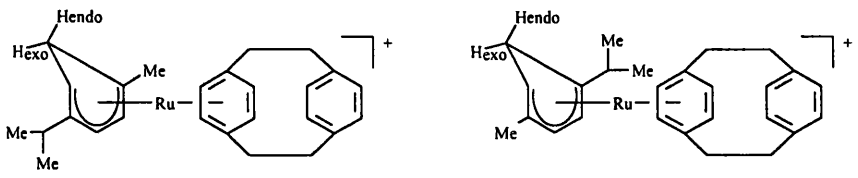


Figure 1.26 Two isomeric forms of the cation $[(\eta^5\text{-}MeC_6H_5{}^{i}Pr)Ru(\eta^6\text{-}C_{16}H_{16})]^+$

1.11 Reactions of nucleophiles with (η^6-arene)Ru(II) complexes containing N-donor ligands

As part of an investigation into the reactions of nucleophiles with (η^6-arene)Ru(II) complexes containing nitrogen and phosphorus ligands, the complex $[(\eta^6\text{-}C_6H_6)RuCl(bipy)]PF_6$ was prepared[8,9] and treated with various nucleophiles (X^-). Rapid decomposition occurred and no well characterised products were obtained. However $[(\eta^6\text{-}C_6H_6)RuCl(bipy)]PF_6$ reacts with tertiary phosphines (PR_3) in methanol to give complex dications of general type $[(\eta^6\text{-}C_6H_6)RuPR_3(bipy)]^{2+}$, which readily undergo nucleophilic addition reactions to give the air-stable, η^5-cyclohexadienyl complexes $[(\eta^5\text{-}C_6H_6X)RuPR_3(bipy)]PF_6$ (X = H, CN, OH; PR_3 = PMe_2Ph, $PMePh_2$). These were characterised by analytical, conductivity and ^1H NMR measurements. The reactivity of the complexes $[(\eta^6\text{-}C_6H_6)RuPR_3(bipy)][PF_6]_2$ towards nucleophiles was explained by the ability of the π-accepting ligands (2,2'-bipyridyl and tertiary phosphines) to enhance the arene's electrophilicity, as well as the complexes' high formal positive charge. The instability of the complex $[(\eta^6\text{-}C_6H_6)RuCl(bipy)]PF_6$ towards nucleophiles was attributed to competing nucleophilic reactions between the arene and the metal *via* chloride ligand substitution.[9]

In studies on the nucleophilic addition reactions of (η^6-arene)Ru(II) complexes with tridentate nitrogen-donor ligands, Shirin and co-workers[130] found that treatment of the complex $[(\eta^6\text{-}C_6H_6)RuL^1][PF_6]_2$ (Figure 1.22)[105] with X^- (X = H (reaction in methanol), CN (2:1 acetonitrile/methanol) or OH (acetone)) gave the compound $[(\eta^5\text{-}C_6H_6X)RuL^1]PF_6$ as the sole product. The X-ray structure of

the cyanide derivative is shown in Figure 1.27. The piano stool geometry present in the parent complex is retained in the

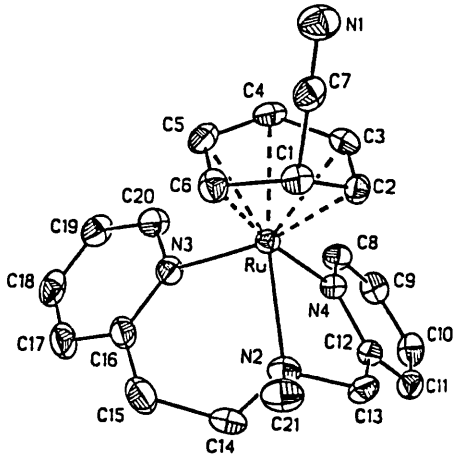
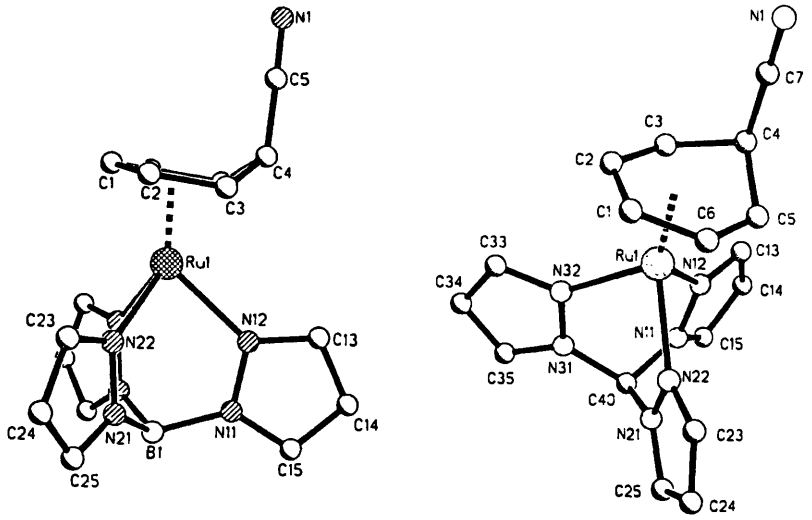


Figure 1.27 Structure of the cation in $[(\eta^5\text{-}C_6H_6CN)RuL^1]PF_6$ [130]

cyclohexadienyl derivative. The cyanide exhibits an *exo* stereochemistry in its attachment to the cyclohexadienyl ring.

Single nucleophilic addition to the complex cations $[(\eta^6\text{-arene})Ru(HB\{Pz\}_3)]^+$ (arene = C_6H_6, $MeC_6H_4{}^iPr$, 1,4-$Me_2C_6H_4$, 1,4-$^iPr_2C_6H_4$ or 1,3,5-$Me_3C_6H_3$) or $[(\eta^6\text{-arene})Ru(HC\{Pz\}_3)]^{2+}$ (arene = C_6H_6, $MeC_6H_4{}^iPr$, 1,4-$Me_2C_6H_4$)[17] gives the neutral or monocationic products $[(\eta^5\text{-cyclohexadienyl})Ru(HB\{Pz\}_3)]$ or $[(\eta^5\text{-cyclohexadienyl})Ru(HC\{Pz\}_3)]^+$ respectively.[18,19] Figure 1.28 shows the crystal structures of the neutral and cationic species $[(\eta^5\text{-}C_6H_6CN)Ru(HB\{Pz\}_3)]$, **A**, and $[(\eta^5\text{-}C_6H_6CN)Ru(HC\{Pz\}_3)]^+$, **B**. Common to both structures, and analogous to the cation shown in Figure 1.27, is the piano stool geometry about the metal and the cyanide addition in an *exo* manner.

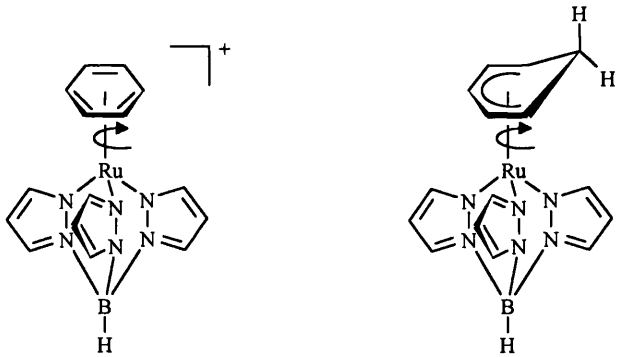


A B

Figure 1.28 Stuctures of $[(\eta^5\text{-}C_6H_6CN)Ru(HB\{Pz\}_3)]$ and $[(\eta^5\text{-}C_6H_6CN)Ru(HC\{Pz\}_3)]^+$ [18,19]

The room temperature ^1H NMR spectrum of the complex $[(\eta^5\text{-}C_6H_7)Ru(HB\{Pz\}_3)]$ exhibits the five expected cyclohexadienyl resonances[127,128] and the ^1H NMR spectra of the hydroxide, deuteride and cyanide analogs are very similar, except for the absence of the H_{exo} doublet and presence of an H_{endo} triplet. Interestingly, unlike the three well-defined pyrazolyl proton resonances in the room temperature ^1H NMR spectrum of the parent complex $[(\eta^6\text{-}C_6H_6)Ru(HB\{Pz\}_3)]PF_6$,[17] all four cyclohexadienyl derivatives exhibit only two broad pyrazolyl resonances, with a relative intensity of 2:1. Cooling the samples to –65 °C resolves these into two sharp sets of three resonances, with a 2:1 integral ratio, whilst heating to 50 °C leads to the observation of three broad, equally intense resonances. Thus at higher temperatures all three pyrazolyl rings are equivalent, whereas at lower temperatures two remain equivalent and one is unique. The cyclohexadienyl resonances remain essentially unchanged throughout the temperature range.

While changes in hapticity of the hydro*tris*(1-pyrazolyl)borate ligand, between the κ^3 and κ^2 binding modes, offers a possible explaination for the fluxionality observed on the ^1H NMR time-scale, this was ruled out on the basis that treating a solution of the cyclohexadienyls with carbon monoxide or $P(OMe)_3$ fails to 'trap out' a complex containing a κ^2-ligand. More convincingly it was proposed that at low temperatures restricted rotation about the Ru-cyclohexadienyl axis was responsible for the two pyrazolyl environments. This theory was computationally investigated *via* extended Hückel molecular orbital (EHMO) calculations. In the case of the cation $[(\eta^6\text{-}C_6H_6)Ru(HB\{Pz\}_3)]^+$ the energy barrier to ring rotation (see Figure 1.29) through 120 ° is calculated



A B

Figure 1.29 Rotation of the benzene and cyclohexadienyl about the Ru-ring centroid vector in $[(\eta^6\text{-}C_6H_6)Ru(HB\{Pz\}_3)]^+$, **A**, and $[(\eta^5\text{-}C_6H_7)Ru(HB\{Pz\}_3)]$, **B**, respectively

to be relatively insignificant, *ca.* 11 $kJmol^{-1}$, while in the complex $[(\eta^5\text{-}C_6H_7)Ru(HB\{Pz\}_3)]$ it is *ca.* 58 $kJmol^{-1}$, a value consistent with the observations made in the variable temperature NMR studies. EHMO calculations were further extended to substituted-cyclohexadienyl complexes of hydro*tris*(1-

pyrazolyl)borate, where it was concluded that the energy barrier to cyclohexadienyl rotation was a function of the number and steric properties of alkyl substituents on the cyclohexadienyl ligand. Subsequently a range of compounds were prepared and variable temperature NMR studies produced results consistent with the predictions of the molecular orbital calculations.[19]

1.12 Summary

In the remainder of this thesis, following Chapter 2 which describes the preparations of a variety of *tris*(2-pyridyl) compounds, studies into (arene)Ru(II) complexes containing *tris*(2-pyridyl) ligands will be described. Comparisons will be drawn with the coordination modes described in this introduction, and the influence of substituents on the pyridyl rings and on the bridgehead carbon atom assessed in Chapters 3 and 4. Studies into the reactions of the new compounds with nucleophiles are described in Chapter 5.

Chapter 2

The synthesis of

Tris(2-pyridyl) compounds

Introduction

A variety of carbon-bridged *tris*(2-pyridyl) compounds were synthesised in the course of our investigations, some of which had been previously reported in the literature, while others were novel and prepared *via* modifications of literature procedures.[25,60] The different chemistries of these organic compounds, with respect to coordination modes and steric properties in their (η^6-arene)Ru(II) complexes, are examined in Chapters 3 and 4.

2.1 Results and discussion

The chloromethane, ethoxymethane and methane derivatives of *tris*(2-pyridyl)methanol with their differing bridgehead substituents, as well as a number of methyl-ring-substituted analogs of these, were prepared (Figure 2.1).

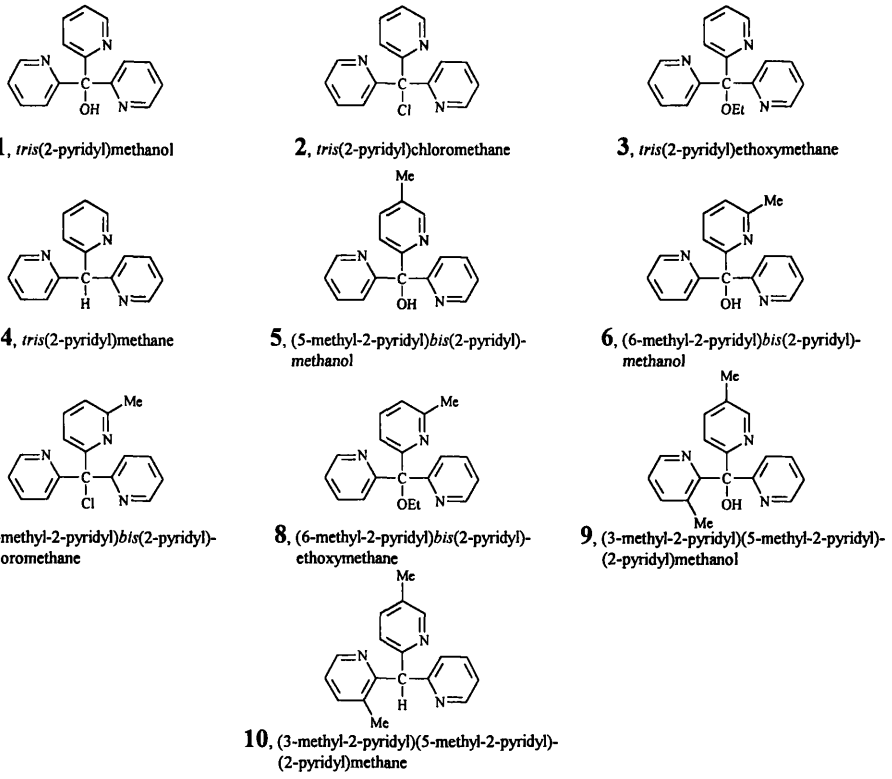
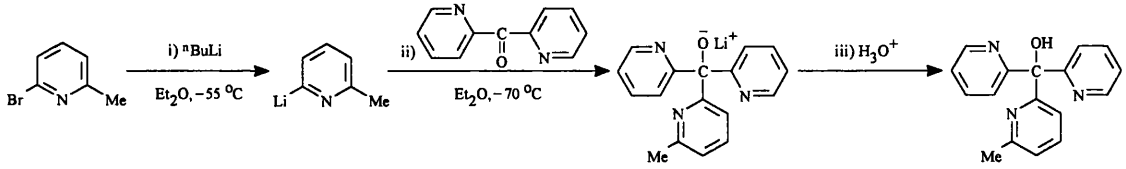


Figure 2.1 Carbon-bridged *tris*(2-pyridyl) compounds

2.1.1 The synthesis of *tris*(2-pyridyl) compounds

Compounds **5**, **6** and **9** were prepared by reacting the appropriate lithiopyridine with a *bis*(2-pyridyl)ketone using an analogous procedure to that used in the preparation of compound **1** (Scheme 1.1). The synthesis of compound **6**, depicted in Scheme 2.1, illustrates the synthetic method for a specific example. In step i of Scheme 2.1, 2-bromo-6-methylpyridine reacts

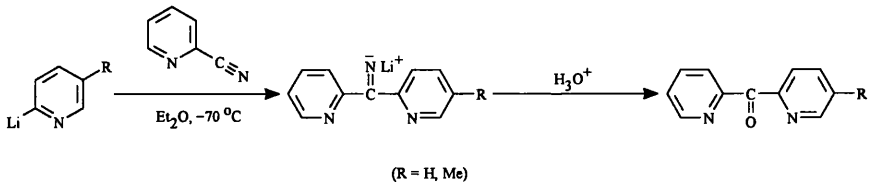


Scheme 2.1 The synthesis of (6-methyl-2-pyridyl)*bis*(2-pyridyl)methanol

with ^{n}butyllithium to give 2-lithio-6-methylpyridine. Reaction of this compound, in step ii, with *bis*(2-pyridyl)ketone *via* nucleophilic attack on the carbonyl carbon by the organolithium compound forms an alkoxide ion, which upon subsequent treatment with dilute acid (step iii) gives the alcohol, (6-methyl-2-pyridyl)*bis*(2-pyridyl)methanol.

Compound **1** was obtained in 44 % yield, whereas compounds **5**, **6** and **9** were achieved in considerably poorer yields (18, 19 and 26 % respectively). Whether or not these lower yields can be directly attributed to the use of substituted pyridines is unknown. Modifications to the general procedure described in Scheme 1.1 were made where necessary e.g. changes to the solvents to facilitate dissolution of reagents. Furthermore the crude mixtures obtained in the syntheses of compounds **5**, **6** and **9** were purified by techniques which may be less than optimum, resulting in lower overall yields.

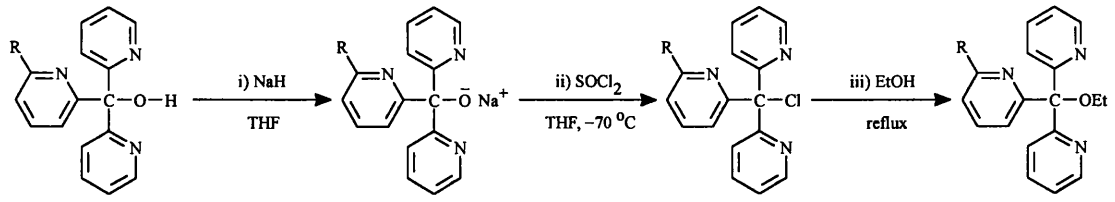
The ketones *bis*(2-pyridyl)ketone and (5-methyl-2-pyridyl)(2-pyridyl)ketone were prepared by the reaction of 2-cyanopyridine with 2-lithiopyridine or 2-lithio-5-methylpyridine, respectively, Scheme 2.2. Intermediate imine often



Scheme 2.2 The synthesis of *bis*(2-pyridyl)ketone and (5-methyl-2-pyridyl)(2-pyridyl) ketone

contaminates the ketonic product, hence once the crude reaction mixture is extracted into dilute sulfuric acid, the solution is heated in order to decompose the imine, before proceeding with the work-up (sub-section 2.2.3).

Compounds **2**, **3**, **7** and **8** were prepared by reacting the appropriate *tris*(2-pyridyl) compound using the methodologies illustrated in Scheme 1.2. Scheme 2.3 depicts the synthetic routes used in the preparation of these

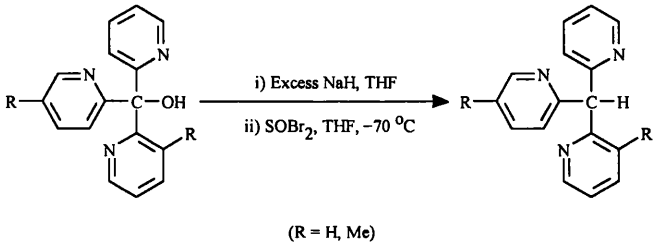


Scheme 2.3 The synthesis of chloro and ethoxy *tris*(2-pyridyl) compounds

compounds. In step i of Scheme 2.3, reaction of the alcohol **1** or **6** with sodium hydride forms the sodium alkoxide which subsequently reacts with thionyl

chloride, step ii, to give the chloromethanes **2** or **7**, respectively. Refluxing compound **2** or **7** in absolute ethanol forms the ethoxymethane compounds **3** or **8** (step iii).

Compounds **4** and **10** were prepared by a modification of step iii of Scheme 1.2. Scheme 2.4 illustrates the synthetic details of this modified procedure. In



Scheme 2.4 The synthesis of *tris*(2-pyridyl)methanes

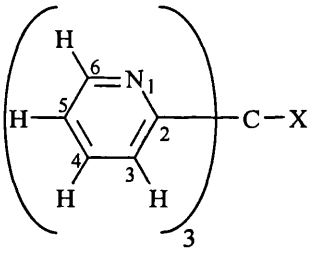
analogy to steps i and ii of Scheme 2.3, reaction of alcohol **1** or **9** with sodium hydride followed by reaction with thionyl bromide gives the bromomethane. This then reacts further with an excess of sodium hydride to give compounds **4** and **10**. (In contrast, use of excess sodium hydride in step i of Scheme 2.3 did not lead to the occurrence of an analogous reaction between the chloromethane and sodium hydride, owing to the increase in carbon-halogen bond strength).

Compound **4** was obtained in 62 % yield, considerably greater than that reported in the literature, 20 %.[25] The most plausible explanation for this increased yield is that the novel procedure (see sub-section 2.2.3) proceeds in fewer steps, *via* the *in situ* use of *tris*(2-pyridyl)bromomethane. In the original

literature preparation *tris*(2-pyridyl)bromomethane is first isolated and purified before its subsequent conversion into *tris*(2-pyridyl)methane.

2.1.2 The characterisation of compounds 1-4 by ^{1}H NMR spectroscopy

Compounds **1-4** have been previously synthesised and characterised,[25,60] and therefore no microanalytical, infrared or mass spectroscopic data are given for them here. However for comparison with compounds **5-10** their ^{1}H NMR spectra will be described. Figure 2.2 illustrates the pyridyl ring atomic numbering scheme employed in the ^{1}H NMR spectral assignments. The



(X = OH (**1**), Cl (**2**), OEt (**3**), H (**4**))

Figure 2.2 The *tris*(2-pyridyl)CX atomic numbering scheme

solution ^{1}H NMR spectra of the four compounds are all similar and exhibit four signals, of equal intensity, in the approximate chemical shift range, δ 7.1-8.6. These correspond to the four non-equivalent protons of the three equivalent pyridyl rings. Figure 2.3 shows the ^{1}H NMR spectrum of compound **2**, in the approximate chemical shift range, which includes an expansion of the 'doublet of doublet of doublets' signal at δ 7.70 due to the proton on the '4' position of the three equivalent pyridyl rings. The coupling between this proton and the

other three non-equivalent protons is resolved to the extent that eight lines are

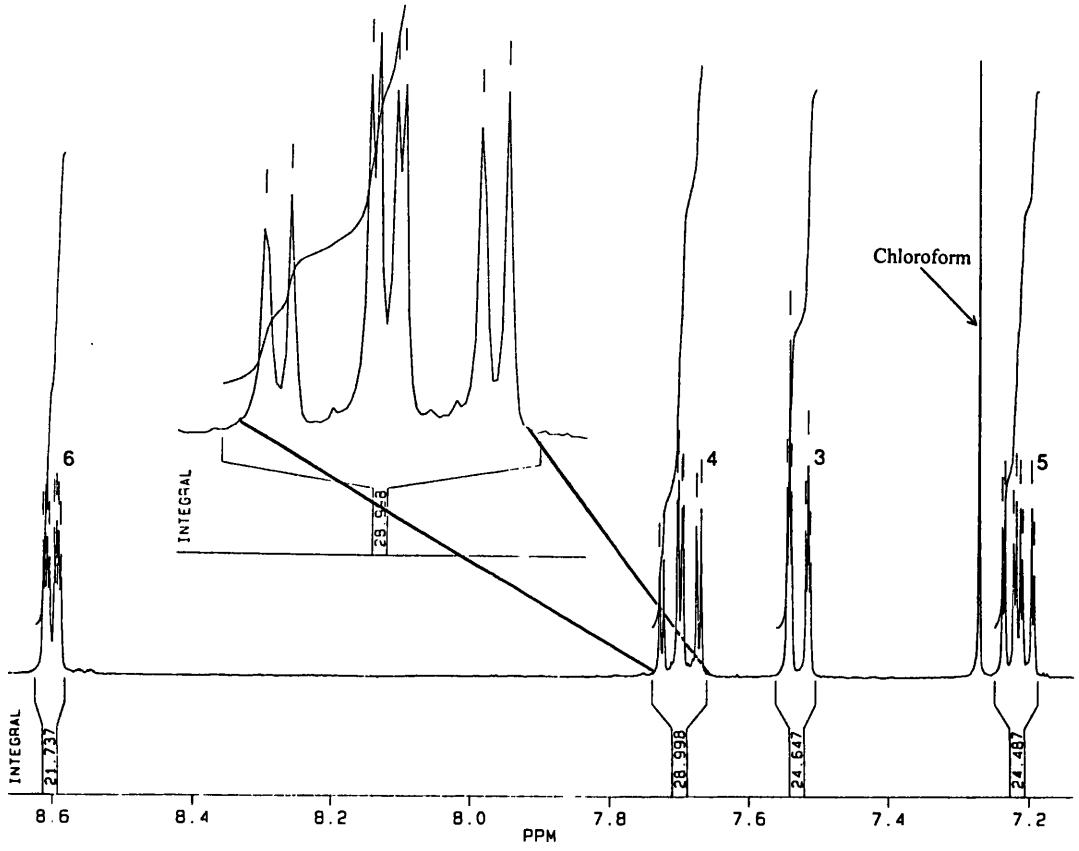


Figure 2.3 Part of the ^{1}H NMR spectrum of *tris*(2-pyridyl)chloromethane

clearly visible. However for most of the *tris*(2-pyridyl) compounds described here, complete resolution of the couplings was not observed. The magnitudes of the coupling constants govern the appearance of a given multiplet, and, with respect to where two ring protons are situated relative to one another, generally follow the trend $J_{ortho} > J_{meta} > J_{para}$. In the case of all four compounds, it is observed that the signal associated with the proton on the pyridyl ring '6' position occurs at the highest chemical shift owing to its position *ortho* to the nitrogen, whilst the proton in the '5' position occurs at the lowest chemical shift. The protons in the '3' and '4' positions tend to have similar

chemical shifts and are often observed to overlap. Additional signals due to the alcoholic, ethyl, and methane protons are observed in the ^{1}H NMR spectra of compounds **1**, **3**, and **4**, respectively.

2.1.3 The characterisation of compounds 5, 6, and 9

The methyl-ring-substituted analogs of compound **1**, that is compounds **5**, **6**, and **9**, were all characterised satisfactorily by elemental analysis. Common to their mass spectra was the observation of three fragments corresponding to the parent molecule (which was also observed) having lost one of the following substituents: i) alcoholic group, ii) pyridyl ring, iii) substituted-pyridyl ring. For example, compound **6** exhibits peaks at *m/z* 260, 199, and 185 due to loss of hydroxyl, pyridyl and 6-methylpyridyl groups respectively from the parent molecule (*m/z* 277).

The infrared spectra of compounds **5-10** are all expected to possess ν(C$\equiv$C), ν(C-H$_{aromatic}$) and ν(C-H$_{alkyl}$) absorption bands, reflecting the presence of both aromatic and aliphatic molecular substituents. Indeed the ν(C$\equiv$C) bands are easily recognisable, however, the lower intensities and occasionally similar stretching frequencies associated with the latter bands often makes their accurate assignment difficult. The alcoholic nature of compounds **5**, **6** and **9** is reflected by the observation of a ν(O-H) band in their infrared spectra.

Compounds **5-10** were all characterised by ^{1}H NMR spectroscopy and proton

assignments for the non-substituted pyridyl rings are based on analogies with the spectra of compounds **1-4**. However, the ^{1}H NMR spectra of compounds **5-10** are considerably more complex owing to the presence of one (compounds **5**, **6**, **7**, **8**) or two (compounds **9**,**10**) unique methyl-substituted pyridyl rings, as well as the non-substituted pyridyl rings. For many of these compounds two-dimensional ^{1}H NMR spectroscopy was called upon in order to make proton assignments. Figure 2.4 shows both the ^{1}H (δ 7.1-8.6) and ^{1}H 'correlated spectroscopy' (COSY) NMR spectra of compound **5** (recorded on separate occasions). As the atomic numbering scheme highlights, the unresolved doublet at δ 8.37 is due to the proton on the '6' position of the 5-methyl-2-pyridyl ring, and is at lowest field, relative to the other protons of the same ring. The '4' and '6' protons of this ring experience slight shielding from the *ortho* methyl group explaining why the resonances due to these protons occur at higher fields than the analogous protons of the other two equivalent rings. This phenomenon was also observed in the ^{1}H NMR spectra of compound **9** and of (5-methyl-2-pyridyl)(2-pyridyl)ketone. There are numerous cross peaks within the δ 7.1-8.6 spectral region, corresponding to many spin-spin couplings between the four non-equivalent protons of the two equivalent pyridyl rings, as well as between the three non-equivalent protons on the unique 5-methyl-2-pyridyl substituent. The signal for the hydroxyl proton also occurs in this region, as a singlet at δ 7.22. Proton assignments for compound **5** were made using the spectra shown in Figure 2.4 and the data obtained from the previously assigned ^{1}H NMR spectra of the analog, **1**, and the precursor compound, (5-methyl-2-pyridyl)(2-pyridyl)ketone.

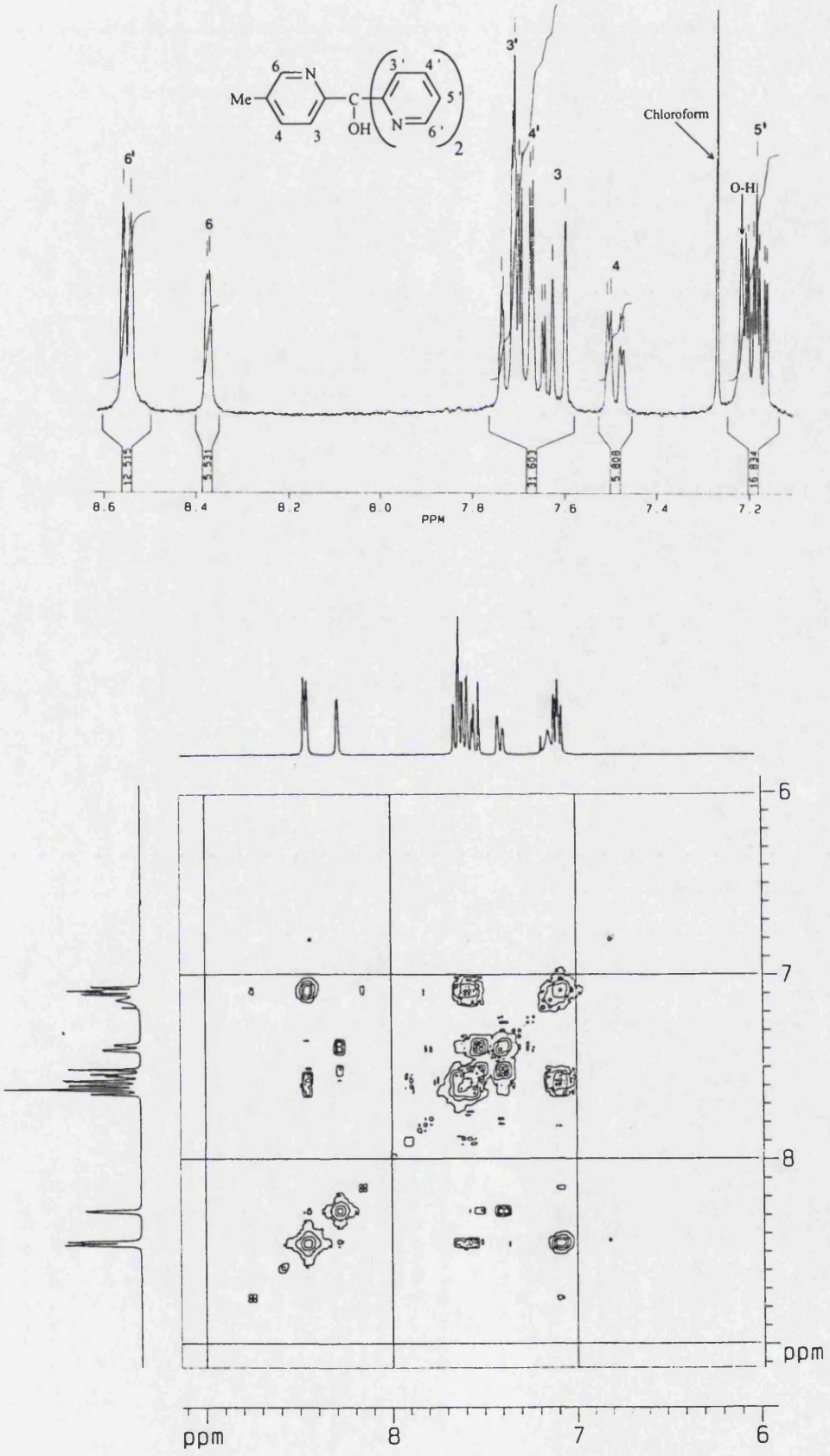
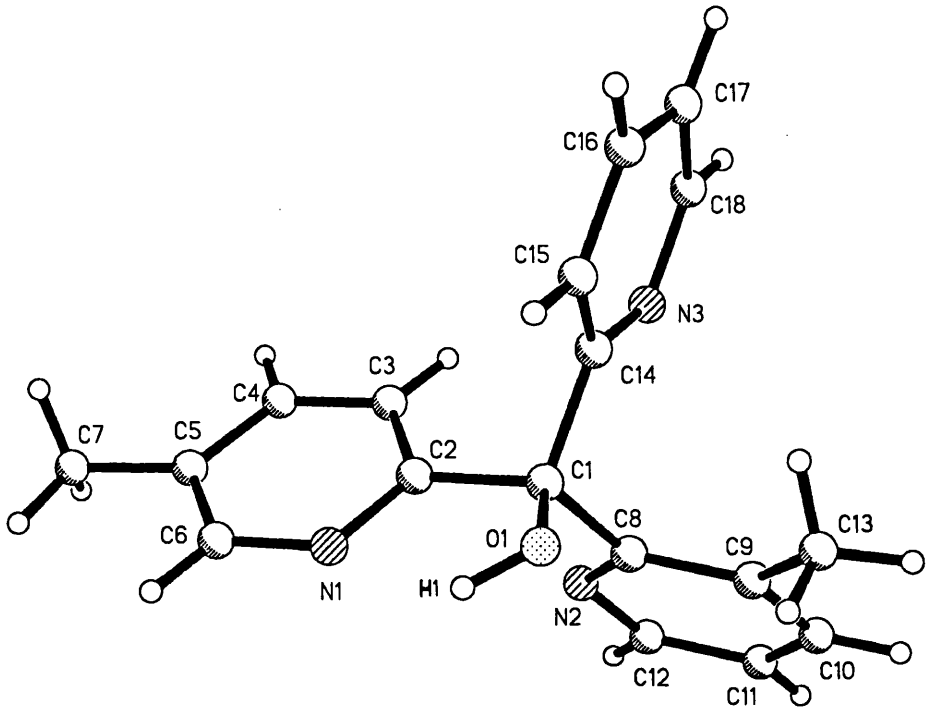


Figure 2.4 ^{1}H and ^{1}H COSY NMR spectra of (5-methyl-2-pyridyl)*bis*(2-pyridyl)methanol

Compound **9** was further characterised crystallographically, Figure 2.5. For

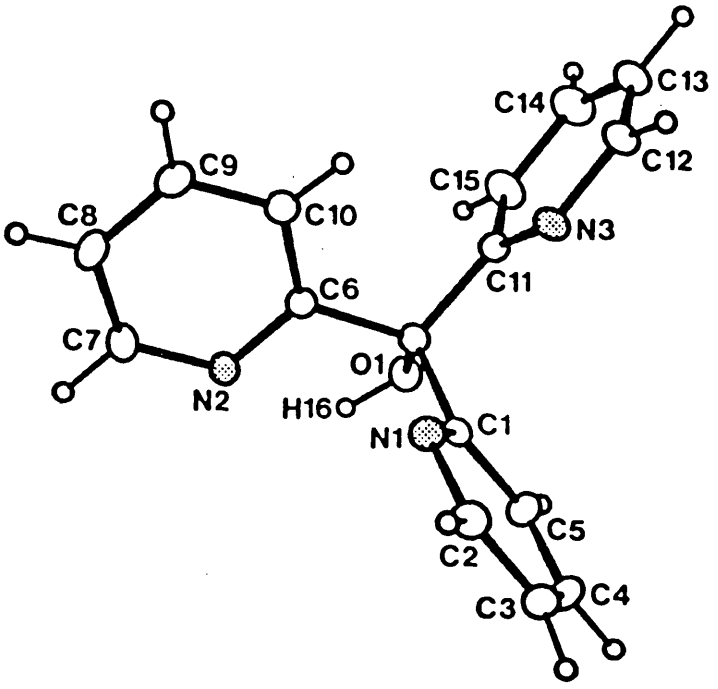


O(1)-H(1)	0.90(3)	C(14)-C(1)-C(8)	110.12(13)
O(1)-C(1)	1.4287(19)	O(1)-C(1)-C(8)	109.16(12)
N(1)-C(2)	1.333(2)	O(1)-C(1)-C(2)	108.32(12)
N(2)-C(8)	1.336(2)	N(1)-C(2)-C(1)	115.05(14)
N(3)-C(14)	1.336(2)	N(2)-C(8)-C(1)	116.43(14)
C(1)-C(14)	1.530(2)	N(3)-C(14)-C(1)	116.51(13)
C(1)-C(8)	1.539(2)	O(1)-C(1)-C(14)	108.82(13)
C(1)-C(2)	1.541(2)	C(8)-C(1)-C(2)	111.73(13)
		C(14)-C(1)-C(2)	108.62(13)

Figure 2.5 Structure of (3-methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol with selected bond lengths (Å) and bond angles (°)

comparative purposes the molecular structure[134] of compound **1**, as determined by X-ray crystallography, is shown in Figure 2.6. Both X-ray studies clearly show three pyridine rings attached *ortho* to the nitrogen to the bridgehead carbon atom which also has a hydroxyl substituent. Unlike compound **1** in which all three pyridyl rings are non-substituted, compound **9** possesses three distinctly different rings, two of which are methyl-substituted,

on the 3 and 5-positions respectively. The bonding parameters within the two structures are very similar to one another. For instance in compounds **9** and **1** the C-O bond length is 1.4287(19) and 1.427(2) Å respectively, and the average $O_{hydroxyl}$-$C_{bridgehead}$-$C_{pyridyl}$ bond angles are 108.77(12) and 108.2(1) °.



O(1)-H(16)	0.88(3)	C(1)-C(16)-C(6)	110.1(1)
C(16)-O(1)	1.427(2)	C(6)-C(16)-C(11)	111.6(1)
C(16)-C(6)	1.530(2)	C(16)-O(1)-H(16)	106.0(2)
C(16)-C(1)	1.524(3)	O(1)-C(16)-C(1)	109.8(1)
C(16)-C(11)	1.526(3)	O(1)-C(16)-C(11)	106.1(2)
N(2)-C(6)	1.333(2)	O(1)-C(16)-C(6)	108.7(1)
N(1)-C(1)	1.333(3)	N(3)-C(11)-C(16)	116.9(2)
N(3)-C(11)	1.329(3)	N(2)-C(6)-C(16)	113.9(1)
		N(1)-C(1)-C(16)	117.4(2)
		C(1)-C(16)-C(11)	110.4(2)

Figure 2.6 Structure of *tris*(2-pyridyl)methanol with selected bond lengths (Å) and bond angles (°)[134]

In both cases the geometry about the bridgehead-carbon atom is that of a tetrahedron. In compound **1** the presence of a weak hydrogen-bonding interaction between the hydroxyl hydrogen atom, H(16), and the pyridyl nitrogen atom, N(2), is implied by the reduced N(2)-C(6)-$C(16)_{bridgehead}$ bond

angle of 113.9(1)° [compared to the average angle (117.2(2)°) for the two related bond angles]. In compound **9** a smaller reduction is seen, 115.05(14)° *vs* 116.47(14)°. The interatomic H(1)....N(1) distance in **9** is 1.94(2) Å, with no equivalent distance being reported for compound **1**. In compound **9** one might argue that sterically hindering methyl groups interfere with any H-bonding interaction between the hydroxyl proton and a pyridyl ring thus giving rise to the 'less reduced' N-C-C angle.

2.1.4 The characterisation of compounds 7, 8 and 10

Compounds **7**, **8** and **10** were characterised by ^{1}H NMR spectroscopy. Figure 2.7 shows the ^{1}H NMR spectrum of compound **8**. Typical of all the *tris*(2-pyridyl) compounds prepared the pyridyl proton signals are located in an approximate δ 7-9 chemical shift range. In Figure 2.7 the ring methyl

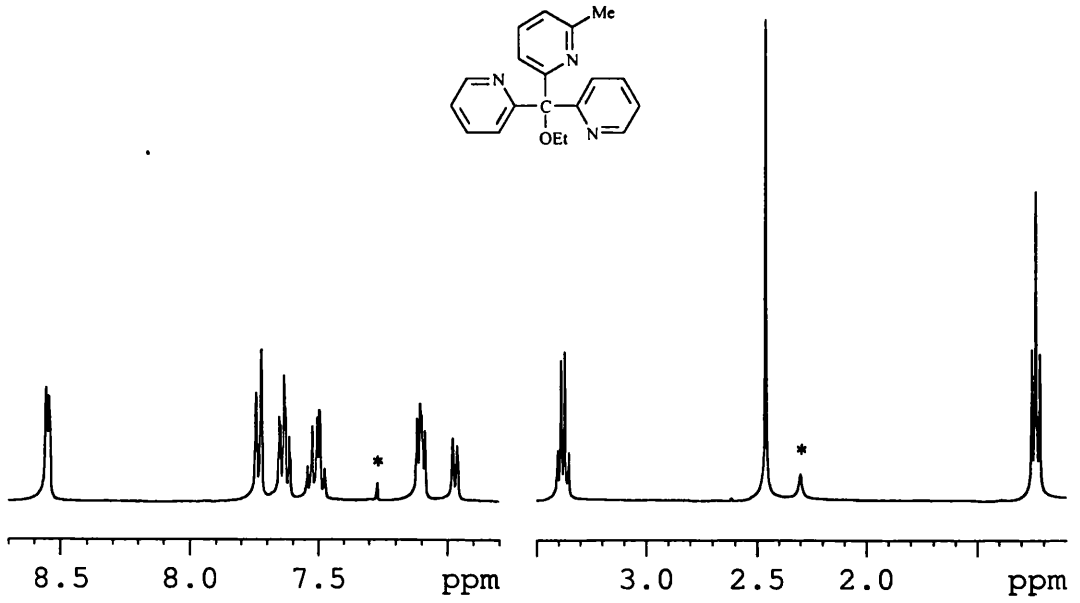


Figure 2.7 ^{1}H NMR spectrum of (6-methyl-2-pyridyl)*bis*(2-pyridyl)ethoxymethane (* signals due to chloroform and water)

proton resonance occurs as a singlet at δ 2.46. By analogy with **3** the presence of the ethoxy substituent on the bridgehead-carbon atom is reflected in the observation of triplet and quartet signals at δ 1.23 and δ 3.38, respectively.

Common to the mass spectra of compounds **7**, **8**, and **10** was the presence of fragments which correspond to the loss of the carbon-bridgehead-substituent (Cl, OEt, and H, respectively) from the parent molecule. Consistent with the formulation of compound **7** is the observation of a ν(C-Cl) band at 766 cm^{-1} in the infrared spectrum.[25] It should be noted, however, that this band was only tentatively assigned as the detection of a carbon-halide bond by infrared spectroscopy is generally unreliable. Unfortunately no satisfactory microanalytical data for compounds **7**, **8** and **10** could be obtained, even though their ^1H NMR spectra were consistently clean, and hence no accurate yields were calculated. However, these compounds were incorporated as ligands into "(η^6-arene)Ru(II)" complexes that were fully characterised, including by the use of microanalytical data (Chapter 4).

2.2 Experimental

2.2.1 Instrumentation

NMR spectra were recorded on Bruker AMX300, 400 and 500 FT spectrometers and chemical shifts are referenced with respect to the residual proton of the deuterated solvent $CDCl_3$, δ 7.27. Infrared spectra were recorded on either a Nicolet 205 or a Shimadzu 8700 FT-IR spectrometer between 4000

and 400 cm^{-1} as KBr discs. Microanalyses were run by the UCL chemistry departmental service. Mass spectra (assignments based on the ^{35}Cl isotope) were run by the UCL chemistry departmental mass spectrometry service. Fast atom bombardment (FAB) and Electron-impact (EI) mass spectra were recorded on a VG ZAB-SE spectrometer, and atmospheric pressure chemical ionisation (APCI) mass spectra were recorded on a Micromass Quattro L/C spectrometer. X-ray structure determinations were carried out at ambient temperature on a Nicolet R3 mV diffractometer (UCL) or at low temperature (150 K) on a Nonius Kappa CCD equipped diffractometer (KCL). Data were processed routinely. Crystal parameters, fractional coordinates, and bond lengths and angles are reported in tables at the end of the Experimental Section.

2.2.2 Materials

Reactions involving lithium reagents were carried out under a dinitrogen atmosphere in degassed solvents using standard Schlenk line techniques. Diethyl ether and tetrahydrofuran were distilled over sodium wire before use. Work-up of reaction mixtures, as well as all the preparations of the other compounds, did not require air-free conditions as all the products were air-stable. The compound 2-bromo-6-methylpyridine was prepared *via* a diazotisation procedure described in the literature.[135] All solvents and other reagents were obtained from the usual commercial sources.

2.2.3 Preparations

(5-Methyl-2-pyridyl)(2-pyridyl)ketone [60] **(modified procedure)**

A 2.5 M solution of ^{n}butyllithium in hexane (34 cm^3, 85 mmol) was added to a

solution of 2-bromo-5-methylpyridine (14.39 g, 84 mmol) in diethyl ether (50 cm^3) which had been pre-cooled to *ca.* –55 °C. The dark brown solution was stirred for 40 minutes before being cooled to *ca.* –70 °C. A solution of 2-cyanopyridine (8.75 g, 84 mmol) in diethyl ether (50 cm^3) was then added and the mixture became dark purple. After stirring for 2 hours the cooling bath was removed and the reaction vessel allowed to reach room temperature. The solution was quenched with water (100 cm^3), followed by the careful addition of 2 M sulfuric acid (50 cm^3), to give a dark red coloration. The diethyl ether layer was separated and extracted several times with dilute sulfuric acid (25 cm^3) until the acid extract was no longer coloured. The combined acid extracts were refluxed for 5 hours, then made alkaline and extracted with diethyl ether. After drying with $MgSO_4$, the solvent was removed and the product was recrystallised three times from diethyl ether. Yield: 5.84 g, 35 % (Found: C, 72.37; H, 4.94; N, 14.17. Calc. for $C_{12}H_{10}N_2O$: C, 72.70; H, 5.09; N, 14.13 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46 ({d,d,d}, $J_{3,5}$=1.19, $J_{4,5}$=7.61, $J_{5,6}$=4.79 Hz, 1H, py-5-H); δ 7.86 ({d,d,d}, $J_{3,4}$=7.86, $J_{4,5}$=7.61, $J_{4,6}$= 1.71 Hz, 1H, py-4-H); δ 8.06 ({d,d}, $J_{3,4}$=7.86, $J_{3,5}$=1.19 Hz, 1H, py-3-H); δ 8.74 ({d,d}, $J_{4,6}$=1.71, $J_{5,6}$=4.79 Hz, 1H, py-6-H); δ 7.67 ({d,d}, $J_{3,4}$=7.95, $J_{4,6}$=1.50 Hz, 1H, 5-Mepy-4-H); δ 8.01 (d, $J_{3,4}$=7.95 Hz, 1H, 5-Mepy-3-H); δ 8.56 (d, $J_{4,6}$=1.50 Hz, 1H, 5-Mepy-6-H); δ 2.41 (s, 3H, CH_3).

Tris(2-pyridyl)methanol, 1 [60]

A 2.5 M solution of ^{n}butyllithium in hexane (19 cm^3, 48 mmol) was added to a pre-cooled (*ca.* –55 °C) solution of 2-bromopyridine (6.06 g, 38 mmol) in diethyl ether (70 cm^3). The mixture was stirred for 40 minutes then the solution

cooled to *ca.* –70 °C. Addition of a solution of *bis*(2-pyridyl)ketone (6.96 g, 38 mmol) in diethyl ether (70 cm^3) gave a dark blue coloration. The solution was stirred for *ca.* 2 hours before the cooling bath was removed and the reaction vessel allowed to warm to room temperature. The reaction mixture was quenched with water (100 cm^3) and 2 M sulfuric acid (25 cm^3) was carefully added. The diethyl ether layer was separated and extracted several times with dilute sulfuric acid (25 cm^3) until the acid extract was no longer coloured. The combined acid extracts were made alkaline and extracted into diethyl ether. After drying with Na_2SO_4, the solvent was removed and the product was recrystallised from 40:60 petroleum spirit and benzene (50:50) to which was added a little activated charcoal. The resultant yellow solid was washed with cold diethyl ether (15 cm^3) and air dried. Yield: 4.39 g, 44 %. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.20 ({d,d,d}, $J_{3,5}$=1.52, $J_{4,5}$=7.05, $J_{5,6}$=4.74 Hz, 3H, py-5-H); δ 7.68 ({d,d,d}, $J_{3,4}$=8.02, $J_{4,5}$=7.05, $J_{4,6}$=1.75 Hz, 3H, py-4-H); δ 7.74 ({d,d,d}, $J_{3,4}$=8.02, $J_{3,5}$=1.52, $J_{3,6}$=1.15 Hz, 3H, py-3-H); δ 8.55 ({d,d,d}, $J_{3,6}$=1.15, $J_{4,6}$=1.75, $J_{5,6}$=4.74 Hz, 3H, py-6-H); δ 7.26 (s, 1H, OH).

Tris(2-pyridyl)chloromethane, 2 [25]

Sodium hydride (0.31 g, 13 mmol) was added to a solution of **1** (0.94 g, 3.6 mmol) in tetrahydrofuran (THF) (30 cm^3), forming a light yellow solution. The reaction mixture was cooled to *ca.* –70 °C and a solution of thionyl chloride (1.65 g, 14 mmol) in THF (10 cm^3) added dropwise. The mixture was stirred for 40 minutes at –70 °C, before the reaction vessel was allowed to warm to room temperature. Water (30 cm^3) was added to the solution, then the organic layer was collected. The aqueous layer was extracted several times with

dichloromethane (25 cm^3) and the combined extracts washed with a 1 M $NaHCO_3$ solution (25 cm^3). The solvent was dried with Na_2SO_4, then the solution evaporated to dryness. The crude product was recrystallised from acetone as a white solid. Yield: 0.77 g, 77 %. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.21 ({d,d,d}, $J_{3,5}$=1.02, $J_{4,5}$=7.56, $J_{5,6}$=4.79 Hz, 3H, py-5-H); δ 7.53 ({d,d,d}, $J_{3,4}$=8.03, $J_{3,5}$=1.02 Hz, 3H, py-3-H); δ 7.70 ({d,d,d}, $J_{3,4}$=8.03, $J_{4,5}$=7.56, $J_{4,6}$=1.83 Hz, 3H, py-4-H); δ 8.60 ({d,d,d}, $J_{3,6}$=0.91, $J_{4,6}$=1.83, $J_{5,6}$=4.79 Hz, 3H, py-6-H).

Tris(2-pyridyl)ethoxymethane, 3 [25]

Compound **2** (0.26 g, 0.92 mmol) was refluxed in absolute ethanol (40 cm^3) for *ca.* 18 hours, to give a yellow solution. The solvent was removed *in vacuo* and the residue treated with 1 M Na_2CO_3 solution (10 cm^3). The solution was extracted several times with dichloromethane (25 cm^3) and the extracts dried with $MgSO_4$. The solvent was removed and the resultant crude product was recrystallised three times from pentane and diethyl ether (50:50). The product was obtained as a white solid. Yield: 0.13 g, 48 %. ^1H NMR ($CDCl_3$, 300 MHz): δ 7,14 ({d,d,d}, $J_{3,5}$=1.35, $J_{4,5}$=7.28, $J_{5,6}$=4.82 Hz, 3H, py-5-H); δ 7.67 ({d,d,d}, $J_{3,4}$=7.97, $J_{4,5}$=7.28, $J_{4,6}$=1.71 Hz, 3H, py-4-H); δ 7.74 ({d,d}, $J_{3,4}$=7.97, $J_{3,5}$=1.35 Hz, 3H, py-3-H); δ 8.58 ({d,d}, $J_{4,6}$=1.71, $J_{5,6}$=4.82 Hz, 3H, py-6-H); δ 1.26 (t, J=6.98 Hz, 3H, $C\underline{H}_3CH_2O$); δ 3.38 (q, J=6.98 Hz, 2H, $CH_3C\underline{H}_2O$).

Tris(2-pyridyl)methane, 4 [25] (modified procedure)

Sodium hydride (0.23 g, 9.6 mmol) was added to a solution of **1** (0.70 g, 2.7 mmol) in THF (20 cm^3), forming a light yellow solution. The mixture was cooled

to *ca.* –70 °C and thionyl bromide (2.02 g, 9.7 mmol) in THF (10 cm^3) added dropwise. The mixture was stirred for 25 minutes, then allowed to warm to room temperature, after which it was stirred for a further 1 hour. Water (40 cm^3) was added to the solution. The organic layer, plus several dichloromethane extracts (25 cm^3) of the aqueous layer, were combined and dried with Na_2SO_4. The solvent was removed and the resultant crude product was recrystallised from diethyl ether as an off-white solid. Yield: 0.41 g, 62 %. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.16 ({d,d,d}, $J_{3,5}$=1.11, $J_{4,5}$=7.51, $J_{5,6}$=4.87 Hz, 3H, py-5-H); δ 7.33 ({d,d}, $J_{3,4}$=7.88, $J_{3,5}$=1.11 Hz, 3H, py-3-H); δ 7.64 ({d,d,d}, $J_{3,4}$=7.88, $J_{4,5}$=7.51, $J_{4,6}$=1.88 Hz, 3H, py-4-H); δ 8.60 ({d,d}, $J_{4,6}$=1.88, $J_{5,6}$=4.87 Hz, 3H, py-6-H); δ 6.00 (s, 1H, CH).

(5-Methyl-2-pyridyl)bis(2-pyridyl)methanol, 5

A 2.5 M solution of ^{n}butyllithium in hexane (7.3 cm^3, 18 mmol) was added to a solution of 2-bromo-5-methylpyridine (3.11 g, 18 mmol) in diethyl ether (70 cm^3) which was pre-cooled to *ca.* –55 °C. The solution was stirred for 45 minutes, then cooled to *ca.* –70 °C. A solution of *bis*(2-pyridyl)ketone (3.33 g, 18 mmol) in diethyl ether (70 cm^3) was added resulting in the development of a purple coloration. The mixture was stirred for 3 hours, then quenched with methanol (80 cm^3). The cooling bath was removed and the reaction vessel allowed to warm to room temperature. A 2 M solution of sulfuric acid (25 cm^3) was carefully added, then the diethyl ether layer was separated and extracted several times with 15 cm^3 of dilute sulfuric acid, until the acid extract was no longer coloured. The combined acid extracts were made alkaline and extracted with diethyl ether. After drying with $MgSO_4$, the solvent was removed

to leave an oil. The pure product was obtained as a colourless oil, following purification by flash chromatography (on silica gel and eluting with ethyl acetate, RF = 0.63). A white solid product was obtained on ageing of the oil. Yield: 0.88 g, 18 % (Found: C, 73.33; H, 5.42; N, 15.03. Calc. for $C_{17}H_{15}N_3O$: C, 73.61; H, 5.46; N, 15.15 %). MS (EI): *m/z* 277 M, 260 [M–OH], 199 [M–py], 185 [M–Mepy]. ^{1}H NMR ($CDCl_3$, 300MHz): δ 7.19 ({d,d,d}, $J_{3,5}$=1.61, $J_{4,5}$=6.90, $J_{5,6}$=5.05 Hz, 2H, py-5-H); δ 7.67 ({d,d,d}, $J_{4,6}$=1.77 Hz, 2H, py-4-H); δ 7.72 (d, $J_{3,4}$=7.97 Hz, 2H, py-3-H); δ 8.55 (d, $J_{5,6}$=5.05 Hz, 2H, py-6-H); δ 7.49 ({d,d}, $J_{3,4}$=8.16, $J_{4,6}$=2.20 Hz, 1H, 5-Mepy-4-H); δ 7.61 (d, $J_{3,4}$=8.16 Hz, 1H, 5-Mepy-3-H); δ 8.37 (d, $J_{4,6}$=2.20 Hz, 1H, 5-Mepy-6-H); δ 7.22 (s, 1H, OH); δ 2.31 (s, 3H, CH_3). IR (KBr): ν(O-H) 3349 (m, br); ν(C-$H_{aromatic}$) 3022 (w); ν(C-H_{alkyl}) 2924 (w); ν(C=C) 1588, 1466 (m) cm^{-1}.

(6-Methyl-2-pyridyl)bis(2-pyridyl)methanol, 6

A 2.5 M solution of ^{n}butyllithium in hexane (15 cm^3, 38 mmol) was added to a pre-cooled (*ca.* –55 °C) solution of 2-bromo-6-methylpyridine (4.90 g, 28 mmol) in diethyl ether (70 cm^3). The mixture was stirred for 40 minutes, then was cooled to *ca.* –70 °C. A solution of *bis*(2-pyridyl)ketone (5.31 g, 29 mmol) in diethyl ether (70 cm^3) was added and the mixture stirred for a further 75 minutes. The reaction vessel was allowed to warm up to room temperature, then the solution was quenched with water (100 cm^3), and 2 M sulfuric acid (25 cm^3) was carefully added. The diethyl ether layer was separated and extracted several times with 25 cm^3 of dilute sulfuric acid until the acid extract was no longer coloured. The combined acid extracts were made alkaline and extracted with diethyl ether. After drying with Na_2SO_4, the volume of solvent

was reduced to *ca.* 25 cm^3. Cooling to –78 °C, resulted in precipitation of a solid. This was collected by filtration, washed with diethyl ether, and air dried. Yield: 1.52 g, 19 % (Found: C, 73.49; H, 5.41; N, 15.00. Calc. for $C_{17}H_{15}N_3O$: C, 73.61; H, 5.46; N, 15.15 %). MS (EI): *m/z* 277 M, 260 [M–OH], 199 [M–py], 185 [M–Mepy]. ^1H NMR ($CDCl_3$, 300MHz): δ 7.17 ({d,d,d}, $J_{3,5}$=2.88, $J_{4,5}$=5.80, $J_{5,6}$=5.09 Hz, 2H, py-5-H); δ 7.67 (m, 4H, py-3,4-H); δ 8.55 ({d,d,d}, $J_{3,6}$=1.27, $J_{4,6}$=1.27, $J_{5,6}$=5.09 Hz, 2H, py-6-H); δ 7.06 ({d,d}, $J_{3,4}$=4.41, $J_{4,5}$=4.41 Hz, 1H, 6-Mepy-4-H); δ 7.57 (m, 2H, 6-Mepy-3,5-H); δ 7.40 (s, 1H, OH); δ 2.53 (s, 3H, CH_3). IR (KBr): ν(O-H) 3188 (m, br); ν(C⎓C) 1576, 1460 (m) cm^{-1}.

(6-Methyl-2-pyridyl)bis(2-pyridyl)chloromethane, 7

Sodium hydride (0.18 g, 7.5 mmol) was added to a solution of **6** (0.29 g, 1.05 mmol) in THF (20 cm^3), with no noticable colour change. The mixture was stirred for 20 minutes, then cooled to *ca.* –70 °C. Thionyl chloride (0.99 g, 8.3 mmol) in THF (10 cm^3) was added dropwise, forming a pale yellow solution. After stirring for a further 35 minutes, the cooling bath was removed and the reaction vessel allowed to warm to room temperature. The mixture was stirred for *ca.* 2 hours, before water (20 cm^3) was added. The organic layer, plus several dichloromethane extracts (25 cm^3) of the aqueous layer, were collected and combined, then dried with Na_2SO_4. The solvent was removed to give an off-white residue. MS (FAB): *m/z* 296 [M+H], 260 [M–Cl], 182 [M–Cl–py]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.19 ({d,d}, $J_{4,5}$=7.44, $J_{5,6}$=4.92 Hz, 2H, py-5-H); δ 7.51 (d, $J_{3,4}$=8.24 Hz, 2H, py-3-H); δ 7.66 ({d,d}, $J_{3,4}$=8.24, $J_{4,5}$=7.44 Hz, 2H, py-4-H); δ 8.58 (d, $J_{5,6}$=4.92 Hz, 2H, py-6-H); δ 7.05 (d, $J_{4,5}$=7.65 Hz, 1H, 6-Mepy-5-H); δ 7.23 (d, $J_{3,4}$=7.96 Hz, 1H, 6-Mepy-3-H); δ

7.54 ({d,d}, $J_{3,4}$=7.96, $J_{4,5}$=7.65 Hz, 1H, 6-Mepy-4-H); δ 2.47 (s, 3H, CH_3). ^{1}H NMR spectroscopy indicated the compound was pure however satisfactory microanalytical data could not be obtained. IR (KBr): ν(C-$H_{aromatic}$) 3048 (w); ν(C-H_{alkyl}) 2963 (w); ν(C⁼C) 1587, 1450 (m); ν(C-Cl) 766 (m) cm^{-1}.

(6-Methyl-2-pyridyl)bis(2-pyridyl)ethoxymethane, 8

Using an analogous method to the synthesis of **3**, compound **7** (0.20 g, 0.68 mmol) was reacted with ethanol to give a yellow residue. MS (FAB): *m/z* 306 [M+H], 276 [M–Et], 260 [M–OEt]. ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.10 ({d,d}, $J_{4,5}$=7.33, $J_{5,6}$=4.86 Hz, 2H, py-5-H); δ 7.63 ({d,d}, $J_{3,4}$=8.10, $J_{4,5}$=7.33 Hz, 2H, py-4-H); δ 7.73 (d, $J_{3,4}$=8.10 Hz, 2H, py-3-H); δ 8.55 (d, $J_{5,6}$=4.86 Hz, 2H, py-6-H); δ 6.97 (d, $J_{4,5}$=7.27 Hz, 1H, 6-Mepy-5-H); δ 7.51 (m, 2H, 6-Mepy-3,4-H); δ 1.23 (t, J=6.80 Hz, 3H, $C\underline{H}_3CH_2O$); δ 3.38 (q, J=6.80 Hz, 2H, $CH_3C\underline{H}_2O$); δ 2.46 (s, 3H, CH_3). ^{1}H NMR spectroscopy indicated the compound was pure however satisfactory microanalytical data could not be obtained. IR (KBr): ν(C-$H_{aromatic}$) 3056 (w); ν(C-H_{alkyl}) 2926 (w); ν(C⁼C) 1589, 1452 (m) cm^{-1}.

(3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol, 9

A 2.5 M solution of ^{n}butyllithium in hexane (12 cm^3, 30 mmol) was added to a pre-cooled (*ca.* –50 °C) solution of 2-bromo-3-methylpyridine (3.26 g, 19 mmol) in THF (100 cm^3). The dark red solution was stirred for 45 minutes, then cooled to *ca.* –65 °C. A solution of (5-methyl-2-pyridyl)(2-pyridyl)ketone (3.76 g, 19 mmol) in THF (50 cm^3) was added. The mixture was stirred for 2.5 hours then allowed to warm to room temperature. The solution was quenched with water (100 cm^3) and 2 M sulfuric acid (50 cm^3) was carefully added. The

THF layer was separated and extracted several times with 25 cm^3 of dilute sulfuric acid until the acid extract was no longer coloured. The combined acid extracts were made alkaline and extracted with diethyl ether, which was subsequently dried with $MgSO_4$. The solvent was removed *in vacuo* to give an orange oil. Trituration with diethyl ether led to precipitation of the product as a beige solid. Yield: 1.45 g, 26% (Found: C, 74.42; H, 5.90; N, 14.07. Calc. for $C_{18}H_{17}N_3O$: C, 74.19; H, 5.89; N, 14.42 %). MS (APCI): *m/z* 292 [M+H], 274 [M–OH], 213 [M–py], 199 [M–Mepy]. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 ({d,d,d}, $J_{3,5}$=2.00, $J_{4,5}$=6.67, $J_{5,6}$=4.79 Hz, 1H, py-5-H); δ 7.68 (m, 2H, py-3,4-H); δ 8.52 ({d,d,d}, $J_{3,6}$=1.29, $J_{4,6}$=1.29, $J_{5,6}$=4.79 Hz, 1H, py-6-H); δ 7.11 ({d,d}, $J_{4,5}$=7.56, $J_{5,6}$=4.79 Hz, 1H, 3-Mepy-5-H); δ 7.46 (m, 2H, 3-Mepy and 5-Mepy-4-H); δ 8.27 (d, $J_{5,6}$=4.79 Hz, 1H, 3-Mepy-6-H); δ 7.58 (d, $J_{3,4}$=8.10 Hz, 1H, 5-Mepy-3-H); δ 8.35 (d, $J_{4,6}$=2.16 Hz, 1H, 5-Mepy-6-H); δ 7.50 (s, 1H, OH); δ 2.01 (s, 3H, 3-Mepy-CH_3); δ 2.32 (s, 3H, 5-Mepy-CH_3). IR (KBr): ν(O-H) 3297 (m, br); ν(C=C) 1586, 1465 (m) cm^{-1}.

(3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methane, 10

Sodium hydride (0.061g, 2.5 mmol) was added to a solution of **9** (0.21 g, 0.72 mmol) in THF (10 cm^3). The mixture was stirred for 1.5 hours at ambient temperature before being cooled to *ca.* –65 °C. Thionyl bromide (0.57 g, 2.7 mmol) in THF (5 cm^3) was added dropwise, giving a dark yellow solution which was stirred for 10 minutes. The reaction vessel was allowed to warm to room temperature, then water (10 cm^3) was added. The organic layer, plus several dichloromethane extracts (25 cm^3) of the aqueous layer, were combined and dried with $MgSO_4$. The solvent was removed *in vacuo* to give a yellow oil. A

yellow solid was obtained on ageing of the oil. MS (EI): *m/z* 275 M, 274 [M–H], 197 [M–py], 183 [M–Mepy]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 ({d,d}, $J_{4,5}$=7.42, $J_{5,6}$=4.78 Hz, 1H, py-5-H); δ 7.16 (d, $J_{3,4}$=8.00 Hz, 1H, py-3-H); δ 7.60 ({d,d}, $J_{3,4}$=8.00, $J_{4,5}$=7.42 Hz, 1H, py-4-H); δ 8.57 (d, $J_{5,6}$=4.78 Hz, 1H, py-6-H); δ 7.06 ({d,d}, $J_{4,5}$=7.62, $J_{5,6}$=4.78 Hz, 1H, 3-Mepy-5-H); δ 7.43 (m, 2H, 3-Mepy and 5-Mepy-4-H); δ 8.41 (m, 2H, 3-Mepy and 5-Mepy-6-H); δ 7.08 (d, $J_{3,4}$=8.02 Hz, 1H, 5-Mepy-3-H); δ 6.15 (s, 1H, CH); δ 2.29 (s, 3H, 3-Mepy-CH_3); δ 2.32 (s, 3H, 5-Mepy-CH_3). ^{1}H NMR spectroscopy indicated the compound was pure however satisfactory microanalytical data could not be obtained. IR (KBr): ν(C⁼⁼C) 1587, 1465 (m) cm^{-1}.

Crystallographic characterisation of (3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol (9)

Table 2.1 **Crystal data and structure refinement for 9.**

Formula	$C_{18}H_{17}N_3O$	
Formula weight	291.38	
Temperature	100(2) K	
Wavelength	0.71070 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4962(9) Å b = 8.8894(7) Å c = 11.9406(14) Å	α= 99.232(2)°. β= 101.503(2)°. γ = 100.642(2)°.
Volume	750.04(14) $Å^3$	
Z	4	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	308	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	3.28 to 26.00°.	
Index ranges	-9<=h<=9, -10<=k<=10, -14<=l<=14	
Reflections collected	6544	
Independent reflections	2752 [R(int) = 0.049]	
Completeness to theta = 26.00°	93.3 %	
Absorption correction	Scalepack	
Max. and min. transmission	0.9918 and 0.9837	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2752 / 0 / 204	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1031	
R indices (all data)	R1 = 0.0595, wR2 = 0.1088	
Extinction coefficient	0.075(10)	
Largest diff. peak and hole	0.203 and -0.175 $e.Å^{-3}$	

Table 2.2 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 9.**

	x	y	z	U(eq)
O(1)	3706(2)	7765(1)	8807(1)	26(1)
N(1)	6621(2)	9919(2)	8980(1)	24(1)
N(2)	3642(2)	8815(2)	6142(1)	28(1)
N(3)	4830(2)	5303(2)	6484(1)	26(1)
C(1)	4456(2)	7565(2)	7796(1)	22(1)
C(2)	6313(2)	8782(2)	8041(1)	22(1)
C(3)	7603(2)	8679(2)	7356(1)	26(1)
C(4)	9254(2)	9792(2)	7662(2)	27(1)
C(5)	9611(2)	10992(2)	8633(1)	26(1)
C(6)	8241(2)	10994(2)	9260(1)	26(1)
C(7)	11383(3)	12232(2)	8993(2)	36(1)
C(8)	3030(2)	7759(2)	6738(1)	23(1)
C(9)	1195(2)	6835(2)	6432(1)	26(1)
C(10)	21(2)	7028(2)	5426(2)	30(1)
C(11)	649(3)	8117(2)	4801(2)	33(1)
C(12)	2454(3)	8999(2)	5193(2)	31(1)
C(13)	454(2)	5704(2)	7136(2)	32(1)
C(14)	4853(2)	5929(2)	7583(1)	22(1)
C(15)	5258(2)	5169(2)	8504(1)	26(1)
C(16)	5630(2)	3695(2)	8277(2)	30(1)
C(17)	5583(2)	3021(2)	7135(2)	28(1)
C(18)	5197(2)	3866(2)	6275(2)	28(1)

Table 2.3 **Bond lengths [Å] and angles [°] for 9.**

O(1)-C(1)	1.4287(19)	C(4)-C(5)	1.388(2)
N(1)-C(2)	1.333(2)	C(5)-C(6)	1.386(2)
N(1)-C(6)	1.344(2)	C(5)-C(7)	1.498(2)
N(2)-C(8)	1.336(2)	C(8)-C(9)	1.409(2)
N(2)-C(12)	1.346(2)	C(9)-C(10)	1.396(2)
N(3)-C(14)	1.336(2)	C(9)-C(13)	1.508(3)
N(3)-C(18)	1.351(2)	C(10)-C(11)	1.385(3)
C(1)-C(14)	1.530(2)	C(11)-C(12)	1.379(3)
C(1)-C(8)	1.539(2)	C(14)-C(15)	1.393(2)
C(1)-C(2)	1.541(2)	C(15)-C(16)	1.386(2)
C(2)-C(3)	1.392(2)	C(16)-C(17)	1.389(2)
C(3)-C(4)	1.376(2)	C(17)-C(18)	1.383(2)
C(2)-N(1)-C(6)	117.99(14)	N(1)-C(6)-C(5)	123.99(16)
C(8)-N(2)-C(12)	118.47(15)	N(2)-C(8)-C(9)	123.38(15)
C(14)-N(3)-C(18)	117.61(14)	N(2)-C(8)-C(1)	116.43(14)
O(1)-C(1)-C(14)	108.82(13)	C(9)-C(8)-C(1)	120.18(15)
O(1)-C(1)-C(8)	109.16(12)	C(10)-C(9)-C(8)	116.42(16)
C(14)-C(1)-C(8)	110.12(13)	C(10)-C(9)-C(13)	119.67(16)
O(1)-C(1)-C(2)	108.32(12)	C(8)-C(9)-C(13)	123.90(15)
C(14)-C(1)-C(2)	108.62(13)	C(11)-C(10)-C(9)	120.46(17)
C(8)-C(1)-C(2)	111.73(13)	C(12)-C(11)-C(10)	118.62(16)
N(1)-C(2)-C(3)	122.32(15)	N(2)-C(12)-C(11)	122.59(18)
N(1)-C(2)-C(1)	115.05(14)	N(3)-C(14)-C(15)	122.69(15)
C(3)-C(2)-C(1)	122.60(14)	N(3)-C(14)-C(1)	116.51(13)
C(4)-C(3)-C(2)	118.61(16)	C(15)-C(14)-C(1)	120.78(14)
C(3)-C(4)-C(5)	120.35(16)	C(16)-C(15)-C(14)	119.04(15)
C(6)-C(5)-C(4)	116.74(16)	C(15)-C(16)-C(17)	118.85(15)
C(6)-C(5)-C(7)	121.18(16)	C(18)-C(17)-C(16)	118.36(16)
C(4)-C(5)-C(7)	122.09(16)	N(3)-C(18)-C(17)	123.44(16)

Chapter 3

(η^6-arene)Ru(II) complexes of *tris*(2-pyridyl)methanol and its analogs

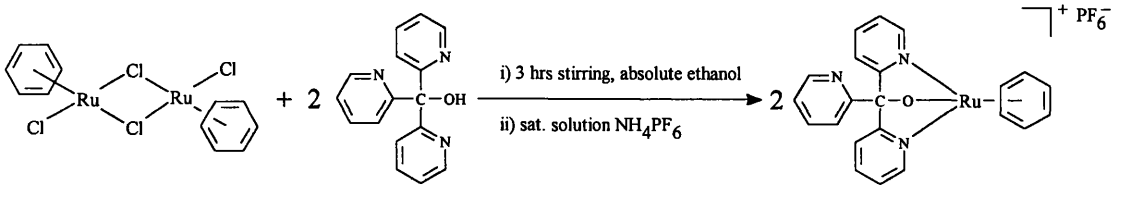
Introduction

Tris(2-pyridyl)methanol and closely related analogs were incorporated into a number of (η^6-arene)Ru(II) complexes *via* modifications of literature procedures.[8,9,105] Mono and dicationic complexes were synthesised depending on whether or not the *tris*(2-pyridyl) ligand had become deprotonated. In addition two complexes were prepared in which the *tris*(2-pyridyl)methoxide ligand bridged between two metal centres.

3.1 Results and Discussion

3.1.1 The synthesis and characterisation of (η^6-arene)-Ru(II) complexes of *tris*(2-pyridyl)methanol

The preparation of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$, **11**, follows general methods already described for the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with a variety of bi and tridentate nitrogen bases.[8,9,105] Thus, treatment of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with two equivalents of *tris*(2-pyridyl)methanol in absolute ethanol results in the slow dissolution of the ruthenium compound and the formation of a yellow solution over a period of 3 hours. Addition of an ethanolic solution of NH_4PF_6 results in the formation of a yellow precipitate of **11**, Scheme 3.1. The polar nature of the reaction medium as well as the



Scheme 3.1 The synthesis of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$ (**11**)

chelate effect of *tris*(2-pyridyl)methanol facilitates chloride loss. Figure 3.1 shows the ^{1}H NMR spectrum of **11** in the chemical shift range 7-10 ppm.

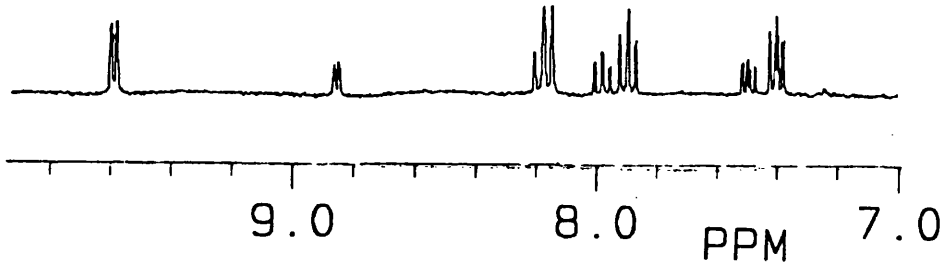
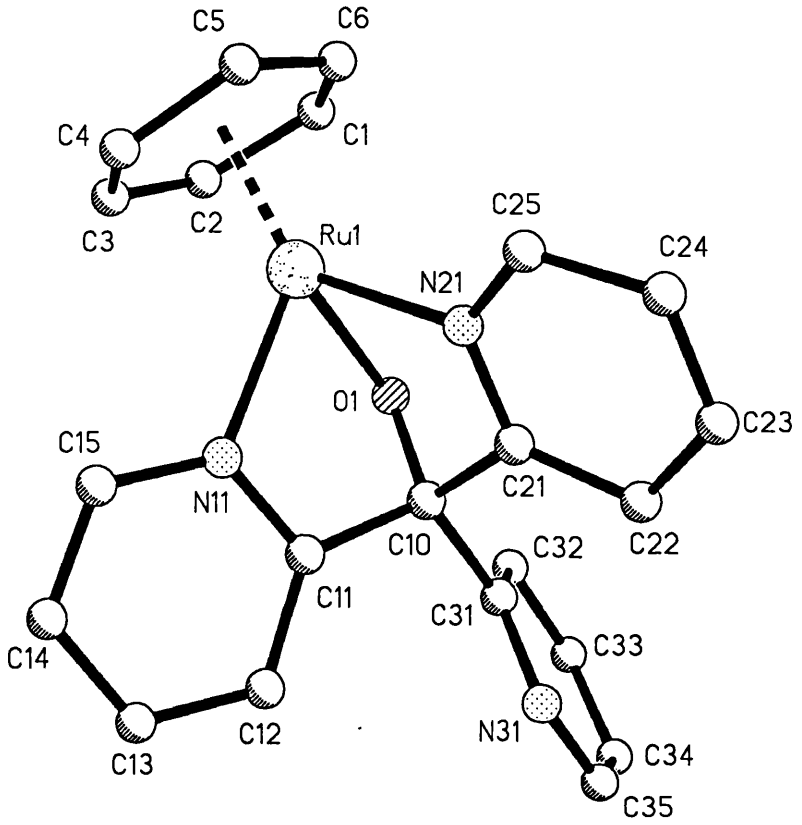


Figure 3.1 Part of the ^{1}H NMR spectrum of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$ **11** (7-10 ppm region)

While four signals are expected from the pyridyl hydrogens of *tris*(2-pyridyl)methanol when it is coordinated in the tridentate N,N',N'' mode, the observation of eight signals, in two sets of four with integral ratio of 2:1 implies an alternative mode of coordination. (NB typical of the ^{1}H NMR spectra of compounds **11-21** is the observation that, relative to the spectra of the free ligands, the pyridyl proton signals are shifted to lower field. This is due to the π-electron density of a metallated pyridyl ring being drawn towards the Ru(II) ion, thus deshielding the ring protons). Bidentate coordination of *tris*(2-pyridyl)methanol to the metal centre (through either two nitrogen atoms or one nitrogen and oxygen atom) was ruled out on the grounds that the infrared spectrum of **11** contains no ν(Ru-Cl) band around 250-350 cm^{-1}, thus implying tridentate coordination of the N,N',O type. As described earlier (sections 1.6 and 1.7) the ligand is known to coordinate both as a neutral alcohol and as an anionic alkoxide. In the former case the complex will be dicationic while in the latter it will exist as a monocation. While the presence/absence of an O-H bond should be apparent in the infrared spectrum our data were not of

sufficient quality to provide a definitive observation. However, microanalytical results were consistent with a monocationic formulation for **11**, with the ligand coordinated in the form of an alkoxide. The cationic constituent of the compound was observed in the mass spectrum at *m/z* 442. Typical to the infrared spectra of all the hexafluorophosphate salts described in this thesis is the observation of a strong ν(P-F) band at ~ 840 cm^{-1}. Conclusive proof for the formulation of **11** was obtained by single crystal X-ray analysis. The crystal structure of **11** contains two crystallographically unique, but chemically indistinguishable cations in the asymmetric unit, one of which is shown in Figure 3.2. The cation exhibits the well known 'piano stool' geometry found for numerous other "(η^6-arene)RuL_3" complexes. The coordination of the tripodal ligand to the ruthenium metal centre through two nitrogens and one oxygen atom is confirmed. While the X-ray data is not of sufficient quality for hydrogen atoms to be found, the presence of only one PF_6^- anion per cation conclusively demonstrates that the ligand is coordinated in the form of an anionic alkoxide, rather than the neutral alcohol. The two Ru-N bond lengths are closely similar (av. 2.123(7) Å) and are noticeably longer than those of the deprotonated ligand in $[Ru\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3CO\}]^+$ (av. 2.063(4) Å) (Figure 1.16, **A**),[75] whereas the two Ru-O bond lengths (2.055(6) and 2.047(5) Å respectively) are indistinguishable and quite typical of Ru-alkoxide bonds.[136,137] The differences between the Ru-N bond lengths may be attributed to the different electronic effects experienced by the *tris*(2-pyridyl)methoxide ligand in the two cations, since the 'spectator ligands', C_6H_6 and $(C_5H_4N)_3COH$, coordinate to the Ru(II) ion in differing manners (η^6-π and N,N',N''-σ respectively). Interestingly however, the Ru-O bond remains

relatively unaltered. In **11** the 'bite' angle formed at the metal by the two



Ru(1)-O(1)	2.055(6)	O(1)-Ru(1)-N(11)	76.8(3)
Ru(1)-N(11)	2.124(7)	O(1)-Ru(1)-N(21)	76.3(3)
Ru(1)-N(21)	2.122(7)	N(11)-Ru(1)-N(21)	82.2(3)
Ru(1)-C(2)	2.185(11)	C(31)-C(10)-C(21)	111.6(7)
Ru(1)-C(3)	2.193(10)	N(11)-C(11)-C(10)	111.0(8)
Ru(1)-C(1)	2.199(12)	N(21)-C(21)-C(10)	109.9(7)
O(1)-C(10)	1.426(9)	N(31)-C(31)-C(10)	116.1(8)

Figure 3.2 Structure of the cation in $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$ with selected bond lengths (Å) and bond angles (°)

nitrogen atoms, 82.2(3) °, is somewhat less than that observed for the deprotonated ligand in $[Ru\{(C_5H_4N)_3COH\}\{(C_5H_4N)_3CO\}]^+$, 85.6(2) °, as is the average O-Ru-N 'bite' angle, 76.6(3) *vs* 78.2(1) °. In both cations the *tris*(2-pyridyl)methoxide ligand donor atoms are unable to take up facial positions associated with an ideal octahedral geometry about the metal. In general this is a consequence of the N,N',O coordination mode, since the bridgehead

carbon atom-oxygen atom bond length is considerably shorter than the two bridgehead carbon atom-nitrogen donor atom distances.[27] However, relative to the cation $[Ru\{(C_5H_4N)_3COH\}\{(C_5H_4N)_3CO\}]^+$, a greater distortion from ideal geometry is observed in $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]^+$ (Figure 3.2) perhaps reflecting greater steric repulsions between the two coordinated ligands. The $C_{bridgehead}$-O bond length in **11**, 1.426(9) Å, is essentially identical to that of the free *tris*(2-pyridyl)methanol ligand, 1.427(2) Å, deprotonation and metallation of the oxygen apparently having no noticable effect on this geometrical parameter. In the free ligand the average $C_{bridgehead}$-$C_{pyridine}$-$N_{pyridine}$ bond angle is 116.1(2) °. In the cation $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]^+$ the equivalent angle is identical for the non-metallated pyridyl ring, 116.1(8)°, but for the two metallated pyridyl rings the average angle is 110.5(8) °. This decrease is not surprising considering the steric constraints of metallation imposed upon these pyridyl rings. There is nothing remarkable about the π-bound benzene ring as the Ru-C distances are all similar and fall in the range typical of other $(\eta^6\text{-}C_6H_6)Ru$ structures.[105,107]

When the reaction shown in Scheme 3.1 is carried out using methanol as a solvent, rather than ethanol, compound **12**, the dicationic non-deprotonated analog of **11**, precipitates out exclusively upon addition of NH_4PF_6. While this observation may tentatively be ascribed to the relative acidity of the solvent, a number of other factors, discussed later, will also play a part. The general appearance of the ^1H NMR spectrum of **12**, Figure 3.3, is similar to that of **11**, Figure 3.1, with two sets of pyridyl resonances being observed. However, for **12** the set of signals corresponding to the non-metallated pyridyl protons have

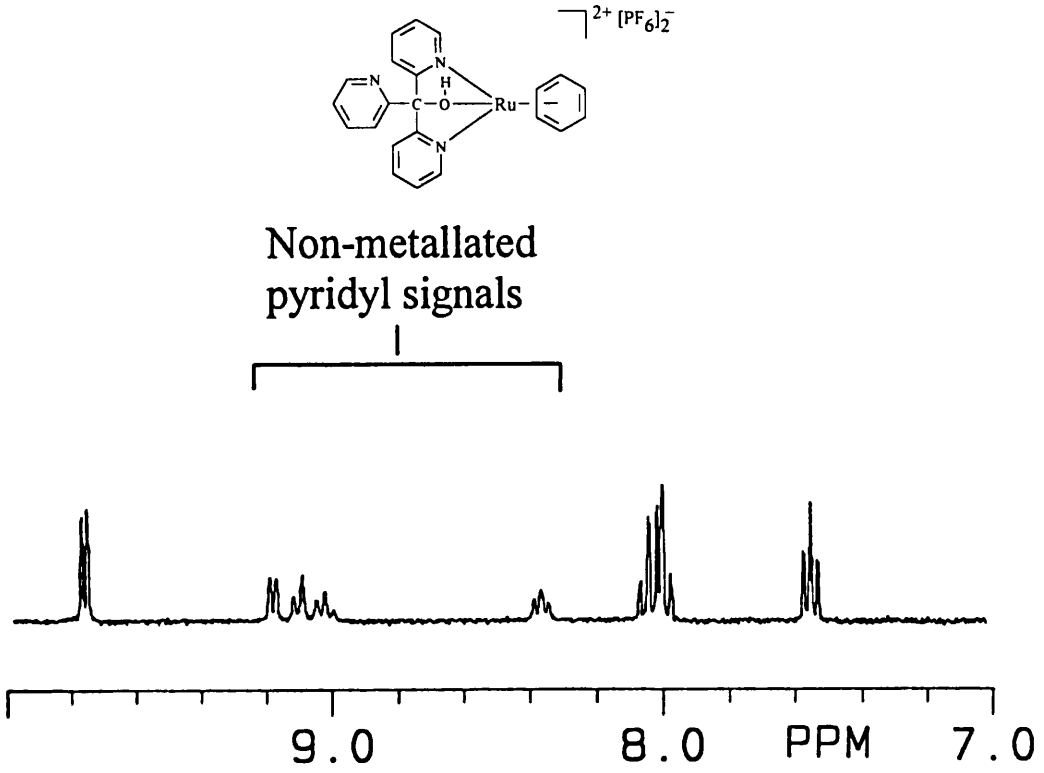


Figure 3.3 Part of the ^{1}H NMR spectrum of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COH\}][PF_6]_2$ **12** (δ 7-10 ppm region)

shifted considerably to lower field and are broadened. Conversion of the ^{1}H NMR spectrum of **12** to that of **11** is readily achieved upon addition of triethylamine to the NMR solution of the former. Similarly when dilute acid is added to an NMR solution of **11** the cation in **12** is generated. Whilst microanalytical data for **12** are consistent with the formulation $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COH\}][PF_6]_2 \cdot Me_2CO$ (crystals grown from acetone) the location of the additional proton, i.e. whether it is on the oxygen or the non-metallated pyridyl nitrogen, is uncertain. The infrared spectrum of **12** was not of a high enough quality for an O-H band to be identified, however previous infrared studies[67] on complexes with protonated pyridyl nitrogens have reported a definitive py-H$^+$ band at 1530 cm^{-1}, this is not observed for **12**.

Therefore tentatively on this basis, and by analogy with the cations $[Ru(NH_3)_3\{N,N',O\text{-}(C_5H_4N)_3COH\}]^{2+}$ [27] and $[Ru\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3COH\}]^{2+}$,[75] compound **12** has been formulated as a dication with the proton residing on the oxygen atom. In contrast to the ^1H NMR spectrum of *tris*(2-pyridyl)methanol, **1**, the absence of an O-H signal from the spectrum of **12** may be due to the acidic alcoholic proton rapidly exchanging with water in, or deuterium from, the NMR solvent. In the literature[75] the protonation of $[Ru\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3CO\}]^{+}$ to give $[Ru\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3COH\}]^{2+}$ was noted as being unusual, in that protonation of the free pyridyl nitrogen had not occured despite the enhanced pK_a values generally associated with non-metallated pyridyl nitrogen atoms in polypyridyl-type ligands monodentately bound to Ru(II). However it was suggested that in solution the metallated hydroxyl group, *via* a hydrogen-bonding interaction with the free pyridyl nitrogen, prevents protonation of that nitrogen. An analogous interaction between the metallated hydroxyl group and non-metallated pyridyl nitrogen atom of **12** may lead to restricted pyridyl group rotation about the $C_{pyridyl}\text{-}C_{bridgehead}$ axis, resulting in the broadened signals observed in the ^1H NMR spectrum of **12**. By analogy with $[Ru\{N,N',N''\text{-}(C_5H_4N)_3COH\}\{N,N',O\text{-}(C_5H_4N)_3COH\}]^{2+}$,[75] further protonation of **12** is prevented, hence explaining why the addition of dilute acid to the NMR solution of **11** does not result in the formation of a tricationic species where both the oxygen and free pyridyl nitrogen atoms have been protonated.

Compound **13**, $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CO\}]PF_6$, was prepared analogously to **11** by reaction of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ with *tris*(2-

pyridyl)methanol. Microanalysis was consistent with the proposed formulation and the monocation was observed in the mass spectrum at *m/z* 498. In comparing the ^{1}H NMR spectrum of **13** with that of **11**, the benzene singlet in **13** is replaced by several signals which correspond to the π-bound *para*-cymene ligand. However it is clear that the pyridyl signals of **11** and **13** occur at very similar chemical shifts, implying that the 'spectator ligands', benzene and *para*-cymene, interact similarly with the N,N',O bound polypyridyl ligand.

The protonation of a solution of **13** with HPF_6, followed by work-up gives the microanalytically pure dicationic analog $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3COH\}][PF_6]_2$, **14**. In view of the relationship between the ^{1}H NMR spectra of compounds **11** and **13**, one would expect a similar pattern for their protonated analogs, **12** and **14**. Indeed the pyridyl proton resonances do occur at similar chemical shifts, but as the ^{1}H NMR spectrum of **14** shows (Figure 3.4, **A**, δ 7-10 ppm), in contrast to that of **12**, both sets of pyridyl signals for **14** are broad. Furthermore, addition of dilute acid to an NMR solution of **13** gives an equivalent spectrum to that of **14**, except that all the pyridyl signals are now resolved (Figure 3.4, **B**). It is likely that in spectrum **A**, compound **14** is in equilibrium with its deprotonated analog, compound **13**, the equilibrium favouring somewhat the protonated product, whereas in spectrum **B** the presence of excess acid exclusively favours the protonated product. However, in the latter spectrum it is unclear why, in contrast to compound **12**, the non-metallated pyridyl signals are not broad relative to the metallated pyridyl signals.

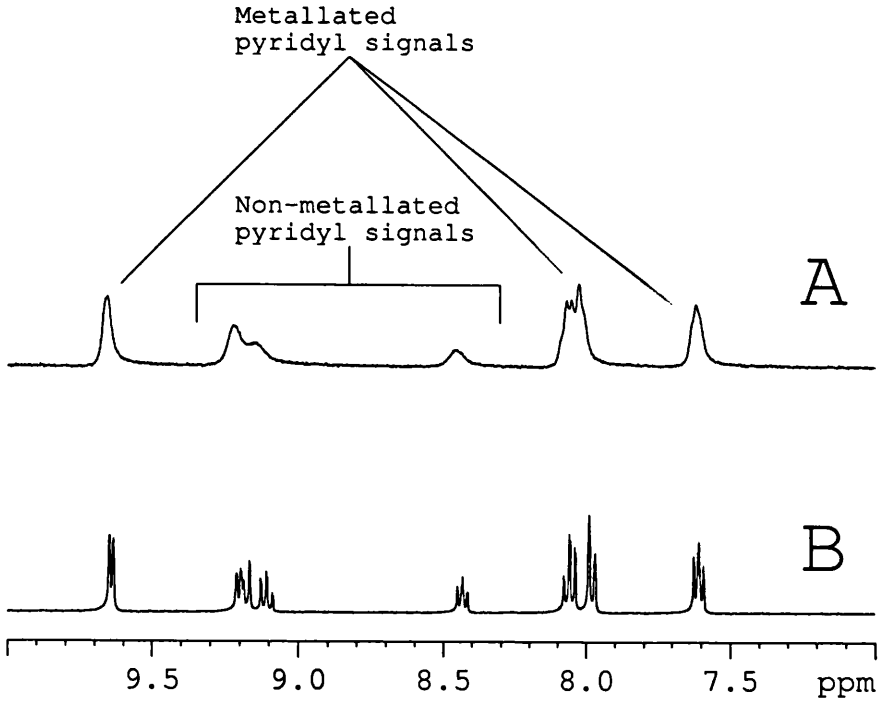
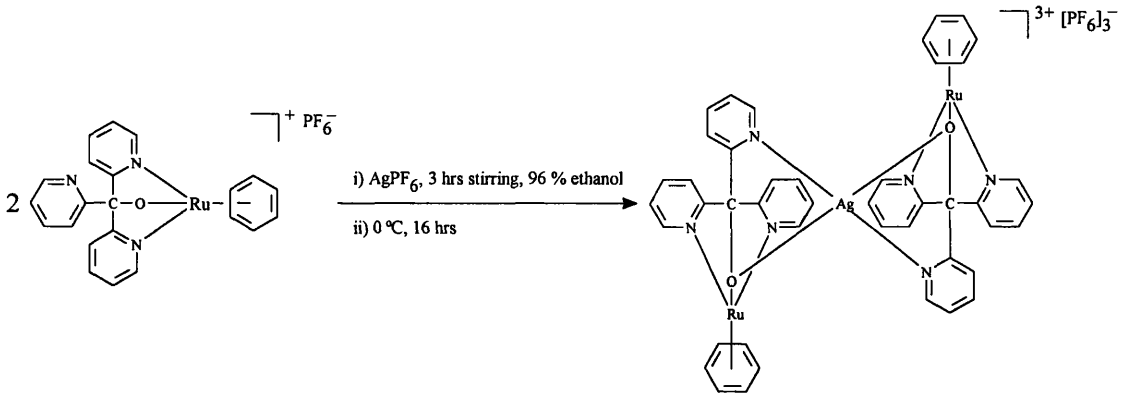


Figure 3.4 Part of the ^{1}H NMR spectra of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3COH\}][PF_6]_2$ **14**, **A**, and $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CO\}]PF_6$ **13** after the addition of dilute acid, **B** (7-10 ppm region)

3.1.2 Heterometallic complexes of *tris*(2-pyridyl)methanol

Compound **11** has been found to act as a metallo ligand for other metals. For example, stirring **11** with an ethanolic suspension of $AgPF_6$ results in the formation of a yellow solution. After removal of unreacted starting materials, that solution will precipitate a yellow solid, **15**, on cooling to 0 °C for several hours, Scheme 3.2. The mass spectrum of **15** exhibits a highest mass peak at *m/z* 1281, with an envelope consistent with the presence of two ruthenium atoms and a single silver atom in the fragment. Compound **15** can be crystallised from acetone to give rather poorly diffracting single crystals which have been examined by X-ray crystallography. The crystallographic analysis reveals **15** to be a hetero-trimetallic complex with the composition [{(η^6-

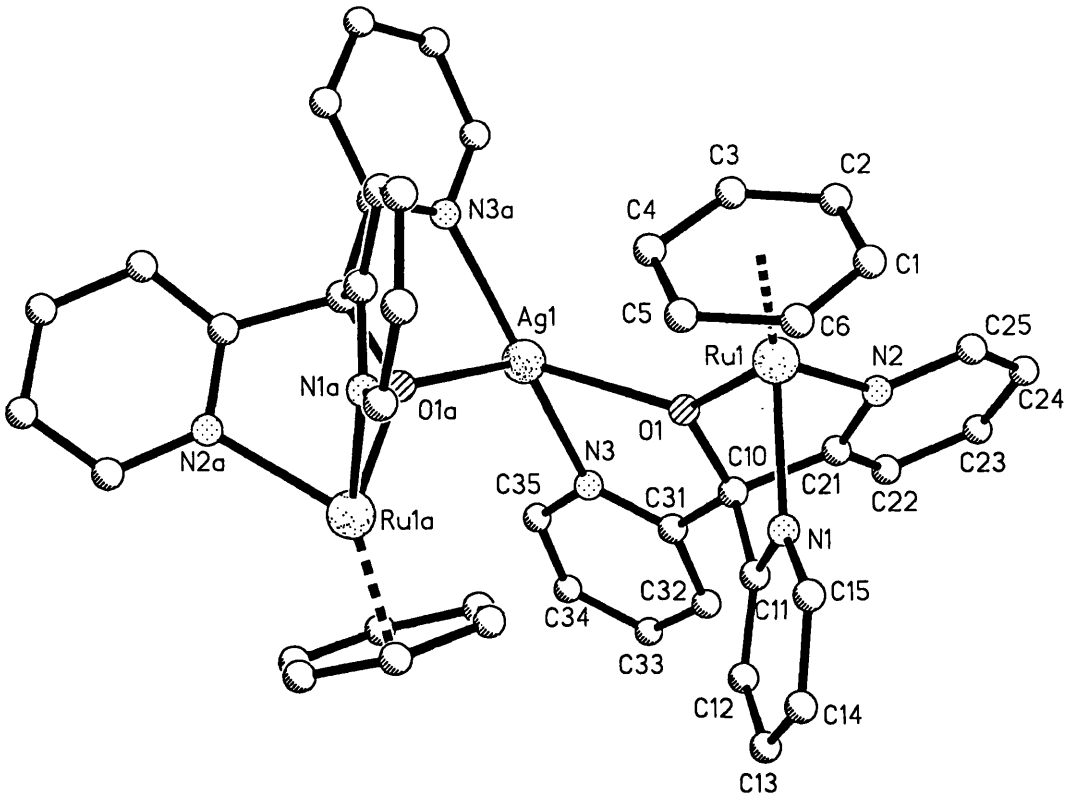
$C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$ and subsequent microanalysis confirms this.



Scheme 3.2 The synthesis of $[\{(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$

The crystal structure of the cation in **15** is shown in Figure 3.5. The structure consists of a central silver ion coordinated by two alkoxide oxygen atoms, which also bridge to the two ruthenium ions, and by two nitrogens of the pyridyl rings which were non-metallated in compound **11**. The geometry around the silver is highly distorted with the donor atom-Ag(I)-donor atom angles covering a wide range, 69.2(2)-162.0(3) °, implying that the geometry is determined by the packing and steric interactions between the two '$(\eta^6$-$C_6H_6)Ru\{(C_5H_4N)_3CO\}$' moieties. Both Ru(II) moieties are equivalent as a consequence of crystal symmetry. A comparison of the bonding parameters in the cationic structures of **11** (Figure 3.2) and **15** (Figure 3.5) reveals that in essence coordination of **11** to silver imposes only a few small structural changes. For instance, coordination of silver to N(3) (N(31) using the atomic numbering scheme of Figure 3.2) has in effect pulled the pyridyl ring toward the metal causing an increase in the C(21)-C(10)-C(31) bond angle (numbering scheme common to both structures) from 111.6(7) ° in **11** to

114.2(6) ° in **15**. However, generally the bonding parameters in the two



Ru(1)-O(1)	2.047(5)	O(1)-Ru(1)-N(1)	76.3(2)
Ru(1)-N(1)	2.139(6)	N(1)-Ru(1)-N(2)	81.1(2)
Ru(1)-N(2)	2.138(6)	O(1)-Ru(1)-N(2)	76.9(2)
O(1)-C(10)	1.414(8)	O(1)-Ag(1)-N(3)	69.2(2)
Ag(1)-O(1)	2.434(5)	O(1)-Ag(1)-O(1a)	104.9(2)
Ag(1)-N(3)	2.282(6)	O(1)-Ag(1)-N(3a)	123.1(2)
Ru(1)-C(1)	2.237(9)	N(3)-Ag(1)-N(3a)	162.0(3)
Ru(1)-C(2)	2.196(9)	C(21)-C(10)-C(31)	114.2(6)
Ru(1)-C(3)	2.182(8)		

Figure 3.5 Structure of the cation in $[\{(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$ with selected bond lengths (Å) and bond angles (°). (Atoms labelled 'a' generated by two-fold rotation about 0, *y*, 0.75).

structures are not significantly different. The similarity between the two structures is further demonstrated in the ^{1}H NMR spectrum of **15** which is closely analogous to that of **11**, except that the set of silver coordinated pyridyl resonances appear somewhat broad. This is due to the d^{10}-Ag(I) ion being labile and hence capable of changing geometry without loss of crystal field

stabilisation energy. The absence of C.F.S.E in the d^{10}-Ag(I) ion explains why it is willing to adopt the highly distorted geometry seen in **15**.

The attempted preparation of the η^6-*para*-cymene analog of **15**, from **13** and $AgPF_6$, proved unsuccessful. This may be due to relatively greater steric interactions between two $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CO\}]^+$ cations preventing their mutual coordination to Ag(I).

By analogy with the synthesis of compound **15**, compound **11** will react with $[(PhCN)_2PdCl_2]$ with displacement of the benzonitrile ligands leading to the formation of the hetero-bimetallic compound $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}PdCl_2]PF_6$, **16**. Elemental analysis is consistent with **16**$\cdot 2H_2O$ and the mass spectrum displays a peak and associated isotope distribution pattern for the cationic constituent at *m/z* 620. The two expected sets of pyridyl signals are observed in the ^1H NMR spectrum of **16** and, in contrast to **15**, the unique pyridyl ring is rigidly bound to the d^8-Pd(II) ion. The coordination of the metallo ligand, *via* the bridging alkoxide and non-ruthenated pyridyl group, to the palladium enforces a *cis* geometry on the metal that is confirmed by the appearance of two weak ν(Pd-Cl) bands, at *ca.* 320 and 300 cm^{-1}.

The compound $[(InMe)_2\{(C_5H_4N)_3CO\}_2(NO_3)(H_2O)]NO_3$ prepared by Canty and co-workers[138] is believed to contain two indium metal centres linked together by two alkoxide bridges from two *tris*(2-pyridyl)methoxide ligands, each of which also has two pyridyl rings bound to the metal centres and a third ring

remaining non-metallated. This is the only previous report of a *tris*(2-pyridyl)methoxide ligand bridging between two metal centres, however the new compounds **15** and **16** are the first in which the ligand bridges two different metal centres.

3.1.3 The synthesis and characterisation of (η^6-arene)-Ru(II) complexes of methyl-substituted *tris*(2-pyridyl)methanols

The reaction of (5-Methyl-2-pyridyl)*bis*(2-pyridyl)methanol, **5**, with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ gave, after work-up with alcoholic NH_4PF_6, a yellow solid which analysed for the dicationic complex $[(\eta^6\text{-}C_6H_6)Ru\{(5\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}][PF_6]_2 \cdot 0.5Me_2CO$ (**17**$\cdot 0.5Me_2CO$, crystals grown from acetone). The ^1H COSY NMR spectrum of **17** is shown in Figure 3.6. The two methyl singlet resonances at δ 2.41 and 2.70 ppm as well as the complicated pyridyl region of the spectrum (δ 7-10 ppm) reflect the presence of two isomeric forms of **17**, **A** and **B**. There are also two benzene singlets due to the two isomers, at δ 6.30 and 6.31 ppm (not clearly shown in Figure 3.6). The metallated pyridyl resonances of isomer **A** occur at very similar chemical shifts to those of the equivalent rings of compound **12**, and not surprisingly overlap signals corresponding to the metallated, non-substituted pyridyl ring of isomer **B**. The methyl singlet resonance at highest field corresponds to the methyl protons of isomer **A** since, relative to those of **B**, the protons experience greater shielding owing to non-metallation of the substituted ring. Long range coupling is observed between these protons and those on the ring 4*and 6*-positions (see Figure 3.6). The signals in the region δ 8.1-9.2 ppm are broad and are due to

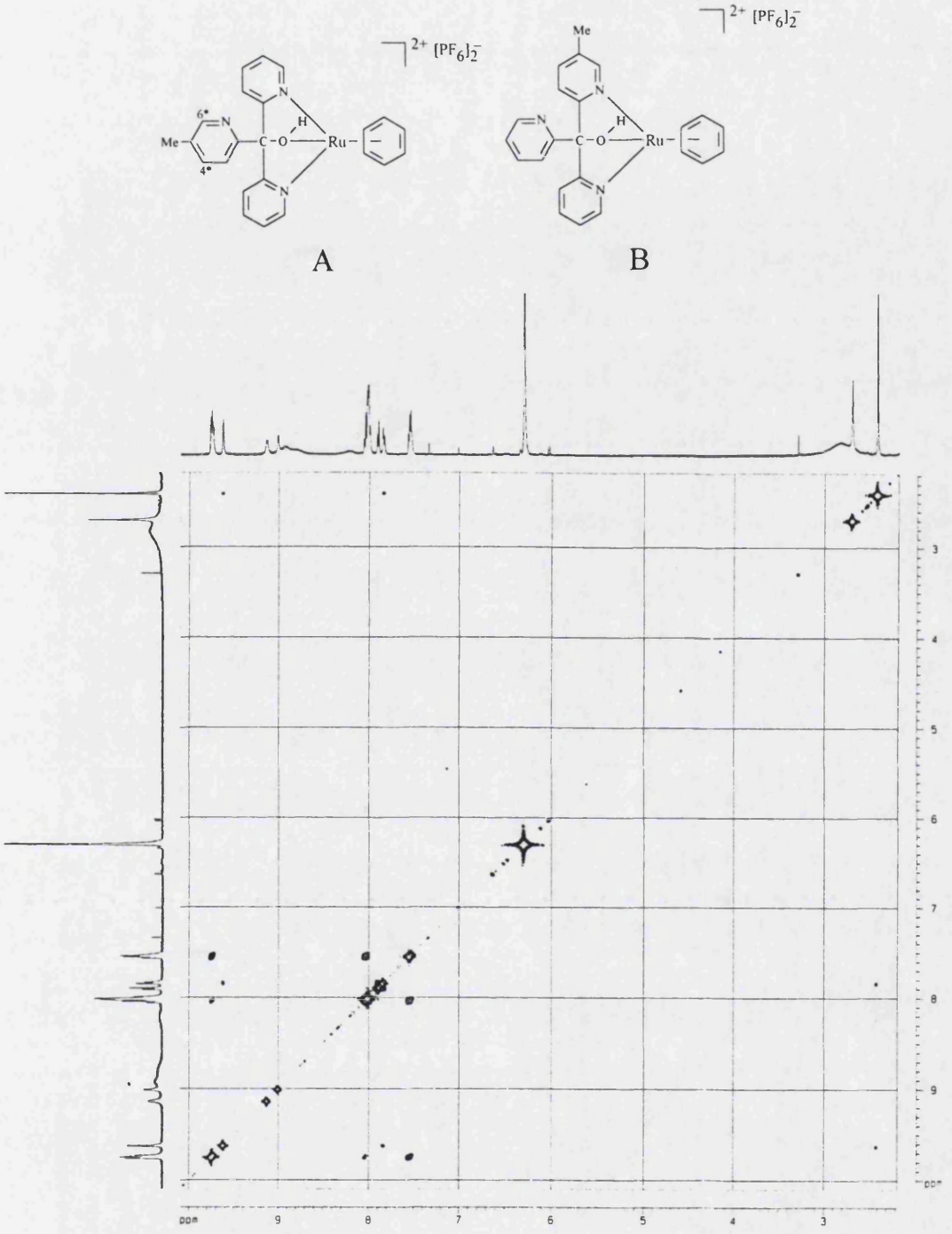


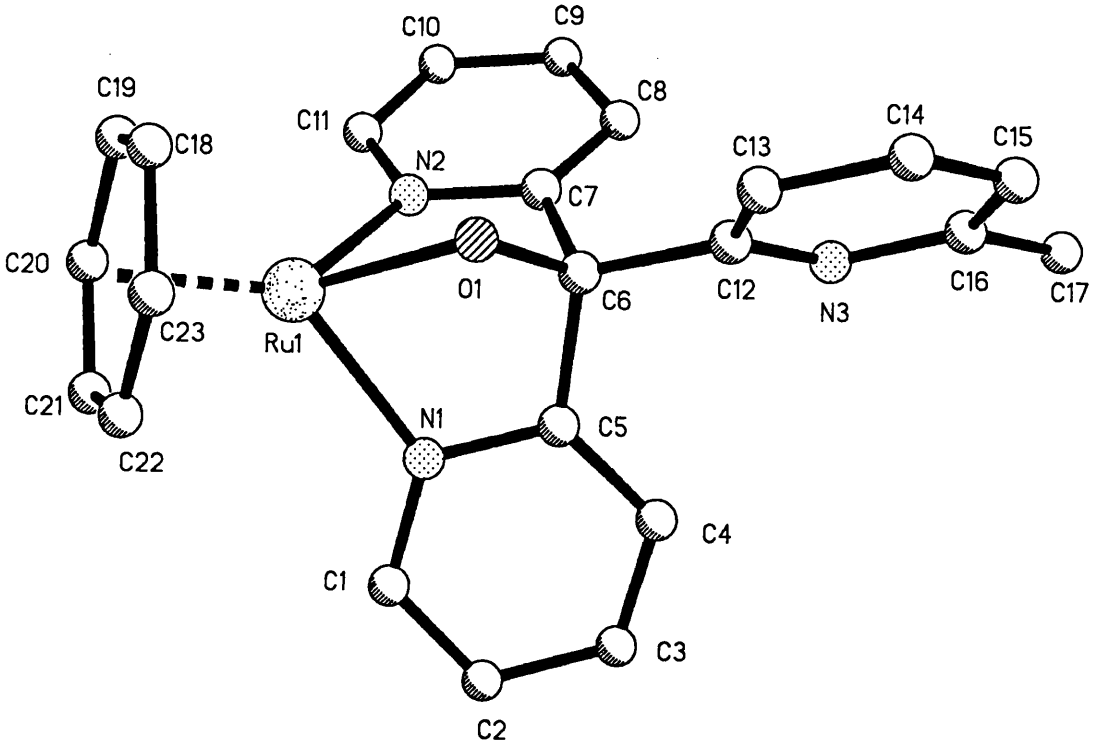
Figure 3.6 ^{1}H COSY spectrum of $[(\eta^{6}\text{-}C_6H_6)Ru\{(5\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}][PF_6]_2$

the metallated substituted pyridyl and non-metallated pyridyl ring protons of isomer **B**. The broadness may be due to the non-metallated pyridyl ring exhibiting restricted rotation due to a hydrogen-bonding interaction with the alcohol, and also interactions with the bulkier metallated ring. Of the two

isomers formed, **A** is marginally the more abundant (*ca.* 6:5), presumably because metallation of the 5-methyl-pyridyl ring in **B** is more sterically unfavourable than metallation of a non-substituted pyridyl ring in **A**.

The reaction of (6-methyl-2-pyridyl)*bis*(2-pyridyl)methanol, **6**, with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ gave, after work-up with ethanolic NH_4PF_6, a yellow solid which analysed for the dicationic complex $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}][PF_6]_2$, **18**. This was found to be a closely related analog of **17** by virtue of very similar mass spectra of the two compounds. The ^1H NMR spectrum of **18** exhibits only two sets of pyridyl signals of relative intensity 2:1. The major set of resonances are due to the two equivalent, metallated non-substituted pyridyl rings, while the minor set of resonances are due to the non-metallated substituted ring. Additionally only two singlets are observed at δ 6.33 and 2.97 ppm respectively due to the benzene and methyl protons. This is consistent with the formation of only a single isomer of **18** and may be due to increased steric hindrance associated with the methyl group located at the pyridyl ring '6' position preventing the nitrogen of that ring from coordinating to the Ru(II) ion.

The deprotonated analog of **18** was prepared by reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with **6** followed by treatment of the reaction mixture with triethylamine before further work-up. Microanalysis was consistent with the formulation $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$, **19**, which was further confirmed by X-ray crystallography. The crystal structure of the cation is shown in Figure 3.7. As was observed for $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]^+$ (Figure 3.2) the tripodal



Ru(1)-O(1)	2.016(2)	O(1)-Ru(1)-N(1)	76.64(9)
Ru(1)-N(1)	2.102(2)	O(1)-Ru(1)-N(2)	76.81(9)
Ru(1)-N(2)	2.114(2)	N(1)-Ru(1)-N(2)	82.72(9)
Ru(1)-C(18)	2.168(3)	N(3)-C(12)-C(6)	117.0(3)
Ru(1)-C(19)	2.180(3)	N(1)-C(5)-C(6)	110.5(2)
Ru(1)-C(20)	2.203(4)	N(2)-C(7)-C(6)	109.4(2)
O(1)-C(6)	1.400(3)		

Figure 3.7 Structure of the cation in $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$ with selected bond lengths (Å) and bond angles (°)

ligand adopts the N,N',O coordination mode, with the 6-methyl-pyridyl ring remaining unmetallated. There are many similarities between the bonding parameters of the two cations in Figures 3.2 and 3.7. For instance, in the cations of **11** and **19** the O-C bond length is 1.426(9) and 1.400(3) Å respectively, and the average O-Ru-N bond angles are 76.6(3) and 76.73(9) °. However, one noteworthy difference between the cations of **11** and **19** is the Ru-O bond lengths, 2.055(6) and 2.016(2) Å respectively. In **19**, the shorter Ru-O bond length may tentatively be ascribed to the electron-releasing effect of the methyl group increasing the basicity of the oxygen. However, the

magnitude of the effect is remarkable with such a long distance separating the two components, hence alternative explanations, such as crystal packing effects, cannot be ruled out.

The compound $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$, **20**, was isolated by work-up of the reaction mixture obtained from $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ and **6**. Microanalysis indicated the composition to be of the monocationic type. By analogy with compounds **18** and **19**, only one isomeric form of compound **20** was observed in the ^1H NMR spectrum (see Experimental).

The reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with (3-methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol, **9**, gave a yellow solid on work-up. Microanalysis indicated the dicationic formulation $[(\eta^6\text{-}C_6H_6)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)COH\}][PF_6]_2$, **21**, in this case. The presence of three isomeric forms of **21** in the ^1H COSY spectrum was reflected by three benzene singlet resonances at δ 6.18, 6.20 and 6.28 ppm, and by six methyl singlet resonances in the δ 1.7-2.6 ppm range. The non-deprotonated nature of **21** was confirmed by three O-H singlet resonances at δ 7.31, 7.48 and 7.66 ppm. Unfortunately the pyridyl region of the spectrum was too complex for any definitive assignments to be made.

To recap, the monocationic compounds **11** and **13** were prepared by the ethanolic reaction of **1** with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ or $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ respectively, followed by treatment with NH_4PF_6. The monocationic compound

20 was prepared analogously from **6** and $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$. In contrast, although following the same general procedure, the dicationic compounds **17**, **18** and **21** were prepared from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, and **5**, **6** and **9** respectively. It is unclear why these *tris*(2-pyridyl)methanol compounds don't give analogous products when reacted under closely similar conditions used to prepare **11**, **13** and **20**. However, it can be definitively stated that each of these compounds was reproducibly synthesised and so it is unlikely that random factors present at the time of the reaction determined the outcome.

The monocationic compound **19** was deliberately synthesised by an alternative route and the X-ray structure demonstrates the influence that the methyl group may have on the Ru-O bond length. Hence, in contrast to the syntheses of the monocationic compounds **11** and **13** derived from **1**, the dicationic nature of compounds **17**, **18** and **21** may be tentatively associated with the presence of methyl groups on the pyridyl rings reducing the acidity of the -OH function *via* an inductive effect. While the ^1H NMR spectra of compounds **17** and **18** show no O-H resonances due to exchange processes, the presence of O-H resonances in the spectrum of **21** may be ascribed to two of the pyridyl rings bearing methyl groups and their inductive effects inhibiting exchange. The infrared spectra of all the dicationic complexes described in this chapter do not exhibit well defined ν(O-H) bands. This may be a consequence of coordination of the alcoholic oxygen to the Ru(II) ion reducing the change in dipole moment associated with an O-H bond vibration, thus reducing the stretching band intensity.

It is surprising that in contrast to the reaction of **6** with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ which gives the dication $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}]^{2+}$ (**18**), the reaction of **6** with $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)RuCl_2]_2$ gives the corresponding monocationic product exclusively (**20**). While the nature of the η^6-bound arene wouldn't be expected to significantly effect the acidity of the ancillary ligand's alcoholic group, it would be expected to influence the overall solubility of the compound. Indeed in each of the reactions described above after the addition of NH_4PF_6 to the reaction mixture, as much solvent as necessary was removed to initiate precipitation of a given product. Therefore a possible explanation for the "inconsistencies" in the chemistries of the differing *tris*(2-pyridyl)methanol compounds is that mono and dicationic products may both be formed in equilibrium in a given reaction, however, owing to their differing solubilities in the reaction medium only one of these preferentially precipitates out with the other remaining in solution.

3.1.4 Summary

A number of mono and dicationic (η^6-arene)Ru(II) complexes of substituted and non-substituted *tris*(2-pyridyl)methanols were synthesised and characterised. In some cases protonation or deprotonation of the tripodal ligand was forcibly achieved by the addition of acid or base respectively to the reaction mixture, whereas in other cases a number of possible factors, such as the nature of the ligands or solvents employed, determined whether or not the isolated compound was dicationic or monocationic.

From the X-ray crystallographic studies it is apparent that the N,N',O

coordination mode adopted by the tripodal ligands in the cations of compounds **11**, **15** and **19** (and presumably in all the other compounds described in this chapter) prevents the donor atoms from taking up facial positions associated with an ideal octahedral geometry at the metal. Furthermore, the crystal structure of the cation in **15** demonstrates the ability of *tris*(2-pyridyl)methoxide to bridge between two different metal centres.

Methyl substitution on a pyridyl ring of a *tris*(2-pyridyl)methanol ligand undoubtedly influences the ligating ability of the ligand to the (η^6-arene)Ru(II) fragment. The closer the methyl group is to a ring nitrogen the less likely that the nitrogen will coordinate. In addition, the presence of methyl substitution appears to decrease the acidity of the coordinated ligand's alcoholic group which may then favour the formation of dicationic products. Unless the methyl group takes up an *ortho* position on a pyridyl ring, thus preventing its coordination (compounds **18-20**), the number of non-equivalent rings within a given compound equals the number of isomeric forms of this compound (two isomers of compound **17** and three isomers of compound **21**).

3.2 Experimental

3.2.1 Instrumentation

As described in sub-section 2.2.1. In addition, some infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer (4000-250 cm^{-1}) on CsI plates, and positive ion electrospray (ES+) mass spectra were recorded on a Micromass Quattro L/C spectrometer (assignments based on the ^{102}Ru, ^{107}Ag and ^{35}Cl isotopes). NMR spectra were referenced internally (d^6-acetone 2.04

ppm). From this point onward, coupling constant data are only given for complexes that are representative of the four main tripodal ligand types (with respect to differing bridgehead substituents). Couplings for the other complexes do not differ significantly from those given, and are not reported.

3.2.2 Materials

All reactions were carried out without use of an inert atmosphere as the products were air-stable. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by repeated dissolution in water and boiling to dryness. The complexes $[(PhCN)_2PdCl_2]$, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)RuCl_2]_2$ were prepared by literature procedures.[5,86,139] Compounds **1**, **5**, **6** and **9** were prepared as described in sub-section 2.2.3. All solvents and other reagents were obtained from the usual commercial sources.

3.2.3 Preparations

$[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$, 11

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.081 g, 0.16 mmol) was added to a solution of **1** (0.084 g, 0.32 mmol) in absolute ethanol (35 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite to remove any insoluble material. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate caused **11** to precipitate out as a yellow solid. Yield: 0.12 g, 64 % (Found: C, 45.30; H, 3.17; N, 6.93. Calc. for $C_{22}H_{18}N_3ORuPF_6$: C, 45.05; H, 3.10; N, 7.17 %). MS (FAB): *m/z* 442 [M–PF_6], 364 [M–py–PF_6]. ^1H NMR (d^6-acetone, 300

MHz): δ 6.23 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.42 ({d,d,d}, 2H, py-5-H); δ 7.91 ({d,d,d}, 2H, py-4-H); δ 8.18 ({d,d,d}, 2H, py-3-H); δ 9.61 ({d,d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.51 ({d,d,d}, 1H, py-5-H); δ 8.00 ({d,d,d}, 1H, py-4-H); δ 8.21 ({d,d,d}, 1H, py-3-H); δ 8.87 ({d,d,d}, 1H, py-6-H). IR (KBr): ν(C-$H_{aromatic}$) 3055 (w); ν(C=C) 1600, 1458 (m); ν(P-F) 840 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru{(C_5H_4N)$_3$COH}][PF_6]$_2$, 12

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.046 g, 0.092 mmol) was added to a solution of **1** (0.043 g, 0.16 mmol) in methanol (40 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite. Addition of a saturated methanolic solution of NH_4PF_6 to the filtrate caused **12** to precipitate out as a yellow solid. Yield: 0.088 g, 74 %. (Yellow crystals of **12**•Me_2CO were grown from acetone prior to microanalysis. Found: C, 37.94; H, 2.84; N, 5.23. Calc. for $C_{22}H_{19}N_3ORuP_2F_{12}$•$Me_2CO$: C, 37.98; H, 3.19; N, 5.32 %). MS (ES+): *m/z* 442 [M–H–2PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 6.33 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.57 ({d,d,d}, 2H, py-5-H); δ 8.01 ({d,d}, 2H, py-3-H); δ 8.05 ({d,d,d}, 2H, py-4-H); δ 9.78 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 8.39 ({d,d}, 1H, py-5-H); δ 9.04 ({d,d}, 1H, py-4-H); δ 9.13 (d, 1H, py-3-H); δ 9.20 (d, 1H, py-6-H). IR (KBr): ν(C=C) 1603, 1458 (m); ν(P-F) 841 (s, br) cm^{-1}.

[(η^6-$MeC_6H_4{}^iPr$)Ru{(C_5H_4N)$_3$CO}]PF_6, 13

Using an analogous method to the synthesis of **11**, [(η^6-$MeC_6H_4{}^iPr$)$RuCl_2$]$_2$ (0.17 g, 0.28 mmol) was reacted with **1** (0.14 g, 0.53 mmol) in a 96 %

ethanolic solution to give **13** as a yellow solid. Yield: 0.22 g, 64 % (Found: C, 48.69; H, 4.06; N, 6.92. Calc. for $C_{26}H_{26}N_3ORuPF_6$: C, 48.59; H, 4.09; N, 6.54 %). MS (FAB): *m/z* 498 [M–PF_6], 420 [M–py–PF_6], 365 [M+H–Ar–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 1.41 (d, J=6.91 Hz, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.50 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.18 (sept, J=6.91 Hz, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 5.92 & 6.11 (AA'BB', J_{AB}=6.25 Hz, 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 7.44 ({d,d,d}, $J_{3,5}$=1.40, $J_{4,5}$=7.38, $J_{5,6}$= 5.67 Hz, 2H, py-5-H); δ 7.90 ({d,d,d}, $J_{3,4}$=7.94, $J_{4,5}$=7.38, $J_{4,6}$=1.50 Hz, 2H, py-4-H); δ 8.20 ({d,d}, $J_{3,4}$=7.94, $J_{3,5}$=1.40 Hz, 2H, py-3-H); δ 9.47 ({d,d}, $J_{4,6}$=1.50, $J_{5,6}$=5.67 Hz, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.51 ({d,d,d}, $J_{3,5}$=1.23, $J_{4,5}$=7.58, $J_{5,6}$=4.80 Hz, 1H, py-5-H); δ 8.00 ({d,d,d}, $J_{3,4}$=8.00, $J_{4,5}$=7.58, $J_{4,6}$=1.85 Hz, 1H, py-4-H); δ 8.27 ({d,d,d}, $J_{3,4}$=8.00, $J_{3,5}$=1.23, $J_{3,6}$=1.01 Hz, 1H, py-3-H); δ 8.88 ({d,d,d}, $J_{3,6}$=1.01, $J_{4,6}$=1.85, $J_{5,6}$=4.80 Hz, 1H, py-6-H). IR (KBr): ν(C-$H_{aromatic}$) 3034 (w); ν(C-H_{alkyl}) 2928 (w); ν(C=C) 1589, 1456 (m); ν(P-F) 843 (s, br) cm^{-1}.

[(η^6-$MeC_6H_4^iPr$)Ru{$(C_5H_4N)_3COH$}][PF_6]$_2$, 14

Compound **13** (0.022 g, 0.034 mmol) was dissolved in acetone (20 cm^3) and the resultant solution filtered through celite before the addition of HPF_6 (0.1 cm^3, 60 % wt. in H_2O) followed by absolute ethanol (10 cm^3). The volume of solution was reduced *in vacuo* and precipitation of **14** occured as a pale yellow solid. The solid was filtered, washed with cold absolute ethanol and diethyl ether, then air-dried. Yield: 0.010 g, 37 % (Found: C, 39.74; H, 3.46; N, 5.24. Calc. for $C_{26}H_{27}N_3ORuP_2F_{12}$: C, 39.60; H, 3.46; N, 5.33 %). MS (FAB): *m/z* 498 [M–H–2PF_6], 420 [M–H–py–2PF_6]. ^{1}H NMR (d^6-acetone, 400 MHz): δ

1.34 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.49 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.23 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 6.00 & 6.28 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 7.62 (br, 2H, py-5-H); δ 8.05 (br m, 4H, py-3,4-H); δ 9.66 (br, 2H, py-6-H). Non-metallated pyridyl ring; δ 8.45 (br, 1H, py-5-H); δ 9.22 (br m, 3H, py-3,4,6-H). IR (KBr): ν(C-$H_{aromatic}$) 3049 (w); ν(C-H_{alkyl}) 2928 (w); ν(C⎓C) 1618, 1466 (m); ν(P-F) 843 (s, br) cm^{-1}.

[{(η^6-C_6H_6)Ru{$(C_5H_4N)_3CO$}}$_2$Ag][PF_6]$_3$, 15

$AgPF_6$ (0.12 g, 0.47 mmol) was added to a suspension of **11** (0.25g, 0.43 mmol) in 96 % ethanol (35 cm^3). The mixture was stirred for 3 hours at ambient temperature then filtered through celite. The filtrate was stored at 0 °C for 16 hours after which time **15** precipitated out as a microcrystalline yellow solid. Yield: 0.21 g, 35 % (Found: C, 37.12; H, 2.63; N, 5.52. Calc. for $C_{44}H_{36}N_6O_2Ru_2AgP_3F_{18}$: C, 37.06; H, 2.55; N, 5.90 %). MS (ES+): *m/z* 1281 [M–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 6.23 (s, 6H, C_6H_6). Ruthenium coordinated pyridyl rings; δ 7.45 ({d,d,d}, 2H, py-5-H); δ 7.94 ({d,d,d}, 2H, py-4-H); δ 8.13 ({d,d}, 2H, py-3-H); δ 9.64 ({d,d}, 2H, py-6-H). Silver coordinated pyridyl ring; δ 7.57 ({d,d,d}, 1H, py-5-H); δ 8.07 ({d,d,d}, 1H, py-4-H); δ 8.25 ({d,d}, 1H, py-3-H); δ 8.88 ({d,d}, 1H, py-6-H). IR (KBr): ν(C-$H_{aromatic}$) 3057 (w); ν(C⎓C) 1605, 1460 (m); ν(P-F) 837 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru{$(C_5H_4N)_3CO$}$PdCl_2$]PF_6, 16

[$(PhCN)_2PdCl_2$] (0.046 g, 0.12 mmol) was added to a suspension of **11** (0.071 g, 0.12 mmol) in 96 % ethanol (25 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite. The celite was washed

with acetone (2 X 10 cm^3) and the washings were combined with the filtrate. Slow evaporation of this solution led to precipitation of **16**•$2H_2O$ as a yellow solid. Yield: 0.027 g, 28 % (Found: C, 32.98; H, 2.47; N, 5.68. Calc. for $C_{22}H_{18}N_3Cl_2ORuPdPF_6$•$2H_2O$: C, 33.03; H, 2.78; N, 5.25 %). MS (ES+): 620 [M–PF_6], 442 [M–$PdCl_2$–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 6.78 (s, 6H, C_6H_6). Ruthenium coordinated pyridyl rings; δ 7.72 ({d,d,d}, 2H, py-5-H); δ 7.86 (m, 2H, py-3-H); δ 8.16 (m, 2H, py-4-H); δ 10.03 ({d,d,d}, 2H, py-6-H). Palladium coordinated pyridyl ring; δ 7.85 (m, 1H, py-5-H, overlapping other signals); δ 8.16 (m, 1H, py-3-H, overlapping other signals); δ 8.48 ({d,d,d}, 1H, py-4-H); δ 9.24 ({d,d,d}, 1H, py-6-H). IR (KBr): ν(C-$H_{aromatic}$) 3074 (w); ν(C=C) 1605, 1460 (m); ν(P-F) 843 (s, br) cm^{-1}. (Nujol): ν(Pd-Cl) *ca.* 320, 300 (w) cm^{-1}.

[(η^6-C_6H_6)Ru{(5-MeC_5H_3N)(C_5H_4N)$_2$COH}][PF_6]$_2$, 17

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.045 g, 0.090 mmol) was added to a solution of **5** (0.047 g, 0.17 mmol) in absolute ethanol (35 cm^3). After stirring for 16 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate, followed by removal of approx. half the solvent led to precipitation of **17** as a dark yellow solid. Yield: 0.020 g, 16 % (Yellow crystals of **17**•0.5Me_2CO were grown from acetone prior to microanalysis. Found: C, 38.01; H, 3.15; N, 5.13. Calc. for $C_{23}H_{21}N_3ORuP_2F_{12}$•0.5$Me_2CO$: C, 37.94; H, 3.13; N, 5.42 %). MS (FAB): *m/z* 456 [M–H–2PF_6], 379 [M–py–2PF_6], 364 [M–H–Mepy–2PF_6]. ^{1}H NMR (d^6-acetone, 500 MHz): (Isomers **A** and **B**) δ 6.30, 6.31 (s, 6H, C_6H_6). Isomer **A**, metallated pyridyl rings; δ 7.55 (m, 2H, py-5-H); δ 8.03 (m, 4H, py-3,4-H); δ 9.76 (d, 2H, py-6-H). Isomer **A**, non-metallated pyridyl ring; δ 7.84 (d, 1H, 5-

Mepy-4-H); δ 7.91 (d, 1H, 5-Mepy-3-H); δ 9.63 (s, 1H, 5-Mepy-6-H); δ 2.41 (s, 3H, CH_3). Isomer **B**, metallated pyridyl ring; δ 7.55 (m, 1H, py-5-H, overlapping other signals); δ 8.03 (m, 2H, py-3,4-H, overlapping other signals); δ 9.74 (d, 1H, py-6-H); Isomer **B**, other metallated pyridyl ring and non-metallated pyridyl ring; δ 8.21, 8.80, 8.93, 9.01, 9.14 (br); δ 2.70 (s, 3H, CH_3). IR (KBr): ν(C-$H_{aromatic}$) 3055 (w); ν(C⎓C) 1605, 1456 (m); ν(P-F) 837 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru{(6-MeC_5H_3N)(C_5H_4N)$_2$COH}][PF_6]$_2$, 18

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.042 g, 0.084 mmol) was added to a solution of **6** (0.032 g, 0.12 mmol) in absolute ethanol (35 cm^3). After stirring for 6 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate, followed by a reduction in the volume of the solvent led to precipitation of **18** as a yellow solid. Yield: 0.031 g, 36 % (Found: C, 37.39; H, 3.20; N, 5.42. Calc. for $C_{23}H_{21}N_3ORuP_2F_{12}$: C, 37.00; H, 2.84; N, 5.63 %). MS (FAB): *m/z* 456 [M–H–2PF_6], 379 [M–py–2PF_6], 364 [M–H–Mepy–2PF_6]. ^{1}H NMR (d^6-acetone, 400 MHz): δ 6.33 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.57 ({d,d,d}, 2H, py-5-H); δ 8.03 (m, 4H, py-3,4-H); δ 9.77 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 8.17 ({d,d}, 1H, 6-Mepy-4-H); δ 8.83 (m, 2H, 6-Mepy-3,5-H); δ 2.97 (s, 3H, CH_3). IR (KBr): ν(C-$H_{aromatic}$) 3055 (w); ν(C-H_{alkyl}) 2928 (w); ν(C⎓C) 1603, 1458 (m); ν(P-F) 839 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru{(6-MeC_5H_3N)(C_5H_4N)$_2$CO}]PF_6, 19

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.033 g, 0.066 mmol) was added to a solution of **6** (0.034 g, 0.12 mmol) in absolute ethanol (35 cm^3). After stirring for 6 hours at room

temperature, triethylamine (0.1 cm^3) was added to the solution which was then filtered through celite. A saturated ethanolic solution of NH_4PF_6 was added to the filtrate and the volume was reduced to *ca.* 5 cm^3. The filtrate was stored at 0 °C for 16 hours, and the resulting precipitate was filtered off and washed with cold absolute ethanol and diethyl ether to give **19** as a microcrystalline pale yellow solid, which was air-dried. Yield: 0.019 g, 26 % (Found: C, 46.25; H, 3.23; N, 6.89. Calc. for $C_{23}H_{20}N_3ORuPF_6$: C, 46.00; H, 3.36; N, 7.00 %). MS (FAB): *m/z* 456 [M–PF_6], 378 [M–py–PF_6], 364 [M–Mepy–PF_6]. ^1H NMR (d^6-acetone, 400 MHz): δ 6.21 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.41 ({d,d,d}, 2H, py-5-H); δ 7.90 ({d,d,d}, 2H, py-4-H); δ 8.24 ({d,d}, 2H, py-3-H); δ 9.59 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.36 (d, 1H, 6-Mepy-5-H); δ 7.86 ({d,d}, 1H, 6-Mepy-4-H); δ 7.99 (d, 1H, 6-Mepy-3-H); δ 2.72 (s, 3H, CH_3). IR (KBr): ν(C⎓C) 1618, 1458 (m); ν(P-F) 835 (s, br) cm^{-1}.

[(η^6-MeC$_6$H$_4$^{i}Pr)Ru{(6-MeC$_5$H$_3$N)(C$_5$H$_4$N)$_2$CO}]PF$_6$, 20

Using an analogous method to the synthesis of **18**, $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ (0.023 g, 0.038 mmol) was reacted with **6** (0.021 g, 0.076 mmol) to give **20** as a yellow solid. Yield: 0.031 g, 62 % (Found: C, 48.67; H, 4.06; N, 5.93. Calc. for $C_{27}H_{28}N_3ORuPF_6$: C, 49.38; H, 4.31; N, 6.40 %). MS (FAB): *m/z* 512 [M–PF_6], 434 [M–py–PF_6]. ^1H NMR (d^6-acetone, 400 MHz): δ 1.40 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.49 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.17 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 5.91 & 6.10 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 7.43 ({d,d}, 2H, py-5-H); δ 7.89 ({d,d}, 2H, py-4-H); δ 8.26 (d, 2H, py-3-H); δ 9.45 (d, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.36 (d, 1H, 6-Mepy-5-H); δ 7.86 ({d,d}, 1H, 6-Mepy-4-H); δ 8.04 (d, 1H, 6-Mepy-3-

H); δ 2.72 (s, 3H, CH_3). IR (KBr): ν(C-$H_{aromatic}$) 3037 (w); ν(C-H_{alkyl}) 2930 (w); ν(C⋯C) 1592, 1454 (m); ν(P-F) 843 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru{(3-MeC_5H_3N)(5-MeC_5H_3N)(C_5H_4N)COH}][PF_6]$_2$, 21

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.047 g, 0.094 mmol) was added to a solution of **9** (0.055 g, 0.19 mmol) in absolute ethanol (35 cm^3). After stirring for 4 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate, followed by removal of most of the solvent led to precipitation of **21** as a pale yellow solid. Yield: 0.032 g, 22 % (Found: C, 38.57; H, 3.24; N, 5.63. Calc. for $C_{24}H_{23}N_3ORuP_2F_{12}$: C, 37.90; H, 3.05; N, 5.53 %). MS (FAB): *m/z* 470 [M–H–2PF_6], 378 [M–H–Mepy–2PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz, NB three isomers are unresolved): δ 1.76, 1.85, 2.06, 2.41, 2.44, 2.57 (s, 3H, 3-Mepy-CH_3 and s, 3H, 5-Mepy-CH_3); δ 6.18, 6.20, 6.28 (s, 6H, C_6H_6); δ 7.31, 7.48, 7.66 (s, 1H, OH); δ 7.38 (m), 7.51 (d,d), 7.58 (br), 7.64 (d), 7.76 (br), 7.80 (d), 7.86 (d), 7.90 (d), 8.05 (d,d), 8.10 (d,d), approx. 8.30, 8.35 (br), 8.43 (d,d), 8.80, 8.83, 9.00 (br), 9.53 (m), 9.65 (d), 9.70, 9.81 (br) (pyridyl signals). Isomeric assignments could not be established for the above signals. IR (KBr): ν(C-H_{alkyl}) 2928 (w); ν(C⋯C) 1611, 1458 (m); ν(P-F) 839 (s, br) cm^{-1}.

Crystallographic characterisation of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$ (11)

Table 3.1 **Crystal data and structure refinement for 11.**

Formula	$C_{22}H_{18}F_6N_3OPRu$
Formula weight	586.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 11.981(2) Å alpha = 90.18(3) °. b = 11.943(2) Å beta = 101.03(3) °. c = 19.565(4) Å gamma = 113.43(3) °.
Volume	2511.5(8) $Å^3$
Z	4
Density (calculated)	1.551 Mg/m^3
Absorption coefficient	0.751 mm^{-1}
F(000)	1168
Crystal size	0.44 x 0.38 x 0.32 mm
Theta range for data collection	2.54 to 25.05 °.
Index ranges	0<=h<=14, -14<=k<=13, -23<=l<=22
Reflections collected	9238
Independent reflections	8784 [R(int) = 0.0505]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8775 / 0 / 613
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0816, wR2 = 0.2224
R indices (all data)	R1 = 0.1119, wR2 = 0.2719
Largest diff. peak and hole	1.550 and -2.035 $e.Å^{-3}$

Table 3.2 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 11.**

	x	y	z	U(eq)
Ru(1)	3112(1)	506(1)	9221(1)	59(1)
Ru(2)	6199(1)	2387(1)	5605(1)	48(1)
O(1)	4724(5)	1244(5)	8849(3)	54(1)
O(51)	4485(5)	2115(5)	5034(3)	52(1)
N(11)	4162(7)	2166(7)	9869(3)	65(2)
N(21)	2778(7)	1719(7)	8500(4)	67(2)
N(31)	6550(9)	4416(7)	8517(4)	83(2)
N(61)	4970(5)	1458(5)	6280(3)	46(1)
N(71)	5907(6)	3908(5)	5976(3)	55(2)
N(81)	2029(9)	1670(10)	4436(5)	93(3)
C(1)	2608(14)	-1401(10)	8838(8)	103(4)
C(2)	3329(12)	-1165(11)	9530(10)	111(5)
C(3)	3004(14)	-736(12)	10053(7)	106(5)
C(4)	1936(15)	-523(13)	9940(7)	114(5)
C(5)	1194(11)	-763(12)	9284(8)	105(4)
C(6)	1526(12)	-1182(11)	8714(6)	102(4)
C(51)	6685(12)	1665(19)	4745(7)	121(6)
C(52)	6814(10)	971(10)	5307(9)	92(4)
C(53)	7570(12)	1575(15)	5927(7)	102(4)
C(54)	8235(9)	2872(16)	5989(7)	102(4)
C(55)	8058(13)	3487(11)	5413(12)	114(6)
C(56)	7333(17)	2955(19)	4811(10)	122(6)
C(10)	5014(9)	2523(7)	8845(4)	59(2)
C(60)	3857(7)	2412(7)	5503(4)	53(2)
C(11)	5088(9)	2990(8)	9578(4)	65(2)
C(12)	6016(11)	4062(9)	9987(5)	80(3)
C(13)	5930(14)	4286(10)	10666(6)	105(4)
C(14)	4999(13)	3461(11)	10965(6)	98(4)
C(15)	4121(13)	2427(12)	10557(5)	92(3)
C(21)	3845(10)	2617(8)	8372(4)	66(2)
C(22)	3800(11)	3421(9)	7859(4)	75(3)
C(23)	2637(13)	3337(12)	7508(5)	91(4)
C(24)	1560(12)	2441(14)	7639(6)	102(4)
C(25)	1642(10)	1638(11)	8144(5)	87(3)
C(31)	6208(9)	3204(8)	8557(4)	64(2)
C(32)	6855(10)	2559(10)	8357(5)	75(3)
C(33)	7941(11)	3219(11)	8107(6)	93(3)
C(34)	8272(13)	4487(13)	8056(6)	110(5)
C(35)	7580(12)	5038(10)	8277(6)	95(4)
C(61)	3862(7)	1572(6)	6109(4)	48(2)
C(62)	2901(8)	973(7)	6459(4)	58(2)
C(63)	3096(9)	225(8)	6983(4)	66(2)
C(64)	4224(9)	119(8)	7167(4)	66(2)
C(65)	5160(8)	770(7)	6799(4)	55(2)
C(71)	4692(8)	3741(7)	5846(4)	55(2)
C(72)	4334(10)	4651(8)	6022(5)	74(2)
C(73)	5267(13)	5790(8)	6348(6)	88(3)
C(74)	6496(13)	5929(9)	6503(6)	91(3)
C(75)	6801(10)	4992(7)	6318(5)	73(2)
C(81)	2532(7)	2216(8)	5127(4)	57(2)
C(82)	1845(8)	2521(9)	5510(5)	69(2)
C(83)	651(12)	2316(14)	5179(9)	118(5)
C(84)	114(11)	1820(14)	4495(7)	108(4)
C(85)	820(9)	1493(13)	4146(6)	99(4)

Table 3.2 **cont.**

P(1)	2254(3)	707(3)	2183(1)	73(1)
F(1)	1682(10)	-653(7)	2410(5)	143(3)
F(2)	3292(7)	414(7)	1895(4)	105(2)
F(3)	1360(9)	300(12)	1437(4)	176(5)
F(4)	3145(8)	1078(7)	2950(3)	118(2)
F(5)	1225(8)	989(9)	2461(4)	130(3)
F(6)	2932(11)	2105(8)	2009(5)	154(4)
P(2)	8598(3)	3936(2)	3012(2)	74(1)
F(7)	7911(11)	2622(7)	3234(7)	187(5)
F(8)	9332(9)	5289(7)	2826(6)	150(3)
F(9)	7840(15)	4434(11)	3380(6)	231(7)
F(10)	7736(16)	3766(13)	2278(7)	251(8)
F(11)	9459(14)	4131(10)	3744(7)	236(7)
F(12)	9517(16)	3572(15)	2749(10)	271(9)

Table 3.3 **Bond lengths [Å] and angles [°] for 11.**

Ru(1)-O(1)	2.055(6)	C(55)-C(56)	1.31(2)
Ru(1)-N(11)	2.124(7)	C(10)-C(11)	1.512(11)
Ru(1)-N(21)	2.122(7)	C(10)-C(31)	1.553(12)
Ru(1)-C(2)	2.185(11)	C(10)-C(21)	1.569(12)
Ru(1)-C(3)	2.193(10)	C(60)-C(81)	1.540(11)
Ru(1)-C(1)	2.199(12)	C(60)-C(61)	1.556(10)
Ru(1)-C(6)	2.208(12)	C(60)-C(71)	1.563(11)
Ru(1)-C(4)	2.205(11)	C(11)-C(12)	1.427(13)
Ru(1)-C(5)	2.220(11)	C(12)-C(13)	1.385(14)
Ru(2)-O(51)	2.040(5)	C(13)-C(14)	1.39(2)
Ru(2)-N(71)	2.131(6)	C(14)-C(15)	1.38(2)
Ru(2)-N(61)	2.144(6)	C(21)-C(22)	1.400(12)
Ru(2)-C(51)	2.163(9)	C(22)-C(23)	1.39(2)
Ru(2)-C(55)	2.195(11)	C(23)-C(24)	1.38(2)
Ru(2)-C(56)	2.191(12)	C(24)-C(25)	1.396(14)
Ru(2)-C(53)	2.215(10)	C(31)-C(32)	1.390(13)
Ru(2)-C(52)	2.211(9)	C(32)-C(33)	1.409(14)
Ru(2)-C(54)	2.241(10)	C(33)-C(34)	1.41(2)
O(1)-C(10)	1.426(9)	C(34)-C(35)	1.37(2)
O(51)-C(60)	1.418(8)	C(61)-C(62)	1.399(10)
N(11)-C(11)	1.378(12)	C(62)-C(63)	1.410(12)
N(11)-C(15)	1.396(11)	C(63)-C(64)	1.386(13)
N(21)-C(21)	1.371(12)	C(64)-C(65)	1.414(12)
N(21)-C(25)	1.372(12)	C(71)-C(72)	1.382(11)
N(31)-C(35)	1.338(14)	C(72)-C(73)	1.42(2)
N(31)-C(31)	1.346(11)	C(73)-C(74)	1.39(2)
N(61)-C(65)	1.352(10)	C(74)-C(75)	1.374(14)
N(61)-C(61)	1.367(10)	C(81)-C(82)	1.357(11)
N(71)-C(71)	1.361(10)	C(82)-C(83)	1.38(2)
N(71)-C(75)	1.374(11)	C(83)-C(84)	1.38(2)
N(81)-C(85)	1.380(13)	C(84)-C(85)	1.35(2)
N(81)-C(81)	1.410(13)	P(1)-F(3)	1.581(8)
C(1)-C(6)	1.40(2)	P(1)-F(1)	1.594(8)
C(1)-C(2)	1.42(2)	P(1)-F(5)	1.586(7)
C(2)-C(3)	1.33(2)	P(1)-F(4)	1.610(7)
C(3)-C(4)	1.38(2)	P(1)-F(2)	1.613(6)
C(4)-C(5)	1.37(2)	P(1)-F(6)	1.610(8)
C(5)-C(6)	1.40(2)	P(2)-F(12)	1.504(10)
C(51)-C(52)	1.40(2)	P(2)-F(9)	1.541(9)
C(51)-C(56)	1.41(2)	P(2)-F(10)	1.561(11)
C(52)-C(53)	1.37(2)	P(2)-F(11)	1.551(11)
C(53)-C(54)	1.42(2)	P(2)-F(7)	1.562(8)
C(54)-C(55)	1.37(2)	P(2)-F(8)	1.586(8)
O(1)-Ru(1)-N(11)	76.8(3)	N(21)-Ru(1)-C(6)	97.1(4)
O(1)-Ru(1)-N(21)	76.3(3)	O(1)-Ru(1)-C(4)	155.1(5)
N(11)-Ru(1)-N(21)	82.2(3)	N(11)-Ru(1)-C(4)	98.6(4)
O(1)-Ru(1)-C(2)	95.7(4)	N(21)-Ru(1)-C(4)	127.8(5)
N(11)-Ru(1)-C(2)	119.4(5)	O(1)-Ru(1)-C(5)	159.1(5)
N(21)-Ru(1)-C(2)	155.2(6)	N(11)-Ru(1)-C(5)	124.0(5)
O(1)-Ru(1)-C(3)	119.0(5)	N(21)-Ru(1)-C(5)	102.1(4)
N(11)-Ru(1)-C(3)	96.9(4)	O(51)-Ru(2)-N(71)	77.1(2)
N(21)-Ru(1)-C(3)	164.2(6)	O(51)-Ru(2)-N(61)	76.6(2)
O(1)-Ru(1)-C(1)	96.1(4)	N(71)-Ru(2)-N(61)	81.8(2)
N(11)-Ru(1)-C(1)	156.1(5)	O(51)-Ru(2)-C(51)	92.7(4)
N(21)-Ru(1)-C(1)	118.7(5)	N(71)-Ru(2)-C(51)	143.7(6)
O(1)-Ru(1)-C(6)	122.1(4)	N(61)-Ru(2)-C(51)	130.2(6)
N(11)-Ru(1)-C(6)	160.6(5)	O(51)-Ru(2)-C(55)	130.2(6)

Table 3.3 **cont.**

N(71)-Ru(2)-C(55)	95.2(4)	C(55)-C(54)-Ru(2)	70.1(7)
N(61)-Ru(2)-C(55)	152.0(7)	C(53)-C(54)-Ru(2)	70.4(6)
O(51)-Ru(2)-C(56)	101.2(5)	C(56)-C(55)-C(54)	124.2(14)
N(71)-Ru(2)-C(56)	109.3(5)	C(56)-C(55)-Ru(2)	72.5(8)
N(61)-Ru(2)-C(56)	168.1(6)	C(54)-C(55)-Ru(2)	73.8(7)
O(51)-Ru(2)-C(53)	145.9(5)	C(55)-C(56)-C(51)	118.2(14)
N(71)-Ru(2)-C(53)	135.8(5)	C(55)-C(56)-Ru(2)	72.8(8)
N(61)-Ru(2)-C(53)	97.1(3)	C(51)-C(56)-Ru(2)	70.0(6)
O(51)-Ru(2)-C(52)	111.8(4)	O(1)-C(10)-C(11)	107.2(6)
N(71)-Ru(2)-C(52)	170.9(4)	O(1)-C(10)-C(31)	111.3(6)
N(61)-Ru(2)-C(52)	102.0(4)	C(11)-C(10)-C(31)	114.1(8)
O(51)-Ru(2)-C(54)	165.7(4)	O(1)-C(10)-C(21)	105.4(7)
N(71)-Ru(2)-C(54)	105.0(4)	C(11)-C(10)-C(21)	106.7(7)
N(61)-Ru(2)-C(54)	117.7(5)	C(31)-C(10)-C(21)	111.6(7)
C(10)-O(1)-Ru(1)	105.5(5)	O(51)-C(60)-C(81)	110.5(6)
C(60)-O(51)-Ru(2)	106.0(4)	O(51)-C(60)-C(61)	105.7(6)
C(11)-N(11)-C(15)	118.8(9)	C(81)-C(60)-C(61)	112.6(6)
C(11)-N(11)-Ru(1)	112.6(5)	O(51)-C(60)-C(71)	107.8(6)
C(15)-N(11)-Ru(1)	128.0(8)	C(81)-C(60)-C(71)	114.8(6)
C(21)-N(21)-C(25)	119.6(8)	C(61)-C(60)-C(71)	105.0(6)
C(21)-N(21)-Ru(1)	113.6(5)	N(11)-C(11)-C(12)	120.2(8)
C(25)-N(21)-Ru(1)	126.7(7)	N(11)-C(11)-C(10)	111.0(8)
C(35)-N(31)-C(31)	118.0(10)	C(12)-C(11)-C(10)	128.5(8)
C(65)-N(61)-C(61)	120.2(6)	C(13)-C(12)-C(11)	118.8(10)
C(65)-N(61)-Ru(2)	127.8(5)	C(12)-C(13)-C(14)	121.4(11)
C(61)-N(61)-Ru(2)	112.0(5)	C(15)-C(14)-C(13)	118.3(10)
C(71)-N(71)-C(75)	119.2(7)	C(14)-C(15)-N(11)	122.4(11)
C(71)-N(71)-Ru(2)	113.9(5)	N(21)-C(21)-C(22)	121.3(9)
C(75)-N(71)-Ru(2)	126.9(6)	N(21)-C(21)-C(10)	109.9(7)
C(85)-N(81)-C(81)	117.9(9)	C(22)-C(21)-C(10)	128.7(9)
C(6)-C(1)-C(2)	118.3(13)	C(21)-C(22)-C(23)	118.3(10)
C(6)-C(1)-Ru(1)	71.9(8)	C(24)-C(23)-C(22)	120.7(9)
C(2)-C(1)-Ru(1)	70.6(7)	C(23)-C(24)-C(25)	119.4(11)
C(3)-C(2)-C(1)	121.6(12)	N(21)-C(25)-C(24)	120.7(11)
C(3)-C(2)-Ru(1)	72.6(7)	N(31)-C(31)-C(32)	123.9(9)
C(1)-C(2)-Ru(1)	71.6(7)	N(31)-C(31)-C(10)	116.1(8)
C(2)-C(3)-C(4)	120.6(12)	C(32)-C(31)-C(10)	120.0(8)
C(2)-C(3)-Ru(1)	72.0(7)	C(31)-C(32)-C(33)	118.0(10)
C(4)-C(3)-Ru(1)	72.2(7)	C(32)-C(33)-C(34)	117.3(11)
C(5)-C(4)-C(3)	119.9(13)	C(35)-C(34)-C(33)	120.1(11)
C(5)-C(4)-Ru(1)	72.6(6)	N(31)-C(35)-C(34)	122.7(11)
C(3)-C(4)-Ru(1)	71.3(7)	N(61)-C(61)-C(62)	121.1(7)
C(4)-C(5)-C(6)	121.0(12)	N(61)-C(61)-C(60)	111.3(6)
C(4)-C(5)-Ru(1)	71.4(7)	C(62)-C(61)-C(60)	127.7(7)
C(6)-C(5)-Ru(1)	71.0(7)	C(63)-C(62)-C(61)	118.2(8)
C(5)-C(6)-C(1)	118.4(11)	C(64)-C(63)-C(62)	121.1(8)
C(5)-C(6)-Ru(1)	72.0(7)	C(63)-C(64)-C(65)	117.5(8)
C(1)-C(6)-Ru(1)	71.1(7)	N(61)-C(65)-C(64)	121.9(8)
C(52)-C(51)-C(56)	121.2(13)	N(71)-C(71)-C(72)	121.9(8)
C(52)-C(51)-Ru(2)	73.2(6)	N(71)-C(71)-C(60)	109.5(6)
C(56)-C(51)-Ru(2)	72.1(7)	C(72)-C(71)-C(60)	128.7(8)
C(53)-C(52)-C(51)	118.2(11)	C(71)-C(72)-C(73)	118.6(9)
C(53)-C(52)-Ru(2)	72.2(6)	C(74)-C(73)-C(72)	118.8(9)
C(51)-C(52)-Ru(2)	69.5(6)	C(75)-C(74)-C(73)	120.1(10)
C(52)-C(53)-C(54)	120.5(11)	C(74)-C(75)-N(71)	121.3(10)
C(52)-C(53)-Ru(2)	71.9(6)	C(82)-C(81)-N(81)	121.7(8)
C(54)-C(53)-Ru(2)	72.4(6)	C(82)-C(81)-C(60)	116.6(7)
C(55)-C(54)-C(53)	117.8(12)	N(81)-C(81)-C(60)	121.6(7)

Table 3.3 **cont..**

C(81)-C(82)-C(83)	116.5(10)	F(1)-P(1)-F(6)	175.1(6)
C(82)-C(83)-C(84)	124.7(11)	F(5)-P(1)-F(6)	91.9(5)
C(85)-C(84)-C(83)	116.5(10)	F(4)-P(1)-F(6)	88.4(5)
C(84)-C(85)-N(81)	122.7(11)	F(2)-P(1)-F(6)	88.3(4)
F(3)-P(1)-F(1)	91.3(6)	F(12)-P(2)-F(10)	94.9(11)
F(3)-P(1)-F(5)	89.2(4)	F(9)-P(2)-F(10)	93.6(9)
F(1)-P(1)-F(5)	89.7(5)	F(12)-P(2)-F(11)	85.7(10)
F(3)-P(1)-F(4)	178.2(6)	F(9)-P(2)-F(11)	85.8(9)
F(1)-P(1)-F(4)	86.9(5)	F(10)-P(2)-F(11)	178.9(7)
F(5)-P(1)-F(4)	90.8(4)	F(12)-P(2)-F(7)	91.9(7)
F(3)-P(1)-F(2)	90.4(4)	F(9)-P(2)-F(7)	91.3(6)
F(1)-P(1)-F(2)	90.2(5)	F(12)-P(2)-F(8)	88.5(6)
F(5)-P(1)-F(2)	179.5(4)	F(9)-P(2)-F(8)	87.9(6)
F(4)-P(1)-F(2)	89.6(4)	F(10)-P(2)-F(8)	85.4(7)
F(3)-P(1)-F(6)	93.4(6)	F(11)-P(2)-F(8)	93.7(6)
		F(7)-P(2)-F(8)	177.2(7)

Crystallographic characterisation of $[\{(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$ (15)

Table 3.4 **Crystal data and structure refinement for 15.**

Formula	$C_{44}H_{36}AgF_{18}N_6O_2P_3Ru_2 \cdot Me_2CO$
Formula weight	1483.87
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 17.920(4) Å alpha = 90 °. b = 20.625(4) Å beta = 107.53(3) °. c = 16.117(3) Å gamma = 90 °.
Volume	5680(2) $Å^3$
Z	4
Density (calculated)	1.735 Mg/m^3
Absorption coefficient	1.055 mm^{-1}
F(000)	2928
Crystal size	0.36 x 0.28 x 0.22 mm
Theta range for data collection	2.65 to 25.03 °.
Index ranges	0<=h<=21, 0<=k<=24, -19<=l<=18
Reflections collected	4992
Independent reflections	4826 [R(int) = 0.0372]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4822 / 0 / 383
Goodness-of-fit on F^2	1.108
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.1116
R indices (all data)	R1 = 0.0917, wR2 = 0.1504
Extinction coefficient	0.00016(5)
Largest diff. peak and hole	1.336 and -0.873 $e.Å^{-3}$

Table 3.5 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 15.**

	x	y	z	U(eq)
Ag(1)	0	3872(1)	7500	52(1)
Ru(1)	1546(1)	2441(1)	7307(1)	40(1)
N(1)	765(3)	2018(3)	6160(4)	44(1)
N(2)	1968(3)	2911(3)	6354(4)	45(1)
N(3)	-329(4)	4045(3)	6035(4)	47(2)
O(1)	733(3)	3153(2)	6834(3)	42(1)
C(1)	2556(6)	1842(6)	8085(6)	81(3)
C(2)	2660(6)	2498(6)	8356(6)	78(3)
C(3)	2093(7)	2827(4)	8610(5)	74(3)
C(4)	1387(6)	2510(5)	8607(6)	67(2)
C(5)	1268(6)	1864(6)	8337(6)	75(3)
C(6)	1862(8)	1532(4)	8082(6)	80(3)
C(10)	595(4)	3176(3)	5924(4)	38(2)
C(11)	326(4)	2470(3)	5591(4)	37(2)
C(12)	-266(5)	2278(4)	4853(5)	50(2)
C(13)	-407(5)	1607(4)	4678(6)	62(2)
C(14)	50(6)	1166(4)	5238(6)	65(2)
C(15)	638(5)	1377(3)	5979(6)	51(2)
C(21)	1413(4)	3266(3)	5763(5)	47(2)
C(22)	1604(5)	3640(4)	5132(5)	55(2)
C(23)	2381(6)	3633(4)	5100(6)	68(2)
C(24)	2941(5)	3258(5)	5693(7)	69(3)
C(25)	2717(4)	2910(4)	6308(5)	54(2)
C(31)	-24(4)	3703(3)	5482(5)	39(2)
C(32)	-259(5)	3820(4)	4589(5)	53(2)
C(33)	-828(5)	4287(4)	4222(6)	61(2)
C(34)	-1150(5)	4625(4)	4774(6)	70(3)
C(35)	-893(5)	4500(4)	5675(6)	61(2)
P(1)	2711(2)	4733(1)	8101(2)	72(1)
F(1)	2711(6)	4471(5)	9018(5)	152(3)
F(2)	3035(5)	4045(3)	7897(5)	117(2)
F(3)	2430(7)	5423(4)	8318(7)	170(4)
F(4)	1844(4)	4493(5)	7728(6)	153(3)
F(5)	2703(6)	4996(4)	7174(6)	154(4)
F(6)	3598(5)	4954(4)	8479(8)	167(4)
P(2)	5000	2257(2)	7500	61(1)
F(7A)	4431(3)	2252(3)	6504(3)	88(2)
F(8A)	4449(15)	1812(18)	7694(17)	174(17)
F(9A)	4455(10)	2851(12)	7704(14)	125(8)
F(7B)	4272(12)	2177(19)	7873(16)	132(15)
F(8B)	5000	1454(14)	7500	141(15)
F(9B)	5000	2962(10)	7500	117(9)
O(50)	5000	5627(5)	7500	93(3)
C(50)	5000	5035(7)	7500	96(6)
C(51)	4508(10)	4664(7)	6735(10)	153(7)

Table 3.6 **Bond lengths [Å] and angles [°] for 15.**

Ag(1)-N(3)#1	2.282(6)	C(12)-C(13)	1.418(11)
Ag(1)-N(3)	2.282(6)	C(13)-C(14)	1.366(12)
Ag(1)-O(1)#1	2.434(5)	C(14)-C(15)	1.404(12)
Ag(1)-O(1)	2.434(5)	C(21)-C(22)	1.397(10)
Ru(1)-O(1)	2.047(5)	C(22)-C(23)	1.408(12)
Ru(1)-N(1)	2.139(6)	C(23)-C(24)	1.393(13)
Ru(1)-N(2)	2.138(6)	C(24)-C(25)	1.377(12)
Ru(1)-C(3)	2.182(8)	C(31)-C(32)	1.392(10)
Ru(1)-C(2)	2.196(9)	C(32)-C(33)	1.399(11)
Ru(1)-C(4)	2.203(9)	C(33)-C(34)	1.386(12)
Ru(1)-C(5)	2.217(9)	C(34)-C(35)	1.408(13)
Ru(1)-C(6)	2.229(8)	P(1)-F(4)	1.567(8)
Ru(1)-C(1)	2.237(9)	P(1)-F(1)	1.574(8)
N(1)-C(15)	1.358(9)	P(1)-F(3)	1.583(7)
N(1)-C(11)	1.376(9)	P(1)-F(5)	1.586(8)
N(2)-C(21)	1.364(9)	P(1)-F(6)	1.588(8)
N(2)-C(25)	1.367(9)	P(1)-F(2)	1.604(7)
N(3)-C(31)	1.373(9)	P(2)-F(9B)	1.45(2)
N(3)-C(35)	1.375(10)	P(2)-F(8A)	1.45(2)
O(1)-C(10)	1.413(8)	P(2)-F(8A)#2	1.45(2)
C(1)-C(6)	1.40(2)	P(2)-F(7B)	1.60(2)
C(1)-C(2)	1.42(2)	P(2)-F(7B)#2	1.60(2)
C(2)-C(3)	1.381(14)	P(2)-F(7A)#2	1.623(5)
C(3)-C(4)	1.423(14)	P(2)-F(7A)	1.623(5)
C(4)-C(5)	1.397(14)	P(2)-F(8B)	1.66(3)
C(5)-C(6)	1.43(2)	P(2)-F(9A)#2	1.66(2)
C(10)-C(31)	1.563(9)	P(2)-F(9A)	1.66(2)
C(10)-C(21)	1.575(10)	O(50)-C(50)	1.22(2)
C(10)-C(11)	1.576(9)	C(50)-C(51)	1.49(2)
C(11)-C(12)	1.392(10)	C(50)-C(51)#2	1.49(2)
N(3)#1-Ag(1)-N(3)	162.0(3)	C(15)-N(1)-C(11)	119.4(6)
N(3)#1-Ag(1)-O(1)#1	69.2(2)	C(15)-N(1)-Ru(1)	127.2(5)
N(3)-Ag(1)-O(1)#1	123.1(2)	C(11)-N(1)-Ru(1)	113.2(4)
N(3)#1-Ag(1)-O(1)	123.1(2)	C(21)-N(2)-C(25)	119.0(7)
N(3)-Ag(1)-O(1)	69.2(2)	C(21)-N(2)-Ru(1)	113.9(5)
O(1)#1-Ag(1)-O(1)	104.9(2)	C(25)-N(2)-Ru(1)	127.1(5)
O(1)-Ru(1)-N(1)	76.3(2)	C(31)-N(3)-C(35)	117.5(7)
O(1)-Ru(1)-N(2)	76.9(2)	C(31)-N(3)-Ag(1)	124.3(5)
N(1)-Ru(1)-N(2)	81.1(2)	C(35)-N(3)-Ag(1)	118.1(5)
O(1)-Ru(1)-C(3)	99.2(3)	C(10)-O(1)-Ru(1)	107.1(4)
N(1)-Ru(1)-C(3)	165.3(4)	C(10)-O(1)-Ag(1)	119.2(4)
N(2)-Ru(1)-C(3)	111.9(3)	Ru(1)-O(1)-Ag(1)	133.7(2)
O(1)-Ru(1)-C(2)	128.9(4)	C(6)-C(1)-C(2)	118.1(10)
N(1)-Ru(1)-C(2)	153.3(4)	C(6)-C(1)-Ru(1)	71.4(5)
N(2)-Ru(1)-C(2)	95.3(3)	C(2)-C(1)-Ru(1)	69.8(5)
O(1)-Ru(1)-C(4)	91.5(3)	C(3)-C(2)-C(1)	121.3(10)
N(1)-Ru(1)-C(4)	127.6(3)	C(3)-C(2)-Ru(1)	71.1(5)
N(2)-Ru(1)-C(4)	146.0(3)	C(1)-C(2)-Ru(1)	72.9(6)
O(1)-Ru(1)-C(5)	111.6(3)	C(2)-C(3)-C(4)	120.4(9)
N(1)-Ru(1)-C(5)	101.1(3)	C(2)-C(3)-Ru(1)	72.2(5)
N(2)-Ru(1)-C(5)	171.5(3)	C(4)-C(3)-Ru(1)	71.9(5)
O(1)-Ru(1)-C(6)	147.5(4)	C(5)-C(4)-C(3)	119.4(9)
N(1)-Ru(1)-C(6)	97.6(3)	C(5)-C(4)-Ru(1)	72.1(6)
N(2)-Ru(1)-C(6)	134.4(4)	C(3)-C(4)-Ru(1)	70.3(5)
O(1)-Ru(1)-C(1)	165.8(4)	C(4)-C(5)-C(6)	119.4(9)
N(1)-Ru(1)-C(1)	117.9(4)	C(4)-C(5)-Ru(1)	71.0(5)
N(2)-Ru(1)-C(1)	104.6(4)	C(6)-C(5)-Ru(1)	71.7(5)

Table 3.6 **cont.**

C(1)-C(6)-C(5)	121.4(9)	F(1)-P(1)-F(5)	179.6(6)
C(1)-C(6)-Ru(1)	72.1(5)	F(3)-P(1)-F(5)	89.3(5)
C(5)-C(6)-Ru(1)	70.9(5)	F(4)-P(1)-F(6)	178.2(5)
O(1)-C(10)-C(31)	112.0(5)	F(1)-P(1)-F(6)	91.2(6)
O(1)-C(10)-C(21)	107.1(5)	F(3)-P(1)-F(6)	90.3(6)
C(31)-C(10)-C(21)	114.2(6)	F(5)-P(1)-F(6)	89.2(6)
O(1)-C(10)-C(11)	105.2(5)	F(4)-P(1)-F(2)	91.1(5)
C(31)-C(10)-C(11)	112.7(5)	F(1)-P(1)-F(2)	89.5(5)
C(21)-C(10)-C(11)	104.9(5)	F(3)-P(1)-F(2)	177.4(6)
N(1)-C(11)-C(12)	120.8(6)	F(5)-P(1)-F(2)	90.6(4)
N(1)-C(11)-C(10)	110.1(6)	F(6)-P(1)-F(2)	87.1(5)
C(12)-C(11)-C(10)	129.1(6)	F(9B)-P(2)-F(7A)#2	90.3(3)
C(11)-C(12)-C(13)	119.5(7)	F(8A)-P(2)-F(7A)#2	92.8(10)
C(14)-C(13)-C(12)	118.8(8)	F(8A)#2-P(2)-F(7A)#2	86.8(10)
C(13)-C(14)-C(15)	120.2(8)	F(7B)-P(2)-F(7A)#2	88.2(9)
N(1)-C(15)-C(14)	121.2(7)	F(7B)#2-P(2)-F(7A)#2	91.7(9)
N(2)-C(21)-C(22)	121.1(7)	F(9B)-P(2)-F(7A)	90.3(3)
N(2)-C(21)-C(10)	109.9(6)	F(8A)-P(2)-F(7A)	86.8(10)
C(22)-C(21)-C(10)	129.0(7)	F(8A)#2-P(2)-F(7A)	92.8(10)
C(21)-C(22)-C(23)	118.9(8)	F(7B)-P(2)-F(7A)	91.7(9)
C(24)-C(23)-C(22)	119.7(8)	F(7B)#2-P(2)-F(7A)	88.2(9)
C(25)-C(24)-C(23)	118.5(8)	F(7A)#2-P(2)-F(7A)	179.4(6)
N(2)-C(25)-C(24)	122.8(8)	F(9B)-P(2)-F(8B)	180.000(7)
N(3)-C(31)-C(32)	121.8(6)	F(7A)#2-P(2)-F(8B)	89.7(3)
N(3)-C(31)-C(10)	115.3(6)	F(7A)-P(2)-F(8B)	89.7(3)
C(32)-C(31)-C(10)	122.9(6)	F(8A)#2-P(2)-F(9A)#2	87(2)
C(31)-C(32)-C(33)	120.8(8)	F(7A)#2-P(2)-F(9A)#2	88.2(7)
C(34)-C(33)-C(32)	117.8(8)	F(7A)-P(2)-F(9A)#2	92.3(7)
C(33)-C(34)-C(35)	120.1(8)	F(8A)-P(2)-F(9A)	87(2)
N(3)-C(35)-C(34)	122.0(8)	F(7A)#2-P(2)-F(9A)	92.3(7)
F(4)-P(1)-F(1)	88.4(5)	F(7A)-P(2)-F(9A)	88.2(7)
F(4)-P(1)-F(3)	91.4(6)	F(9A)#2-P(2)-F(9A)	85(2)
F(1)-P(1)-F(3)	90.6(5)	O(50)-C(50)-C(51)	120.8(8)
F(4)-P(1)-F(5)	91.2(6)	O(50)-C(50)-C(51)#2	120.8(8)
		C(51)-C(50)-C(51)#2	118(2)

Crystallographic characterisation of $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$ (19)

Table 3.7 **Crystal data and structure refinement for 19.**

Formula	$C_{23}H_{20}F_6N_3OPRu$	
Formula weight	600.50	
Temperature	100(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9787(16) Å b = 22.698(5) Å c = 12.580(3) Å	α= 90°. β= 94.980(2)°. γ = 90°.
Volume	2269.6(8) $Å^3$	
Z	4	
Density (calculated)	1.757 Mg/m^3	
Absorption coefficient	0.833 mm^{-1}	
F(000)	1200	
Crystal size	0.50 x 0.20 x 0.03 mm^3	
Theta range for data collection	3.05 to 27.50°.	
Index ranges	-10<=h<=9, -27<=k<=29, -16<=l<=16	
Reflections collected	16666	
Independent reflections	5203 [R(int) = 0.0763]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Scalepack	
Max. and min. transmission	0.9754 and 0.6808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5203 / 0 / 318	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0790	
R indices (all data)	R1 = 0.0651, wR2 = 0.0872	
Extinction coefficient	0.0024(3)	
Largest diff. peak and hole	0.602 and -0.882 $e.Å^{-3}$	

Table 3.8 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 19.**

	x	y	z	U(eq)
Ru(1)	4515(1)	6996(1)	4299(1)	15(1)
O(1)	3416(2)	6665(1)	2923(2)	15(1)
C(16)	3112(4)	4965(1)	750(3)	21(1)
C(4)	7103(4)	5820(1)	2385(2)	18(1)
C(6)	4048(3)	6093(1)	2840(2)	15(1)
N(1)	6510(3)	6575(1)	3618(2)	17(1)
C(8)	2991(4)	5203(1)	3957(3)	19(1)
N(3)	3755(3)	5235(1)	1648(2)	17(1)
C(12)	3325(4)	5803(1)	1805(2)	16(1)
N(2)	3908(3)	6125(1)	4715(2)	17(1)
C(11)	3590(4)	5928(1)	5684(3)	22(1)
C(3)	8802(4)	5942(1)	2552(3)	24(1)
C(13)	2271(4)	6120(1)	1085(3)	19(1)
C(5)	5979(4)	6144(1)	2919(2)	16(1)
C(10)	2930(4)	5375(1)	5831(3)	27(1)
C(15)	2046(4)	5258(1)	-10(3)	23(1)
C(7)	3617(3)	5764(1)	3854(2)	15(1)
C(1)	8169(4)	6695(1)	3767(3)	22(1)
C(14)	1639(4)	5841(1)	156(3)	23(1)
C(9)	2621(4)	5012(1)	4960(3)	25(1)
C(20)	4709(6)	7401(2)	5897(3)	38(1)
C(17)	3593(4)	4330(1)	629(3)	27(1)
C(23)	3910(5)	7904(1)	3891(3)	30(1)
C(21)	5964(5)	7628(2)	5332(3)	37(1)
C(22)	5559(5)	7883(1)	4327(3)	34(1)
C(18)	2616(4)	7666(1)	4460(3)	33(1)
C(19)	3015(5)	7415(2)	5455(3)	36(1)
C(2)	9344(4)	6391(1)	3240(3)	26(1)
P(1)	727(1)	3542(1)	2839(1)	26(1)
F(4)	810(2)	3282(1)	1655(2)	34(1)
F(5)	-1285(2)	3527(1)	2674(2)	42(1)
F(1)	718(3)	4192(1)	2370(2)	41(1)
F(2)	718(3)	2886(1)	3304(2)	53(1)
F(6)	2736(2)	3554(1)	2988(2)	51(1)
F(3)	631(3)	3797(1)	4011(2)	60(1)

Table 3.9 **Bond lengths [Å] and angles [°] for 19.**

Ru(1)-O(1)	2.016(2)	N(3)-C(12)	1.355(4)
Ru(1)-N(1)	2.102(2)	C(12)-C(13)	1.384(4)
Ru(1)-N(2)	2.114(2)	N(2)-C(11)	1.342(4)
Ru(1)-C(23)	2.167(3)	N(2)-C(7)	1.361(4)
Ru(1)-C(18)	2.168(3)	C(11)-C(10)	1.379(4)
Ru(1)-C(22)	2.178(3)	C(3)-C(2)	1.382(4)
Ru(1)-C(19)	2.180(3)	C(13)-C(14)	1.385(4)
Ru(1)-C(21)	2.196(3)	C(10)-C(9)	1.375(5)
Ru(1)-C(20)	2.203(4)	C(15)-C(14)	1.382(4)
O(1)-C(6)	1.400(3)	C(1)-C(2)	1.378(5)
C(16)-N(3)	1.346(4)	C(20)-C(21)	1.377(6)
C(16)-C(15)	1.394(4)	C(20)-C(19)	1.417(5)
C(16)-C(17)	1.502(4)	C(23)-C(22)	1.382(5)
C(4)-C(5)	1.379(4)	C(23)-C(18)	1.413(5)
C(4)-C(3)	1.381(4)	C(21)-C(22)	1.402(6)
C(6)-C(12)	1.526(4)	C(18)-C(19)	1.387(6)
C(6)-C(5)	1.540(4)	P(1)-F(1)	1.590(2)
C(6)-C(7)	1.542(4)	P(1)-F(3)	1.592(3)
N(1)-C(1)	1.348(4)	P(1)-F(6)	1.597(2)
N(1)-C(5)	1.358(4)	P(1)-F(2)	1.600(2)
C(8)-C(7)	1.379(4)	P(1)-F(5)	1.601(2)
C(8)-C(9)	1.389(4)	P(1)-F(4)	1.609(2)
O(1)-Ru(1)-N(1)	76.64(9)	C(7)-C(8)-C(9)	118.7(3)
O(1)-Ru(1)-N(2)	76.81(9)	C(16)-N(3)-C(12)	118.2(3)
N(1)-Ru(1)-N(2)	82.72(9)	N(3)-C(12)-C(13)	123.1(3)
O(1)-Ru(1)-C(23)	94.57(11)	N(3)-C(12)-C(6)	117.0(3)
N(1)-Ru(1)-C(23)	119.78(12)	C(13)-C(12)-C(6)	119.9(3)
N(2)-Ru(1)-C(23)	153.81(12)	C(11)-N(2)-C(7)	119.3(3)
O(1)-Ru(1)-C(18)	94.96(12)	C(11)-N(2)-Ru(1)	127.0(2)
N(1)-Ru(1)-C(18)	156.48(13)	C(7)-N(2)-Ru(1)	113.10(19)
N(2)-Ru(1)-C(18)	117.16(12)	N(2)-C(11)-C(10)	121.9(3)
O(1)-Ru(1)-C(22)	119.71(13)	C(4)-C(3)-C(2)	119.5(3)
N(1)-Ru(1)-C(22)	97.14(11)	C(12)-C(13)-C(14)	118.1(3)
N(2)-Ru(1)-C(22)	163.11(14)	N(1)-C(5)-C(4)	121.3(3)
O(1)-Ru(1)-C(19)	120.82(13)	N(1)-C(5)-C(6)	110.5(2)
N(1)-Ru(1)-C(19)	161.64(14)	C(4)-C(5)-C(6)	128.2(3)
N(2)-Ru(1)-C(19)	95.28(12)	C(9)-C(10)-C(11)	118.8(3)
O(1)-Ru(1)-C(21)	156.74(14)	C(14)-C(15)-C(16)	119.5(3)
N(1)-Ru(1)-C(21)	99.18(12)	N(2)-C(7)-C(8)	121.2(3)
N(2)-Ru(1)-C(21)	125.81(13)	N(2)-C(7)-C(6)	109.4(2)
O(1)-Ru(1)-C(20)	158.37(13)	C(8)-C(7)-C(6)	129.3(3)
N(1)-Ru(1)-C(20)	124.44(13)	N(1)-C(1)-C(2)	122.2(3)
N(2)-Ru(1)-C(20)	99.46(12)	C(15)-C(14)-C(13)	119.4(3)
C(6)-O(1)-Ru(1)	106.11(16)	C(10)-C(9)-C(8)	120.0(3)
N(3)-C(16)-C(15)	121.6(3)	C(21)-C(20)-C(19)	120.1(4)
N(3)-C(16)-C(17)	116.1(3)	C(21)-C(20)-Ru(1)	71.5(2)
C(15)-C(16)-C(17)	122.3(3)	C(19)-C(20)-Ru(1)	70.2(2)
C(5)-C(4)-C(3)	119.4(3)	C(22)-C(23)-C(18)	119.9(4)
O(1)-C(6)-C(12)	110.6(2)	C(22)-C(23)-Ru(1)	71.88(19)
O(1)-C(6)-C(5)	106.8(2)	C(18)-C(23)-Ru(1)	71.03(18)
C(12)-C(6)-C(5)	112.9(2)	C(20)-C(21)-C(22)	119.9(3)
O(1)-C(6)-C(7)	106.2(2)	C(20)-C(21)-Ru(1)	72.1(2)
C(12)-C(6)-C(7)	113.7(2)	C(22)-C(21)-Ru(1)	70.6(2)
C(5)-C(6)-C(7)	106.1(2)	C(23)-C(22)-C(21)	120.5(3)
C(1)-N(1)-C(5)	118.8(3)	C(23)-C(22)-Ru(1)	71.02(18)
C(1)-N(1)-Ru(1)	128.4(2)	C(21)-C(22)-Ru(1)	72.0(2)
C(5)-N(1)-Ru(1)	112.74(19)	C(19)-C(18)-C(23)	119.6(3)

Table 3.9 **cont.**

C(19)-C(18)-Ru(1)	71.86(19)	F(3)-P(1)-F(2)	89.91(15)
C(23)-C(18)-Ru(1)	70.93(18)	F(6)-P(1)-F(2)	90.57(13)
C(18)-C(19)-C(20)	119.9(3)	F(1)-P(1)-F(5)	89.95(12)
C(18)-C(19)-Ru(1)	70.9(2)	F(3)-P(1)-F(5)	89.99(13)
C(20)-C(19)-Ru(1)	72.1(2)	F(6)-P(1)-F(5)	179.22(15)
C(1)-C(2)-C(3)	118.7(3)	F(2)-P(1)-F(5)	89.52(13)
F(1)-P(1)-F(3)	90.43(14)	F(1)-P(1)-F(4)	89.70(12)
F(1)-P(1)-F(6)	89.96(12)	F(3)-P(1)-F(4)	179.57(14)
F(3)-P(1)-F(6)	90.79(14)	F(6)-P(1)-F(4)	89.62(13)
F(1)-P(1)-F(2)	179.36(14)	F(2)-P(1)-F(4)	89.95(13)
		F(5)-P(1)-F(4)	89.60(11)

Chapter 4

(η^6-arene)Ru(II) complexes of the derivatives of *tris*(2-pyridyl)methanol and its analogs

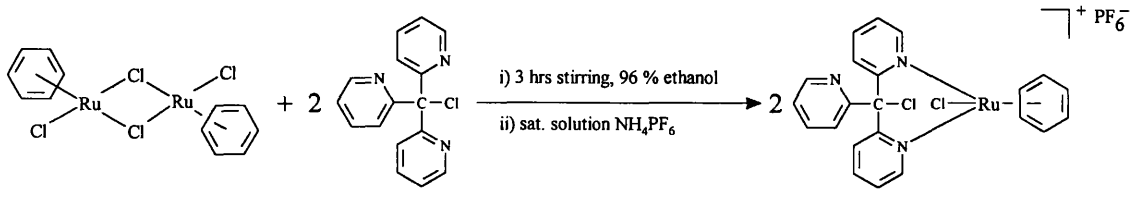
Introduction

A variety of (η^6-arene)Ru(II) complexes of the chloromethane, ethoxymethane and methane derivatives of *tris*(2-pyridyl)methanol and its closely related analogs were prepared. Mono or dicationic complexes were obtained depending upon the coordination mode adopted by the *tris*(2-pyridyl) ligand, this being a function of both the nature of the ligand and the choice of the preparative method.

4.1 Results and Discussion

4.1.1 (η^6-benzene)ruthenium(II) complexes of *tris*(2-pyridyl)chloromethanes

By analogy with the preparation of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$, **11**, described in sub-section 3.2.3, the preparation of $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3CCl\}]PF_6$, **22**, follows the general methods described in the literature.[8,9,105] Therefore, the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with two equivalents of *tris*(2-pyridyl)chloromethane, **2**, in ethanol, followed by work-up with NH_4PF_6 gave **22** as a pale yellow solid, Scheme 4.1. Microanalysis was



Scheme 4.1 The synthesis of $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3CCl\}]PF_6$

consistent with the monocationic formulation for **22**. Typical of all the (η^6-

benzene)ruthenium(II) complexes described in this thesis, the presence of a benzene ligand in **22** was reflected in the observation of a sharp singlet resonance (δ 6.21 ppm) in the ^{1}H NMR spectrum. In the infrared spectrum the ν(P-F) and ν(C-Cl) bands appear at 839 and 762 cm^{-1} respectively. Bidentate coordination of the *tris*(2-pyridyl) ligand through two pyridyl nitrogen atoms was jointly confirmed by the observation of two sets of pyridyl signals (integral ratio 2:1) in the ^{1}H NMR spectrum of **22**, as well as the presence of a ν(Ru-Cl) band at ~ 295 cm^{-1} in the infrared spectrum.

The methyl-substituted analog of **22**, $[(\eta^6\text{-}C_6H_6)RuCl\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CCl\}]PF_6$ **29**, was prepared analogously by reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with (6-methyl-2-pyridyl)*bis*(2-pyridyl)chloromethane, **7**. Microanalysis was consistent with the formulation **29**$\cdot 2H_2O$, and the monocation was observed in the mass spectrum at *m/z* 510. Unsurprisingly, given the observations presented in Chapter 3, the ^{1}H NMR spectrum of **29** indicated that the methyl-substituted pyridyl ring was not metallated. The ^{1}H NMR spectra of **22** and **29** are closely similar with regards to both the benzene and metallated pyridyl ring signals.

In an attempt to convert **22** (which possesses an N,N'-bound tripodal ligand) into its dicationic analog (which would exhibit N,N',N'' coordination), an ethanolic solution of **22** was treated with a stoichiometric amount of $AgPF_6$, with the intention of replacing the chloride ligand with the third pyridyl ring. Unfortunately, attempting to bring about this transformation led to the facile decomposition of **22**, probably owing to the non-selective nature of the

chloride removal. An alternative synthetic method involving the *in situ* reaction of $[(\eta^6\text{-}C_6H_6)Ru(EtOH)_3]^{2+}$ (formed by the treatment of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with four equivalents of $AgPF_6$ in ethanol) with **2** led to the formation of a mixture of products, including the desired one (as identified by ^1H NMR spectroscopy), which, unfortunately, could not be separated and purified.

4.1.2 (η^6-arene)ruthenium(II) complexes of *tris*(2-pyridyl)ethoxymethanes

The reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with two equivalents of *tris*(2-pyridyl)ethoxymethane, **3**, in ethanol gave, after work-up with NH_4PF_6, $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3COEt\}]PF_6$, **23**, as a dark yellow solid. Microanalysis indicated the composition to be of the monocationic type, the compound differing from **22** only in its bridgehead substituent. By analogy with **22** the bidentate N,N'-coordination mode adopted by the *tris*(2-pyridyl)ethoxymethane ligand was confirmed by the presence of a ν(Ru-Cl) band at ~ 290 cm^{-1} in the infrared spectrum and the observation of two sets of pyridyl signals (integral ratio 2:1) in the ^1H NMR spectrum (Figure 4.1). The ethoxy substituent of **23**

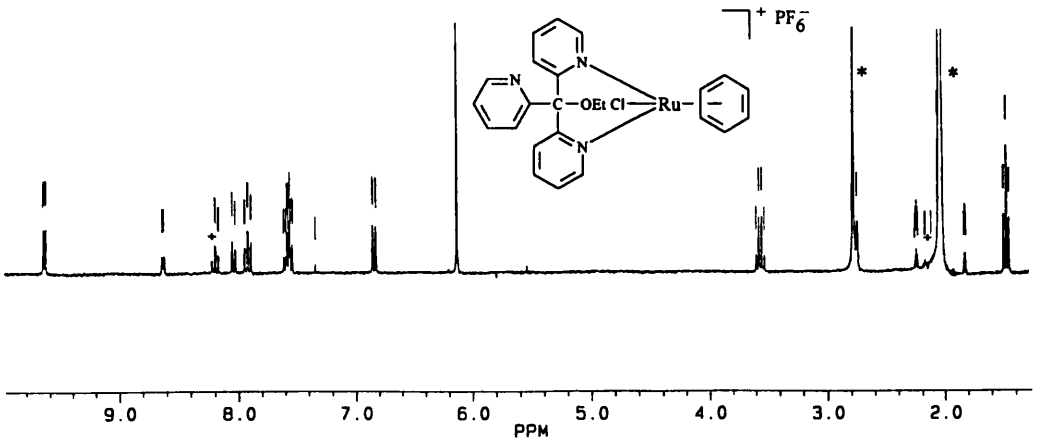


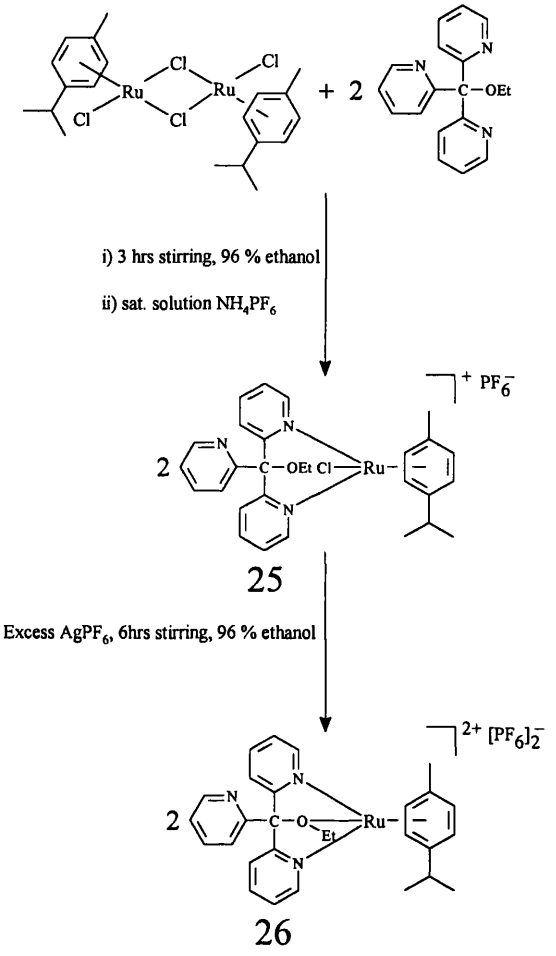
Figure 4.1 ^1H NMR spectrum of $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3COEt\}]PF_6$ (* signals due to water and acetone)

appears as a triplet and quartet at δ 1.48 and 3.56 ppm respectively.

In contrast to the reaction of **22**, treatment of an ethanolic solution of **23** with $AgPF_6$ and subsequent work-up gave exclusively the dicationic analog $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$, **24**, which was confirmed by microanalytical data. A ν(Ru-Cl) band was not observed in the infrared spectrum of **24** and two sets of pyridyl signals, with integral ratio 2:1, were observed in the ^1H NMR spectrum. These observations are consistent with the tripodal ligand adopting the N,N',O-coordination mode, through two pyridyl nitrogens and the ethoxy oxygen atom. In comparing the ^1H NMR spectrum of **24** with that of **23**, it is clear that the ethoxy quartet signal in **23** has dramatically shifted to lower field in **24** (δ 3.56 *vs* 4.42 ppm), whilst the ethoxy triplet signal has shifted to higher field (δ 1.48 *vs* 1.15 ppm) to a lesser extent. The former observation may be attributed to the $-CH_2-$ protons being deshielded upon metallation of the adjacent oxygen atom, whereas the latter may be attributed to the CH_3-protons adopting a position within the molecule that subjects them to greater shielding.

Compound **25**, $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl\{(C_5H_4N)_3COEt\}]PF_6$, was prepared analogously to **23** by reaction of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ with **3**, and compound **26**, $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$, was prepared analogously to **24** by reaction of **25** with $AgPF_6$, Scheme 4.2. In comparing the ^1H NMR spectra of the *para*-cymene complexes (**25** and **26**) with those of their benzene analogs (**23** and **24** respectively) it is found that generally the spectra are very similar, implying that the *tris*(2-pyridyl)ethoxymethane ligands are in a similar

environment in both compounds. Of course, each compound also exhibits its own characteristic set of signals for the π-bound arene.



Scheme 4.2 The synthesis of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl\{(C_5H_4N)_3COEt\}]PF_6$, **25**, and $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$, **26**

The methyl-substituted analog of **23**, $[(\eta^6\text{-}C_6H_6)RuCl\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2COEt\}]PF_6$ **30**, was prepared by reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with (6-methyl-2-pyridyl)*bis*(2-pyridyl)ethoxymethane, **8**, using the general method described above. Microanalytical results were consistent with the formulation $\mathbf{30}\cdot 2H_2O$. In view of the close similarity between the ^1H NMR spectra of compounds **22** and **29** (the chloromethane analogs of **23** and

30 respectively), it is not surprising that the ^{1}H NMR spectra of **23** and **30** are also closely similar to one another, except of course when considering the non-metallated pyridyl ring, which in **30** bears a methyl group in the '6' position.

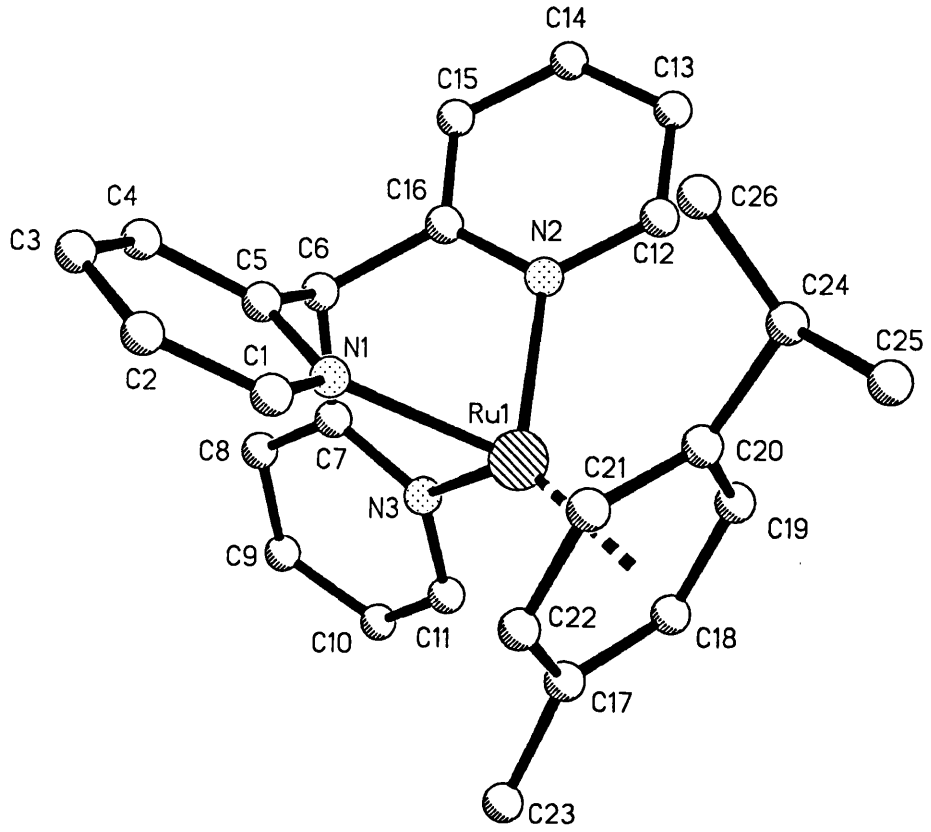
At this point it is appropriate to discuss the different ligation properties of *tris*(2-pyridyl)methanols and *tris*(2-pyridyl)ethoxymethanes in their (η^6-arene)ruthenium(II) complexes. In Chapter 3 all preparations involving the reaction of a given *tris*(2-pyridyl)methanol with an arene-containing ruthenium dimer led to the formation of products containing an N,N',O-bound tripodal ligand, regardless of whether or not alcoholic deprotonation had occurred. In this chapter analogous reactions involving *tris*(2-pyridyl)ethoxymethanes led to the formation of compounds **23**, **25** and **30**, in each of which the tripodal ligand had adopted the N,N'-bidentate mode of coordination. Compounds **23** and **25** could be converted into their dicationic analogs, **24** and **26** respectively, by treatment with $AgPF_6$. Indeed, it was only under such 'forcing' conditions that the *tris*(2-pyridyl)ethoxymethane ligand would adopt the N,N',O-coordination mode. The reluctance of *tris*(2-pyridyl)ethoxymethanes to readily adopt the N,N',O-coordination mode may tentatively be associated with the ethyl group effectively hindering the oxygen atoms approach to the coordination site occupied by the chloride ligand. However, removal of the chloride ligand, as AgCl, followed by its replacement with a more labile ethanol molecule (from the solvent) increasingly favours the occupation of this site by the ethoxy oxygen atom which binds irreversibly.

4.1.3 (η^6-*para*-cymene)ruthenium(II) complexes of *tris*(2-pyridyl)methanes

The reaction of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ with two equivalents of *tris*(2-pyridyl)methane, **4**, in ethanol, followed by work-up with NH_4PF_6 gave $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl\{(C_5H_4N)_3CH\}]PF_6$, **27**, as a yellow solid. Microanalysis confirmed the monocationic formulation, and the mass spectrum exhibited an envelope of peaks at *m/z* 518 due to the cation. By analogy with the previously described compounds in this chapter, two sets of pyridyl signals, with integral ratio 2:1, were observed in the ^1H NMR spectrum of **27**. In addition, the methane proton singlet resonance was observed (δ 6.04 ppm), as were resonances due to the π-bound arene. Bidentate coordination of the *tris*(2-pyridyl)methane ligand in **27** was confirmed by the appearance of a ν(Ru-Cl) band at ~ 305 cm^{-1} in the infrared spectrum.

The *in situ* reaction of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru(EtOH)_3]^{2+}$ (formed by the treatment of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ with a large excess of $AgPF_6$ in ethanol) with **4** gave, after work-up, the dicationic analog of **27**, namely $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CH\}][PF_6]_2$ **28**. An alternative route to **28** involved the treatment of an acetone solution of **27** with $AgPF_6$, however yields were poorer using this method. The FAB mass spectrum of **28** contains fragments at *m/z* 628 and 483, corresponding to the parent compound having lost one and two hexafluorophosphate counteranions respectively. The observation of only one set of pyridyl signals in the ^1H NMR spectrum of **28**, coupled with the absence of a ν(Ru-Cl) band in the infrared spectrum, suggested tridentate N,N',N''-coordination of the *tris*(2-pyridyl)methane ligand in **28**. The crystal structure of

the cation in **28** is shown in Figure 4.2. Coordination of the *tris*(2-pyridyl)methane ligand *via* the three pyridyl nitrogen



Ru(1)-N(3)	2.129(2)	N(3)-Ru(1)-N(2)	80.77(8)
Ru(1)-N(2)	2.137(2)	N(3)-Ru(1)-N(1)	86.20(9)
Ru(1)-N(1)	2.155(2)	N(2)-Ru(1)-N(1)	85.40(9)

Figure 4.2 Structure of the cation in $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CH\}][PF_6]_2$ (**28**) with selected bond lengths (Å) and bond angles (°)

atoms to the Ru(II) ion is confirmed, with the cation exhibiting a 'piano-stool' geometry. The *iso*propyl substituent of the *para*-cymene ring straddles the aromatic plane, with the pyridyl ring containing N(2) having the closest approach to the arene. It is therefore surprising to find that, of the three Ru-N bonds, the Ru(1)-N(1) bond is the longest, 2.155(2) Å, and not that to N(2), 2.137(2) Å. As a consequence of these dissimilar bond lengths, the N(3)-Ru(1)-N(2) angle, 80.77(8) °, is significantly smaller than the other two, av.

85.80(9) °. In **28** the average Ru-N bond length (2.140(2) Å) is noticeably longer than that observed in $[Ru\{(C_5H_4N)_3CH\}_2]^{2+}$ (2.066(3) Å) (Figure 1.6, **A**),[28] while at the same time the average N-Ru-N bond angle in **28** is smaller, 84.12(9) *vs* 87.4(1) °. These structural differences may be due to the differing electronic and steric properties associated with the 'spectator ligands', $MeC_6H_4{}^iPr$ and $(C_5H_4N)_3CH$.

Compound **31**, $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)CH\}][PF_6]_2$, was prepared analogously to **28** *via* the *in situ* reaction of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru(EtOH)_3]^{2+}$ with (3-methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methane, **10**. The dicationic formulation for **31** was confirmed *via* elemental analysis. The ^1H NMR spectrum of **31** is shown in Figure 4.3.

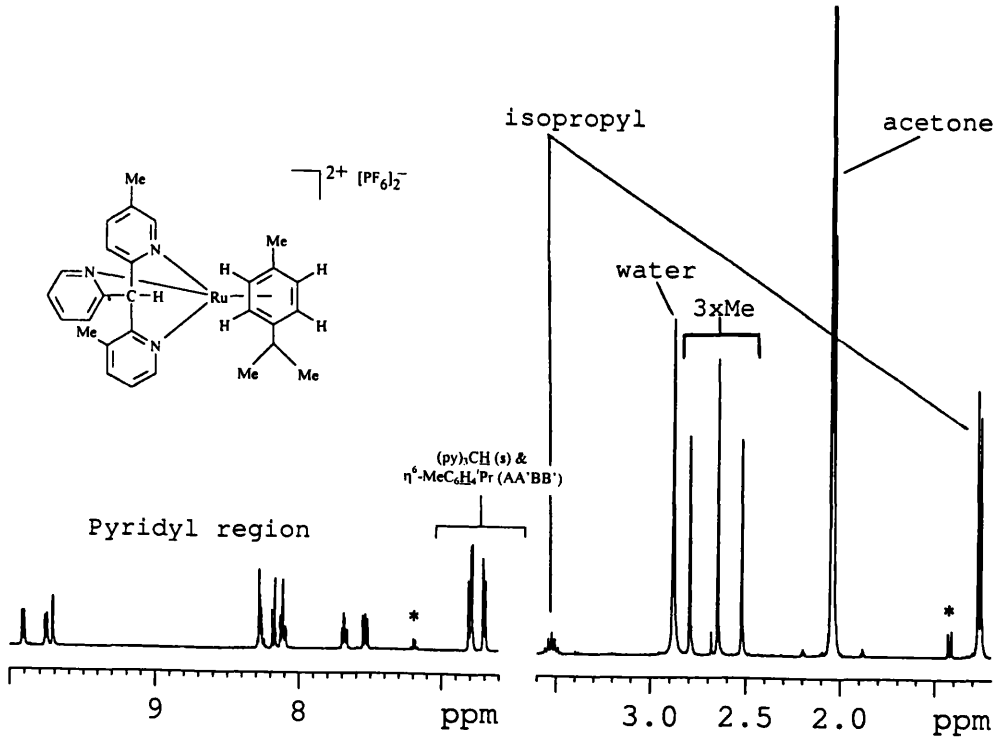


Figure 4.3 ^1H NMR spectrum of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)CH\}][PF_6]_2$ **(31)** (* signals due to impurities)

Tridentate N,N',N''-coordination of the tripodal ligand to the Ru(II) ion was implied by the observation in the ^{1}H NMR spectrum of a unique set of *tris*(pyridyl)methane signals. This clearly contrasts with the three isomeric forms of the related compound **21**, $[(\eta^6\text{-}C_6H_6)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)COH\}][PF_6]_2$ (containing the N,N',O-bound *tris*(pyridyl)methanol analog of **10**), observed by ^{1}H NMR spectroscopy (sub-section 3.2.3). Indeed, an equally complex ^{1}H NMR spectrum would have been observed for **31**, had bidentate coordination of ligand **10** occured. Furthermore, as no ν(Ru-Cl) band was observed in the infrared spectrum of **31** it can firmly be concluded that **10** has complexed *via* all three pyridyl nitrogen atoms.

As discussed previously for *tris*(2-pyridyl)ethoxymethanes, it is only with the use of $AgPF_6$ that *tris*(2-pyridyl)methane ligands adopt the tridentate coordination mode. However, in contrast to *tris*(2-pyridyl)ethoxymethanes, the *tris*(2-pyridyl)methane ligands do not possess a bridgehead substituent capable of metallation, but instead coordinate to the metal through the third pyridyl nitrogen atom.

The preference for the N,N',O-coordination mode, over the N,N',N'' one, in the complexes of *tris*(2-pyridyl)ethoxymethane (**24** and **26**) is unlikely to be due to steric effects, since the latter coordination mode is adopted by *tris*(2-pyridyl)methanes in complexes **28** and **31**. Instead, by analogy with the conclusions drawn from studies on *bis*(*tris*(2-pyridyl)methanol)Ru(II) complexes conducted by Keene and co-workers,[75] it is likely that on the

synthetic pathway kinetic effects play a crucial role in determining the coordination mode adopted by the tripodal ligand in the isolated complexes.

4.1.4 Summary

In this chapter all syntheses involving the reaction of a *tris*(2-pyridyl) compound with $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = benzene, *para*-cymene) led to the formation of a monocationic product, in which the tripodal ligand adopted a bidentate N,N'-coordination mode. Displacement of the second chloride ligand from the metal had not occurred (as detected by infrared spectroscopy), possibly due to steric effects. Dicationic complexes were prepared by using $AgPF_6$, either to generate *tris* solvento species *in situ*, which were then reacted with the *tris*(2-pyridyl) compounds, or to remove a chloride ligand from monocationic complexes. Dicationic complexes of *tris*(2-pyridyl)ethoxymethane were found to possess a tripodal ligand coordinated in an N,N',O-fashion possibly due to kinetic effects, while dicationic complexes of *tris*(2-pyridyl)methanes were found to incorporate an N,N',N''-bound tripodal ligand. Unfortunately, attempts to isolate the pure dicationic analog of **22** were unsuccessful.

4.2 Experimental

4.2.1 Instrumentation

As described in sub-section 3.2.1.

4.2.2 Materials

As described in sub-section 3.2.2. In addition, reactions involving silver hexafluorophosphate were carried out in the dark. Work-up of these reaction

mixtures, as well as all the other preparations, did not require special conditions. Compounds **2**, **3**, **4**, **7**, **8** and **10** were prepared as described in sub-section 2.2.3.

4.2.3 Preparations

[(η^6-C_6H_6)RuCl{(C_5H_4N)$_3$CCl}]PF_6, 22

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.082 g, 0.16 mmol) was added to a solution of **2** (0.092 g, 0.33 mmol) in 96 % ethanol (15 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite to remove any insoluble material. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate caused **22** to precipitate out as a pale yellow solid. Yield: 0.11 g, 53 % (Found: C, 40.86; H, 2.63; N, 6.45. Calc. for $C_{22}H_{18}N_3Cl_2RuPF_6$: C, 41.20; H, 2.83; N, 6.55 %). MS (FAB): *m/z* 496 [M–PF_6], 461 [M–Cl–PF_6], 418 [M–py–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 6.21 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 6.80 ({d,d,d}, $J_{3,4}$=8.24, $J_{3,5}$=1.50, $J_{3,6}$=0.95 Hz, 2H, py-3-H); δ 7.59 ({d,d,d}, $J_{3,5}$=1.50, $J_{4,5}$=7.54, $J_{5,6}$=5.83 Hz, 2H, py-5-H); δ 7.97 ({d,d,d}, $J_{3,4}$=8.24, $J_{4,5}$=7.54, $J_{4,6}$=1.63 Hz, 2H, py-4-H); δ 9.60 ({d,d,d}, $J_{3,6}$=0.95, $J_{4,6}$=1.63, $J_{5,6}$=5.83 Hz, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.62 ({d,d,d}, $J_{3,5}$=0.92, $J_{4,5}$=7.78, $J_{5,6}$=4.52 Hz, 1H, py-5-H); δ 8.28, 8.48, approx. 8.65 (br, 3H, py-3,4,6-H). IR (KBr): ν(C⎓C) 1589, 1458 (m); ν(P-F) 839 (s, br); ν(C-Cl) 762 (m) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 295 (w, br) cm^{-1}.

[(η^6-C_6H_6)RuCl{(C_5H_4N)$_3$COEt}]PF_6, 23

[(η^6-C_6H_6)$RuCl_2$]$_2$ (0.16 g, 0.32 mmol) was added to a solution of **3** (0.19 g,

0.65 mmol) in 96 % ethanol (70 cm^3). After stirring for 4 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate caused **23** to precipitate out as a dark yellow solid. Yield: 0.30 g, 71 % (Found: C, 44.25; H, 3.37; N, 6.32. Calc. for $C_{24}H_{23}N_3OClRuPF_6$: C, 44.28; H, 3.57; N, 6.46 %). MS (FAB): *m/z* 506 [M–PF_6], 471 [M–Cl–PF_6], 428 [M–py–PF_6]. ^1H NMR (d^6-acetone, 300 MHz): δ 6.14 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 6.84 ({d,d}, 2H, py-3-H); δ 7.57 (m, 2H, py-5-H); δ 7.92 ({d,d,d}, 2H, py-4-H); δ 9.64 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.57 (m, 1H, py-5-H, overlapping other signals); δ 8.04 ({d,d}, 1H, py-3-H); δ 8.19 ({d,d,d}, 1H, py-4-H); δ 8.63 ({d,d}, 1H, py-6-H); δ 1.48 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.56 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν($C\text{-}H_{aromatic}$) 3058 (w); ν($C\text{-}H_{alkyl}$) 2903 (w); ν(C=C) 1592, 1463 (m); ν(P-F) 836 (s, br) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 290 (w, br) cm^{-1}.

[(η^6-C_6H_6)Ru{(C_5H_4N)$_3$COEt}][PF_6]$_2$, 24

$AgPF_6$ (0.31 g, 1.2 mmol) was added to a solution of **23** (0.25 g, 0.38 mmol) in 96 % ethanol (150 cm^3). After stirring for 6 hours at room temperature the mixture was filtered through celite to remove AgCl. The celite was washed with acetone (2 x 20 cm^3) and the washings were combined with the filtrate. The volume of solvent was reduced *in vacuo* until **24** precipitated out as a yellow solid. Yield: 0.26 g, 89 % (Found: C, 37.42; H, 2.71; N, 5.36. Calc. for $C_{24}H_{23}N_3ORuP_2F_{12}$: C, 37.90; H, 3.05; N, 5.53 %). MS (FAB): *m/z* 616 [M–PF_6], 471 [M–2PF_6], 442 [M–Et–2PF_6], 426 [M–OEt–2PF_6]. ^1H NMR (d^6-acetone, 300 MHz): δ 6.88 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.77 ({d,d,d}, 2H, py-5-H); δ 8.22 ({d,d,d}, 2H, py-4-H); δ 8.27 (m, 2H, py-3-H); δ

10.04 ({d,d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.82 ({d,d,d}, 1H, py-5-H); δ 7.89 ({d,d,d}, 1H, py-3-H); δ 8.27 (m, 1H, py-4-H, overlapping other signals); δ 8.96 ({d,d,d}, 1H, py-6-H); δ 1.15 (t, 3H, $C\underline{H}_3CH_2O$); δ 4.42 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{alkyl}) 2941 (w); ν(C⁻⁻C) 1605, 1460 (m); ν(P-F) 837 (s, br) cm^{-1}.

[(η^6-$MeC_6H_4{}^iPr$)RuCl{$(C_5H_4N)_3COEt$}]PF_6, 25

Compound **3** (0.068 g, 0.23 mmol) was added to a solution of [(η^6-$MeC_6H_4{}^iPr$)$RuCl_2$]$_2$ (0.071 g, 0.12 mmol) in 96 % ethanol (40 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate, followed by removal of *ca.* 70 % of the solvent *in vacuo* led to precipitation of **25** as a dark yellow solid. Yield: 0.11 g, 67 % (Found: C, 47.12; H, 4.57; N, 5.98. Calc. for $C_{28}H_{31}N_3OClRuPF_6$: C, 47.56; H, 4.43; N, 5.94 %). MS (FAB): *m/z* 562 [M–PF_6], 526 [M–Cl–H–PF_6], 428 [M–Ar–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 1.30 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 1.95 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.03 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 5.77 & 6.10 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 6.85 ({d,d,d}, 2H, py-3-H); δ 7.64 ({d,d,d}, 2H, py-5-H); δ 7.93 ({d,d,d}, 2H, py-4-H); δ 9.47 ({d,d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.58 ({d,d,d}, 1H, py-5-H); δ 8.07 ({d,d,d}, 1H, py-3-H); δ 8.19 ({d,d,d}, 1H, py-4-H); δ 8.57 ({d,d,d}, 1H, py-6-H); δ 1.53 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.59 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{alkyl}) 2933 (w); ν(C⁻⁻C) 1590, 1464 (m); ν(P-F) 848 (s, br) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 300 (w) cm^{-1}.

[(η^6-MeC$_6$H$_4$^{i}Pr)Ru{(C$_5$H$_4$N)$_3$COEt}][PF$_6$]$_2$, 26

$AgPF_6$ (0.086 g, 0.34 mmol) was added to a solution of **25** (0.049 g, 0.069 mmol) in 96 % ethanol (35 cm^3). After stirring for 6 hours at room temperature the mixture was filtered through celite . The celite was washed with acetone (2 x 20 cm^3) and the washings were combined with the filtrate. *Ca.* 70 % of the solvent was removed *in vacuo* then diethyl ether (5 cm^3) added to the solution. **26** precipitated as a dark orange solid. Yield: 0.055 g, 97 % (Found: C, 40.80; H, 3.73; N, 4.87. Calc. for $C_{28}H_{31}N_3ORuP_2F_{12}$: C, 41.18; H, 3.83; N, 5.15 %). MS (FAB): *m/z* 671 [M–H–PF_6], 527 [M–2PF_6], 498 [M–Et–2PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 1.38 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.70 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.55 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 6.54 & 6.71 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 7.82 (m, 2H, py-5-H); δ 8.21 ({d,d,d}, 2H, py-4-H); δ 8.27 (m, 2H, py-3-H); δ 9.88 ({d,d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.82 (m, 1H, py-5-H, overlapping other signals); δ 7.96 ({d,d,d}, 1H, py-3-H); δ 8.27 (m, 1H, py-4-H, overlapping other signals); δ 8.96 ({d,d,d}, 1H, py-6-H); δ 1.04 (t, 3H, $C\underline{H}_3CH_2O$); δ 4.41 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{alkyl}) 2932 (w); ν(C=C) 1607, 1462 (m); ν(P-F) 839 (s, br) cm^{-1}.

[(η^6-MeC$_6$H$_4$^{i}Pr)RuCl{(C$_5$H$_4$N)$_3$CH}]PF$_6$, 27

Compound **4** (0.044 g, 0.18 mmol) was added to a solution of [(η^6-$MeC_6H_4{}^iPr)RuCl_2]_2$ (0.053 g, 0.087 mmol) in 96 % ethanol (35 cm^3). After stirring for 16 hours at room temperature the mixture was filtered through celite. Addition of a saturated ethanolic solution of NH_4PF_6 to the filtrate, followed by removal of *ca.* 50 % of the solvent led to precipitation of **27** as a

yellow solid. Yield: 0.034 g, 29 % (Found: C, 46.67; H, 3.97; N, 6.34. Calc. for $C_{26}H_{27}N_3ClRuPF_6$: C, 47.09; H, 4.11; N, 6.34 %). MS (FAB): 518 [M–PF_6], 483 [M–Cl–PF_6], 384 [M–Ar–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 1.30 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.24 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.04 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 6.11 & 6.21 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$). Metallated pyridyl rings; δ 7.52 ({d,d,d}, 2H, py-5-H); δ 7.70 ({d,d,d}, 2H, py-3-H); δ 7.95 ({d,d,d}, 2H, py-4-H); δ 9.22 ({d,d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.65 ({d,d,d}, 1H, py-5-H); δ 7.90 ({d,d,d}, 1H, py-3-H); δ 8.09 ({d,d,d}, 1H, py-4-H); δ 8.99 ({d,d,d}, 1H, py-6-H); δ 6.04 (s, 1H, CH). IR (KBr): ν(C-$H_{aromatic}$) 3036 (w); ν(C-H_{alkyl}) 2948 (w); ν(C=C) 1604, 1468 (m); ν(P-F) 846 (s, br) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 305 (w, br) cm^{-1}.

[(η^6-$MeC_6H_4{}^iPr$)Ru{$(C_5H_4N)_3CH$}][PF_6]$_2$, 28

$AgPF_6$ (0.27 g, 1.1 mmol) was added to a solution of [(η^6-$MeC_6H_4{}^iPr$)$RuCl_2$]$_2$ (0.098 g, 0.16 mmol) in 96 % ethanol (40 cm^3). After stirring for 16 hours at room temperature the mixture was filtered through celite to remove AgCl and compound **4** (0.083 g, 0.34 mmol) added to the filtrate. The mixture was stirred for 5 hours then filtered through celite. The volume of the filtrate was reduced to approx. half at which point precipitation of **28** occurred, as a yellow solid. Yield: 0.093 g, 36 % (Found: C, 40.89; H, 3.41; N, 5.37. Calc. for $C_{26}H_{27}N_3RuP_2F_{12}$: C, 40.42; H, 3.53; N, 5.44 %). MS (FAB): *m/z* 628 [M–PF_6], 483 [M–2PF_6], 405 [M–py–2PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz): δ 1.28 (d, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.68 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.56 (sept, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 6.71 & 6.81 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$); δ 7.69 ({d,d,d}, 3H, py-5-H); δ 8.21 ({d,d}, 3H, py-3-H); δ 8.29 ({d,d,d}, 3H, py-4-

H); δ 9.92 ({d,d}, 3H, py-6-H); δ 6.72 (s, 1H, CH, overlapping other signals). IR (KBr): ν(C-H_{alkyl}) 2928 (w); ν(C=C) 1609, 1477 (m); ν(P-F) 839 (s, br) cm^{-1}.

[(η⁶-C₆H₆)RuCl{(6-MeC₅H₃N)(C₅H₄N)₂CCl}]PF₆, 29

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.066 g, 0.13 mmol) was added to a solution of **7** (0.080 g, 0.27 mmol)† in absolute ethanol (30 cm^3). After stirring for 3 hours at room temperature the mixture was filtered through celite and a saturated ethanolic solution of NH_4PF_6 was added to the filtrate. *Ca.* 70 % of the solvent was removed and then the solution stored at 0 °C for 16 hours. Precipitation of **29**•$2H_2O$ occurred as a yellow solid. Yield: 0.015 g, 8 %† (Found: C, 40.38; H, 3.11; N, 6.34. Calc. for $C_{23}H_{20}N_3Cl_2RuPF_6 \bullet 2H_2O$: C, 39.95; H, 3.51; N, 6.08 %). MS (FAB): *m/z* 510 [M–PF_6], 475 [M–Cl–PF_6], 432 [M–py–PF_6]. ^{1}H NMR (d^6-acetone, 400 MHz): δ 6.21 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 6.82 ({d,d}, 2H, py-3-H); δ 7.58 ({d,d,d}, 2H, py-5-H); δ 7.96 ({d,d,d}, 2H, py-4-H); δ 9.61 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.48 (d, 1H, 6-Mepy-5-H); δ 8.14, 8.45 (br, 2H, 6-Mepy-3,4-H); δ 2.22 (s, 3H, CH_3). IR (KBr): ν(C=C) 1598, 1459 (m); ν(P-F) 844 (s, br); ν(C-Cl) 761 (m) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 300 (w, br) cm^{-1}.

[(η⁶-C₆H₆)RuCl{(6-MeC₅H₃N)(C₅H₄N)₂COEt}]PF₆, 30

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.081 g, 0.16 mmol) was added to a solution of **8** (0.10 g, 0.33 mmol)† in absolute ethanol (30 cm^3). After stirring for 5 hours at room temperature the mixture was filtered through celite and a saturated ethanolic solution of NH_4PF_6 was added to the filtrate. *Ca.* 70 % of the solvent was removed at which point precipitation of **30**•$2H_2O$ occurred as an orange solid.

Yield: 0.015 g, 7 %† (Found: C, 42.74; H, 3.63; N, 6.13. Calc. for $C_{25}H_{25}N_3OClRuPF_6 \cdot 2H_2O$: C, 42.83; H, 4.18; N, 6.00 %). MS (FAB): *m/z* 520 [M–PF_6], 485 [M–Cl–PF_6], 442 [M–py–PF_6]. ^{1}H NMR (d^6-acetone, 400 MHz): δ 6.13 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 6.88 ({d,d}, $J_{3,4}$=8.15, $J_{3,5}$=1.13 Hz, 2H, py-3-H); δ 7.56 ({d,d,d}, $J_{3,5}$=1.13, $J_{4,5}$=7.43, $J_{5,6}$=5.90 Hz, 2H, py-5-H); δ 7.91 ({d,d,d}, $J_{3,4}$=8.15, $J_{4,5}$=7.43, $J_{4,6}$=1.66 Hz, 2H, py-4-H); δ 9.64 ({d,d}, $J_{4,6}$=1.66, $J_{5,6}$=5.90 Hz, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.45 (d, $J_{4,5}$=7.79 Hz, 1H, 6-Mepy-5-H); δ 7.82 (d, $J_{3,4}$=7.75 Hz, 1H, 6-Mepy-3-H); δ 8.06 ({d,d}, $J_{3,4}$=7.75, $J_{4,5}$=7.79 Hz, 1H, 6-Mepy-4-H); δ 1.46 (t, J=7.01 Hz, 3H, $C\underline{H}_3CH_2O$); δ 3.52 (q, J=7.01 Hz, 2H, $CH_3C\underline{H}_2O$); δ 2.34 (s, 3H, CH_3). IR (KBr): ν(C-H_{alkyl}) 2931 (w); ν(C=C) 1597, 1458 (m); ν(P-F) 842 (s, br) cm^{-1}. (Nujol): ν(Ru-Cl) *ca.* 300 (w) cm^{-1}.

[(η^6-MeC$_6$H$_4$^{i}Pr)Ru{(3-MeC$_5$H$_3$N)(5-MeC$_5$H$_3$N)(C$_5$H$_4$N)CH}][PF$_6$]$_2$, 31

$AgPF_6$ (0.43 g, 1.7 mmol) was added to a solution of $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ (0.20 g, 0.33 mmol) in 96 % ethanol (40 cm^3). After stirring for 16 hours at room temperature the mixture was filtered through celite and compound **10** (0.16 g, 0.58 mmol)† added to the filtrate. The mixture was stirred for 6 hours then filtered through celite. *Ca.* 50 % of the solvent was removed before the solution was stored at 0 °C for 16 hours. Precipitation of **31** occurred as a yellow solid. Yield: 0.13 g, 28 %† (Found: C, 41.68; H, 3.76; N, 5.08. Calc. for $C_{28}H_{31}N_3RuP_2F_{12}$: C, 42.00; H, 3.91; N, 5.25 %). MS (APCI): *m/z* 522

† **NB** Satisfactory microanalytical data could not be obtained for the precursor compounds **7**, **8** and **10** (sub-section 2.2.3), and therefore molar and yield calculations related to the use of these compounds (i.e. the preparations of compounds **29**, **30** and **31** respectively) are not necessarily accurate.

[M–Ar–PF_6], 510 [M–H–$2PF_6$]. ^{1}H NMR (d^6-acetone, 400 MHz): δ 1.26 (d, J=6.76 Hz, 6H, $(CH_3)C_6H_4CH(C\underline{H}_3)_2$); δ 2.65 (s, 3H, $(C\underline{H}_3)C_6H_4CH(CH_3)_2$); δ 3.52 (sept, J=6.76 Hz, 1H, $(CH_3)C_6H_4C\underline{H}(CH_3)_2$); δ 6.70 & 6.80 (AA'BB', J_{AB}=6.55 Hz, 4H, $(CH_3)C_6\underline{H}_4CH(CH_3)_2$); δ 7.68 ({d,d,d}, $J_{3,5}$=2.98, $J_{4,5}$=6.02, $J_{5,6}$=6.02 Hz, 1H, py-5-H); δ 8.27 (m, 2H, py-3,4-H); δ 9.91 (d, $J_{5,6}$=6.02 Hz, 1H, py-6-H); δ 7.54 ({d,d}, $J_{4,5}$=7.62, $J_{5,6}$=6.02 Hz, 1H, 3-Mepy-5-H); δ 8.11 (m, 2H, 3-Mepy-4-H and 5-Mepy-4-H); δ 9.76 (d, $J_{5,6}$=6.02 Hz, 1H, 3-Mepy-6-H); δ 8.18 (d, $J_{3,4}$=7.92 Hz, 1H, 5-Mepy-3-H); δ 9.71 (s, 1H, 5-Mepy-6-H); δ 6.79 (s, 1H, CH); δ 2.52 (s, 3H, 5-Mepy-CH_3); δ 2.79 (s, 3H, 3-Mepy-CH_3). IR (KBr): ν(C-H_{alkyl}) 2934 (w); ν(C⋯C) 1611, 1458 (m); ν(P-F) 837 (s, br) cm^{-1}.

Crystallographic characterisation of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CH\}][PF_6]_2$ (28)

Table 4.1 **Crystal data and structure refinement for 28.**

Formula	$C_{26}H_{27}F_{12}N_3P_2Ru$	
Formula weight	772.57	
Temperature	100(2) K	
Wavelength	0.71070 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3403(4) Å	α= 109.31°.
	b = 11.4237(5) Å	β= 93.127(2)°.
	c = 13.7441(6) Å	γ = 118.10°.
Volume	1434.19(10) $Å^3$	
Z	2	
Density (calculated)	1.752 Mg/m^3	
Absorption coefficient	0.744 mm^{-1}	
F(000)	762	
Crystal size	0.40 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.56 to 26.00°.	
Index ranges	-13<=h<=13, -13<=k<=14, -16<=l<=16	
Reflections collected	8917	
Independent reflections	5247 [R(int) = 0.0293]	
Completeness to theta = 26.00°	93.2 %	
Absorption correction	Scalepack	
Max. and min. transmission	0.8655 and 0.7551	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5247 / 0 / 398	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0849	
R indices (all data)	R1 = 0.0370, wR2 = 0.0870	
Extinction coefficient	0.0127(12)	
Largest diff. peak and hole	1.040 and -0.745 $e.Å^{-3}$	

Table 4.2 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 28.**

	x	y	z	U(eq)
Ru(1)	3730(1)	12876(1)	-2679(1)	15(1)
P(1)	-98(1)	5721(1)	-1954(1)	23(1)
P(2)	4180(1)	11183(1)	-7358(1)	25(1)
F(1)	77(3)	5778(3)	-3071(2)	75(1)
F(2)	-1450(2)	4144(2)	-2541(2)	43(1)
F(3)	874(3)	5084(3)	-1974(2)	62(1)
F(4)	-1056(2)	6402(3)	-1889(3)	72(1)
F(5)	1227(2)	7322(2)	-1367(2)	46(1)
F(6)	-274(3)	5663(3)	-832(2)	59(1)
F(7)	4485(2)	9980(2)	-7296(2)	36(1)
F(8)	2783(2)	10432(2)	-6992(1)	30(1)
F(9)	5004(2)	12190(2)	-6129(2)	40(1)
F(10)	5573(2)	11917(2)	-7713(2)	47(1)
F(11)	3830(3)	12360(2)	-7408(2)	53(1)
F(12)	3338(2)	10173(2)	-8583(1)	40(1)
N(1)	2026(2)	11943(2)	-2002(2)	19(1)
N(2)	3059(2)	10682(2)	-3683(2)	18(1)
N(3)	4828(2)	12451(2)	-1670(2)	17(1)
C(1)	1194(3)	12492(3)	-1741(2)	23(1)
C(2)	79(3)	11875(3)	-1346(2)	28(1)
C(3)	-238(3)	10624(4)	-1199(3)	29(1)
C(4)	603(3)	10057(3)	-1451(2)	25(1)
C(5)	1717(3)	10741(3)	-1841(2)	18(1)
C(6)	2671(3)	10170(3)	-2093(2)	18(1)
C(7)	4128(3)	11300(3)	-1422(2)	17(1)
C(8)	4710(3)	11140(3)	-595(2)	21(1)
C(9)	6084(3)	12106(3)	-73(2)	23(1)
C(10)	6859(3)	13190(3)	-415(2)	23(1)
C(11)	6200(3)	13339(3)	-1199(2)	20(1)
C(12)	3083(3)	10246(3)	-4721(2)	22(1)
C(13)	2683(3)	8841(3)	-5361(2)	26(1)
C(14)	2244(3)	7817(3)	-4930(2)	28(1)
C(15)	2226(3)	8243(3)	-3867(2)	23(1)
C(16)	2646(3)	9678(3)	-3266(2)	19(1)
C(17)	5254(3)	15297(3)	-1920(2)	21(1)
C(18)	5618(3)	14626(3)	-2829(2)	19(1)
C(19)	4661(3)	13769(3)	-3828(2)	19(1)
C(20)	3307(3)	13558(3)	-3976(2)	20(1)
C(21)	2941(3)	14168(3)	-3071(2)	21(1)
C(22)	3907(3)	15021(3)	-2053(2)	22(1)
C(23)	6279(3)	16313(3)	-854(2)	29(1)
C(24)	2323(3)	12771(3)	-5072(2)	28(1)
C(25)	2276(5)	13904(5)	-5403(4)	65(1)
C(26)	914(4)	11608(5)	-5149(4)	57(1)

Table 4.3 **Bond lengths [Å] and angles [°] for 28.**

Ru(1)-N(3)	2.129(2)	N(3)-C(11)	1.356(4)
Ru(1)-N(2)	2.137(2)	C(1)-C(2)	1.371(4)
Ru(1)-N(1)	2.155(2)	C(2)-C(3)	1.388(5)
Ru(1)-C(19)	2.210(3)	C(3)-C(4)	1.385(4)
Ru(1)-C(22)	2.216(3)	C(4)-C(5)	1.384(4)
Ru(1)-C(18)	2.218(3)	C(5)-C(6)	1.507(4)
Ru(1)-C(21)	2.233(3)	C(6)-C(7)	1.511(4)
Ru(1)-C(17)	2.262(3)	C(6)-C(16)	1.516(4)
Ru(1)-C(20)	2.280(3)	C(7)-C(8)	1.388(4)
P(1)-F(3)	1.578(2)	C(8)-C(9)	1.377(4)
P(1)-F(1)	1.578(2)	C(9)-C(10)	1.389(4)
P(1)-F(6)	1.584(2)	C(10)-C(11)	1.379(4)
P(1)-F(2)	1.597(2)	C(12)-C(13)	1.375(4)
P(1)-F(4)	1.599(2)	C(13)-C(14)	1.381(4)
P(1)-F(5)	1.599(2)	C(14)-C(15)	1.384(4)
P(2)-F(11)	1.591(2)	C(15)-C(16)	1.386(4)
P(2)-F(7)	1.593(2)	C(17)-C(22)	1.395(4)
P(2)-F(10)	1.595(2)	C(17)-C(18)	1.428(4)
P(2)-F(12)	1.606(2)	C(17)-C(23)	1.504(4)
P(2)-F(9)	1.606(2)	C(18)-C(19)	1.402(4)
P(2)-F(8)	1.609(2)	C(19)-C(20)	1.430(4)
N(1)-C(5)	1.346(4)	C(20)-C(21)	1.400(4)
N(1)-C(1)	1.363(3)	C(20)-C(24)	1.515(4)
N(2)-C(16)	1.349(4)	C(21)-C(22)	1.426(4)
N(2)-C(12)	1.353(4)	C(24)-C(26)	1.489(5)
N(3)-C(7)	1.348(3)	C(24)-C(25)	1.529(5)
N(3)-Ru(1)-N(2)	80.77(8)	F(3)-P(1)-F(5)	89.26(13)
N(3)-Ru(1)-N(1)	86.20(9)	F(1)-P(1)-F(5)	90.24(14)
N(2)-Ru(1)-N(1)	85.40(9)	F(6)-P(1)-F(5)	89.81(13)
N(3)-Ru(1)-C(19)	120.96(9)	F(2)-P(1)-F(5)	178.21(12)
N(2)-Ru(1)-C(19)	94.83(9)	F(4)-P(1)-F(5)	89.41(12)
N(1)-Ru(1)-C(19)	152.59(9)	F(11)-P(2)-F(7)	178.11(13)
N(3)-Ru(1)-C(22)	117.75(10)	F(11)-P(2)-F(10)	91.79(13)
N(2)-Ru(1)-C(22)	161.28(10)	F(7)-P(2)-F(10)	90.10(12)
N(1)-Ru(1)-C(22)	92.85(10)	F(11)-P(2)-F(12)	89.70(13)
N(3)-Ru(1)-C(18)	94.53(9)	F(7)-P(2)-F(12)	90.33(11)
N(2)-Ru(1)-C(18)	117.89(10)	F(10)-P(2)-F(12)	90.38(12)
N(1)-Ru(1)-C(18)	156.56(9)	F(11)-P(2)-F(9)	90.04(13)
N(3)-Ru(1)-C(21)	154.91(9)	F(7)-P(2)-F(9)	89.91(11)
N(2)-Ru(1)-C(21)	123.95(10)	F(10)-P(2)-F(9)	90.27(12)
N(1)-Ru(1)-C(21)	91.27(10)	F(12)-P(2)-F(9)	179.31(11)
N(3)-Ru(1)-C(17)	93.25(9)	F(11)-P(2)-F(8)	88.95(11)
N(2)-Ru(1)-C(17)	154.24(10)	F(7)-P(2)-F(8)	89.16(11)
N(1)-Ru(1)-C(17)	119.40(10)	F(10)-P(2)-F(8)	179.20(12)
N(3)-Ru(1)-C(20)	158.02(10)	F(12)-P(2)-F(8)	89.93(11)
N(2)-Ru(1)-C(20)	97.63(9)	F(9)-P(2)-F(8)	89.42(10)
N(1)-Ru(1)-C(20)	115.63(9)	C(5)-N(1)-C(1)	116.6(3)
F(3)-P(1)-F(1)	90.66(17)	C(5)-N(1)-Ru(1)	120.23(18)
F(3)-P(1)-F(6)	89.36(16)	C(1)-N(1)-Ru(1)	123.1(2)
F(1)-P(1)-F(6)	179.9(2)	C(16)-N(2)-C(12)	117.3(2)
F(3)-P(1)-F(2)	92.53(13)	C(16)-N(2)-Ru(1)	119.38(18)
F(1)-P(1)-F(2)	89.63(13)	C(12)-N(2)-Ru(1)	123.20(19)
F(6)-P(1)-F(2)	90.32(12)	C(7)-N(3)-C(11)	117.3(2)
F(3)-P(1)-F(4)	177.96(16)	C(7)-N(3)-Ru(1)	119.35(17)
F(1)-P(1)-F(4)	90.89(18)	C(11)-N(3)-Ru(1)	123.17(18)
F(6)-P(1)-F(4)	89.10(17)	N(1)-C(1)-C(2)	123.4(3)
F(2)-P(1)-F(4)	88.81(12)	C(1)-C(2)-C(3)	119.2(3)

Table 4.3 **cont.**

C(4)-C(3)-C(2)	118.2(3)	C(18)-C(17)-C(23)	122.4(3)
C(5)-C(4)-C(3)	119.5(3)	C(22)-C(17)-Ru(1)	70.07(15)
N(1)-C(5)-C(4)	123.0(3)	C(18)-C(17)-Ru(1)	69.71(15)
N(1)-C(5)-C(6)	116.4(2)	C(23)-C(17)-Ru(1)	133.55(19)
C(4)-C(5)-C(6)	120.6(3)	C(19)-C(18)-C(17)	120.6(3)
C(5)-C(6)-C(7)	110.6(2)	C(19)-C(18)-Ru(1)	71.24(16)
C(5)-C(6)-C(16)	111.9(2)	C(17)-C(18)-Ru(1)	73.12(16)
C(7)-C(6)-C(16)	110.4(2)	C(18)-C(19)-C(20)	121.6(2)
N(3)-C(7)-C(8)	122.1(2)	C(18)-C(19)-Ru(1)	71.83(15)
N(3)-C(7)-C(6)	116.9(2)	C(20)-C(19)-Ru(1)	74.13(16)
C(8)-C(7)-C(6)	121.0(2)	C(21)-C(20)-C(19)	117.3(2)
C(9)-C(8)-C(7)	119.5(3)	C(21)-C(20)-C(24)	120.9(3)
C(8)-C(9)-C(10)	118.6(3)	C(19)-C(20)-C(24)	121.8(2)
C(11)-C(10)-C(9)	118.9(3)	C(21)-C(20)-Ru(1)	70.10(15)
N(3)-C(11)-C(10)	122.8(3)	C(19)-C(20)-Ru(1)	68.78(15)
N(2)-C(12)-C(13)	123.2(3)	C(24)-C(20)-Ru(1)	134.8(2)
C(12)-C(13)-C(14)	119.0(3)	C(20)-C(21)-C(22)	121.1(3)
C(13)-C(14)-C(15)	118.7(3)	C(20)-C(21)-Ru(1)	73.77(15)
C(14)-C(15)-C(16)	119.3(3)	C(22)-C(21)-Ru(1)	70.67(15)
N(2)-C(16)-C(15)	122.4(3)	C(17)-C(22)-C(21)	121.5(3)
N(2)-C(16)-C(6)	117.7(2)	C(17)-C(22)-Ru(1)	73.66(15)
C(15)-C(16)-C(6)	119.9(2)	C(21)-C(22)-Ru(1)	71.96(15)
C(22)-C(17)-C(18)	117.8(3)	C(26)-C(24)-C(20)	114.4(3)
C(22)-C(17)-C(23)	119.8(3)	C(26)-C(24)-C(25)	111.6(3)
		C(20)-C(24)-C(25)	108.0(3)

Chapter 5

Nucleophilic attack on (η^6-arene)Ru(II) complexes

Introduction

The treatment of dicationic (η^6-arene)Ru(II) complexes, containing either *tris*(2-pyridyl)methane or *tris*(2-pyridyl)ethoxymethane as ancillary ligands, with nucleophiles led exclusively to the formation of monocationic (η^5-cyclohexadienyl)Ru(II) products. In the case of some (η^6-benzene)Ru(II) precursor complexes containing both a *tris*(2-pyridyl)ethoxymethane and a tertiary phosphine ligand, either of two isomers of a given cyclohexadienyl product could be obtained depending upon the reaction conditions employed.

5.1 Results and Discussion

5.1.1 The reactions of $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$ (24) with nucleophiles

Treatment of a yellow suspension of complex **24** in THF with the hydride source $NaBH_4$ immediately resulted in the formation of a dark brown solution from which a dark yellow solid, **32**, was isolated following work-up. Unfortunately **32** is highly air-sensitive, with complete decomposition of the solid occurring in *ca.* 2 hours. The spectroscopic characterisation described below was conducted immediately following the isolation of **32** and is consistent with the formulation $[(\eta^5\text{-}C_6H_7)Ru\{(C_5H_4N)_3COEt\}]PF_6$, however microanalytical data were inconclusive.

The ^1H NMR spectrum of **32** (in the δ 1.5 - 6.0 chemical shift range) is shown in Figure 5.1. By analogy with previous studies[8,9,18,19,96,128,130] on (η^5-C_6H_7)Ru(II) complexes, the singlet resonance for the benzene

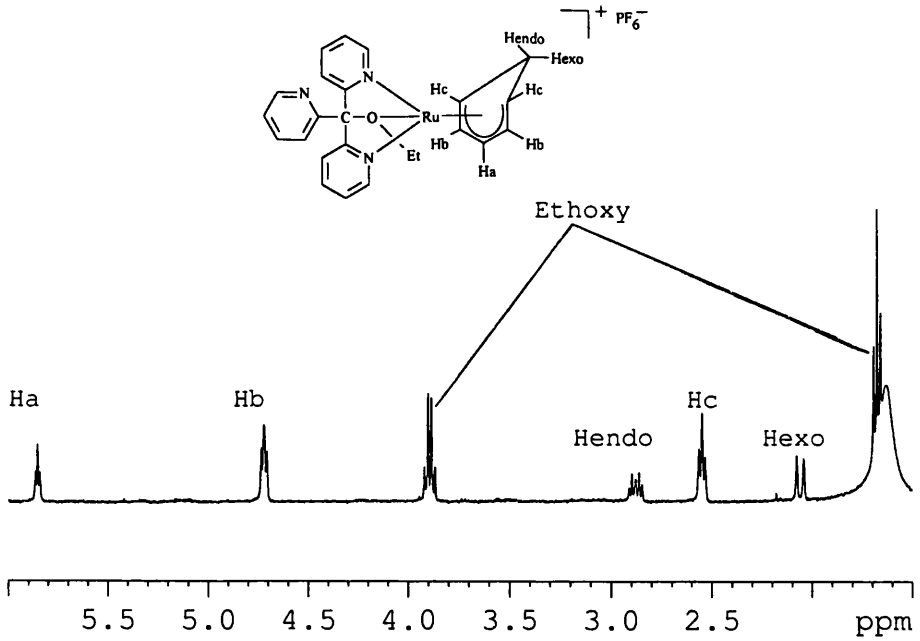


Figure 5.1 ^{1}H NMR spectrum of **32** (δ 1.5 - 6.0 ppm region, 300 K). For clarity purposes, and owing to the instability of **32** in solution, impurities due to decomposition have been omitted from the spectrum.

ligand in the parent compound (**24**) is replaced by five signals covering a wide chemical shift range (δ 2.06 (d), 2.55 (d,d), 2.88 (m), 4.72 (d,d) and 5.85 (t) ppm), indicative of a cyclohexadienyl product. (**NB**. The cyclohexadienyl ring atomic labelling scheme shown in Figure 5.1 has been applied to all the C_6H_6X-cyclohexadienyl complexes described herein). In Figure 5.1 the H_{endo} signal appears as a multiplet while the H_{exo} signal appears as a widely spaced doublet (J = 13.9 Hz), the latter proton showing no vicinal coupling to H_c due to the dihedral angle between these protons being close to 90 °.[128] The ethoxy substituent on **32** appears as a triplet and quartet at δ 1.68 and 3.89 ppm respectively.

Figure 5.2 shows the variable temperature ^{1}H NMR spectra of **32** in the pyridyl

region of the spectrum. (**NB**. As indicated by *, additional signals most

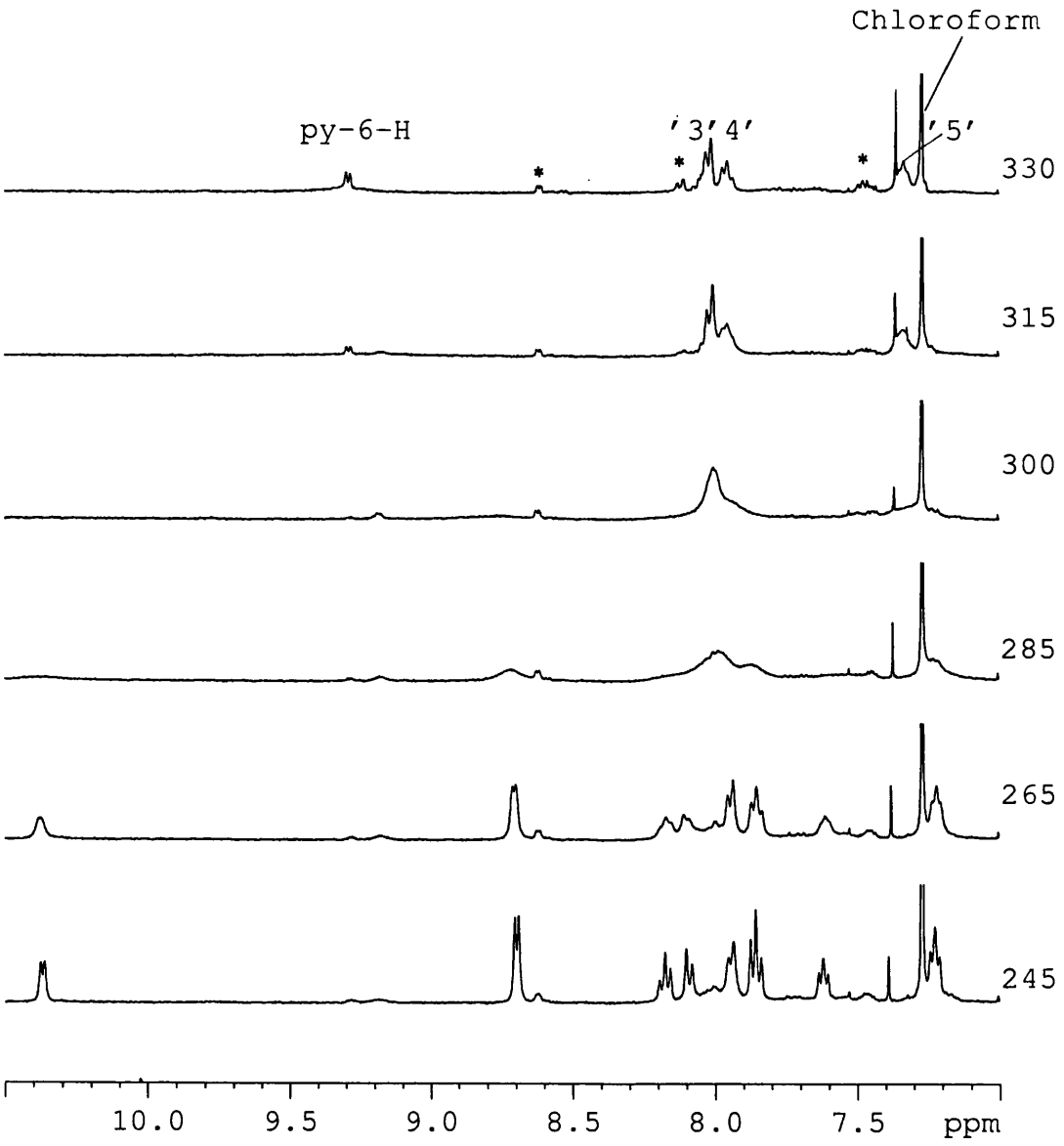


Figure 5.2 Variable temperature (K) ^{1}H NMR spectra of **32** (δ 7.0 - 10.5 ppm region)

probably due to decomposition products are also observed in the spectra). At 300 K the spectrum of **32** is dominated by a broad pyridyl signal at δ 8.01 ppm. As the temperature of the sample is lowered additional signals emerge from the baseline, and collectively the resonances sharpen until at 245 K two distinct sets of four pyridyl signals are observed, with an integral ratio of 2:1. In

contrast, when the temperature is increased to 330 K, only one set of pyridyl signals is observed. Hence a fluxional process must be operating such that at higher temperatures all three pyridyl rings are rendered equivalent, while at lower temperatures two are equivalent and one is unique. By analogy with previous NMR studies on (η^5-cyclohexadienyl)*tris*(pyrazolyl)Ru(II) complexes,[19] the cyclohexadienyl resonances remain essentially unchanged throughout the temperature range. Two distinct sets of pyridyl signals, with integral ratio 2:1, were observed in the room temperature ^{1}H NMR spectrum of the parent complex, **24**, due to the N,N',O-coordination mode adopted by the *tris*(2-pyridyl)ethoxymethane ligand (sub-section 4.2.3). However, Figure 5.2 clearly shows that at higher temperatures all three pyridyl rings of the cyclohexadienyl derivative, **32**, are in an equivalent environment. It is unlikely that these observations are due to the *tris*(2-pyridyl)ethoxymethane ligand in **32** undergoing a rapid change in coordination, between N,N',O and N,N',N'' modes, since the ethoxy resonances remain invariant with changes in temperature. Instead it is likely that at higher temperatures a rapid exchange process is occurring whereby any two of the three pyridyl rings may be coordinated to the metal centre at any one instant, while at lower temperatures this process is slow and thus one of the pyridyl rings is rendered unique.

The infrared spectrum of **32** was not of a high enough quality that ν(C-$H_{endo/exo}$) bands were clearly observed, however the presence of a strong, broad ν(P-F) band at 842 cm^{-1} reflected the presence of the hexafluorophosphate counteranion. In the FAB mass spectrum a fragment at *m/z* 472 was consistent with the presence of the cation [(η^5-

C_6H_7)Ru{$(C_5H_4N)_3COEt$}]$^+$.

Using analogous methods to the preparation of **32**, treatment of **24** with the nucleophiles CN^- or OH^- led to the formation of products that decomposed very rapidly and could not be convincingly and reproducibly characterised.

5.1.2 Tertiary phosphine derivatives of $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3COEt\}]PF_6$ (23)

Treatment of **23** with nucleophiles leads to facile decomposition, the instability of the complex being attributed to competing nucleophilic reactions between the arene and the metal *via* chloride ligand substitution.[9] It has previously been shown that (arene)ruthenium(II) complexes bearing bidentate nitrogen donors can be stabilised towards nucleophilc attack by replacement of chloride ligands with tertiary phosphines.[8,9] Therefore, using the general method described in these studies, a number of tertiary phosphine derivatives of **23** were prepared in the hope that subsequent cyclohexadienyl products would be stabilised by the π-accepting ability of the phosphine ligands. Thus, treatment of **23** with a number of tertiary phosphines in methanol, followed by work-up with NH_4PF_6 results in the formation of the complexes $[(\eta^6\text{-}C_6H_6)Ru(PR_3)\{(C_5H_4N)_3COEt\}][PF_6]_2$ (PR_3 = PEt_3 (**33**), PMe_2Ph (**34**), $PMePh_2$ (**35**)) as yellow solids. Microanalytical data were consistent with the dicationic formulations **33**•Me_2CO, **34**•0.5Me_2CO (crystals grown from acetone) and **35**.

The ^1H NMR spectrum of **35** is shown in Figure 5.3.

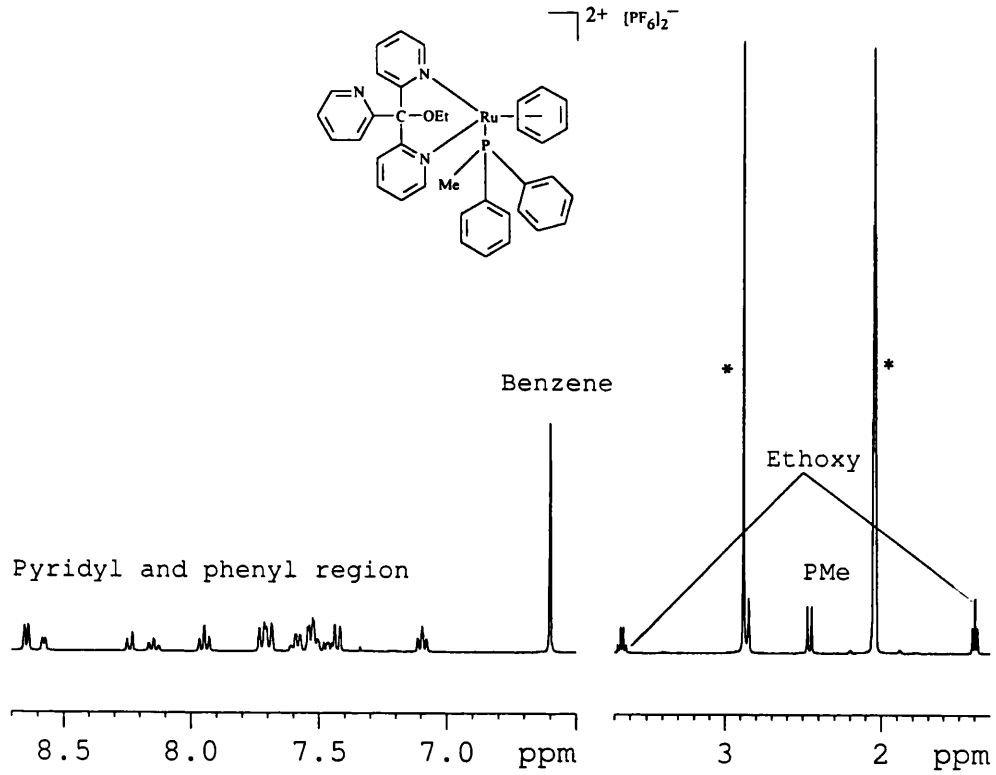


Figure 5.3 ^{1}H NMR spectrum of **35** (* signals due to water and acetone)

The spectrum exhibits resonances that are characteristic of the η^6-benzene ligand, the two sets of pyridyl rings (integral ratio 2:1), and the ethoxy substituent of the *tris*(2-pyridyl)ethoxymethane ligand. In addition there are signals at δ 2.45 (d), 7.52 (m), 7.59 (m) and 7.71 (m) ppm due to the phosphine ligand. The ^{1}H NMR spectra of **33** and **34** are analogous to that of **35** (full characterisation is presented in sub-section 5.2.3). Attempts to prepare the triphenylphosphine derivative of **23** proved unsuccessful, probably owing to the phosphine ligand's greater steric bulk hindering its coordination to the metal.

5.1.3 Nucleophilic attack on complexes 33, 34 and 35

Treatment of a suspension of complex **33** in methanol with $NaBH_4$ immediately resulted in the formation of a bright yellow solution, from which a dark yellow,

air-stable solid, **36**, was isolated following work-up. Microanalytical data were consistent with the monocationic formulation $[(\eta^5\text{-}C_6H_7)Ru(PEt_3)\{(C_5H_4N)_3COEt\}]PF_6$ for **36**. The infrared spectrum of **36** exhibits two bands of medium intensity at 2939 and 2807 cm^{-1} which may be assigned as $\nu(C\text{-}H_{endo})$ and $\nu(C\text{-}H_{exo})$ respectively.[124,131] The variable temperature ^1H NMR spectra of **36** are shown in Figure 5.4. By analogy with the

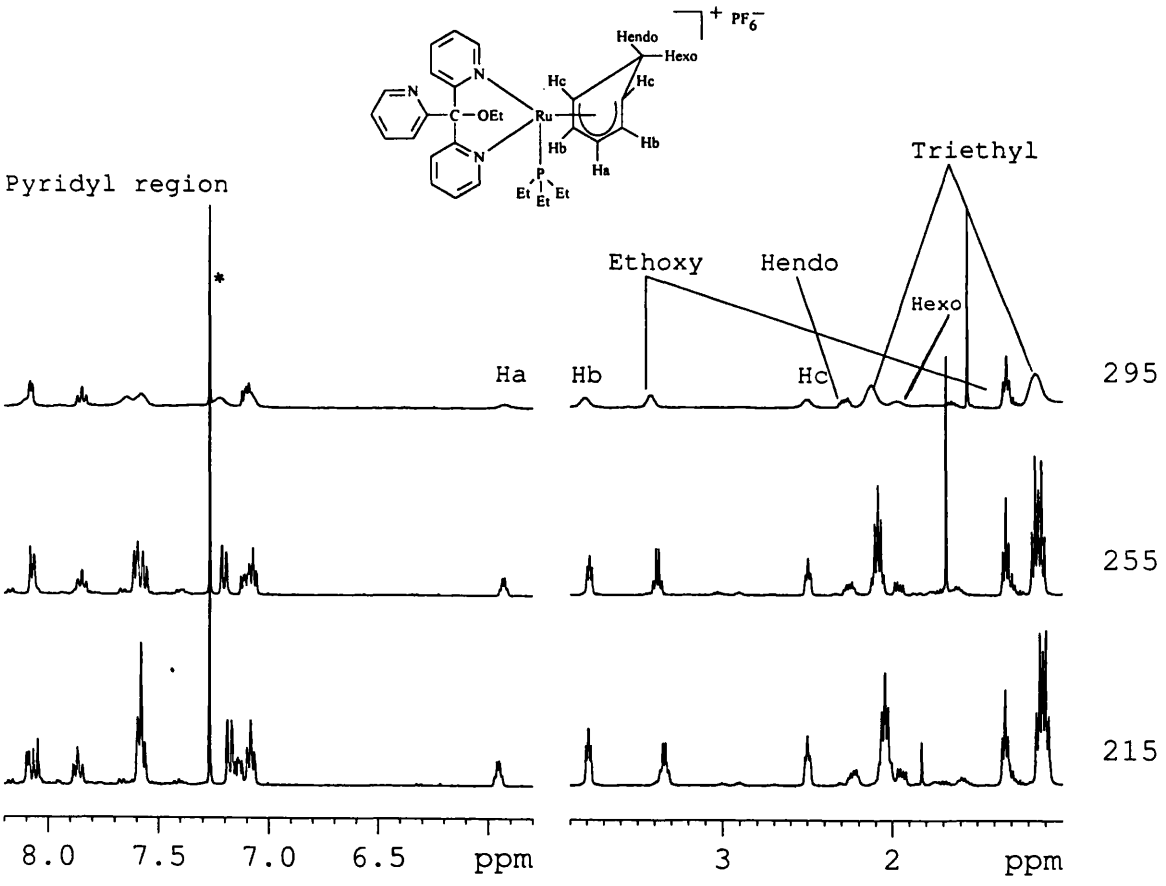
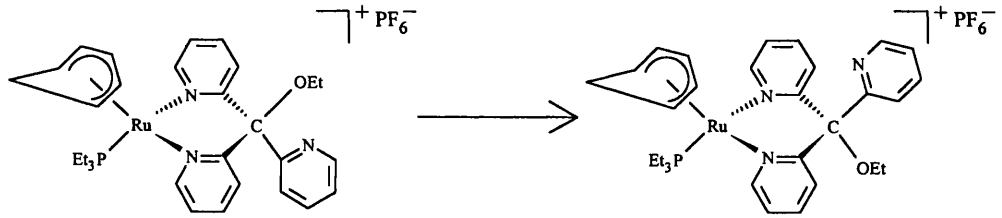


Figure 5.4 Variable temperature (K) ^1H NMR spectra of **36** (* signal due to chloroform)

cyclohexadienyl compound **32**, the singlet resonance for the benzene ligand in the parent compound is replaced by five signals covering a wide chemical shift range. At low temperatures, the observation of one sharp set of phosphine-

ethyl signals is consistent with rapid rotation of the phosphine ligand about the Ru-P bond, equilibriating the three ethyl environments. Interestingly, increasing the sample temperature to 295 K results in the broadening of these signals, indicating phosphine dissociation. Furthermore, as the temperature is increased above 295 K (not shown in Figure 5.4) the intensity of all the signals due to **36** dramatically decreases, and a second set of sharp signals due to a new product (**39**) are observed. These increasingly dominate the spectrum. This would suggest that, above 295 K, compound **36** starts to decompose into a second compound (**39**) (Figure 5.5). It is likely that the formation of **39** requires the dissociation of the phosphine ligand (see above),



36 39

Figure 5.5 Cationic rearrangement of compound **36** to give compound **39**.

and may proceed *via* the formation of a pseudo-tri-dentate (N,N',N") intermediate, however, this remains unproven. Evidence for the cationic conformations illustrated in Figure 5.5 will be discussed later, as will compound **39**.

At low temperatures the signals due to the H_{endo}, H_b and H_c protons of **36** (Figure 5.4) are of a similar appearance to those of **32** (Figure 5.1). However, while in **32** the H_{exo} and H_a proton resonances appear as a doublet and triplet

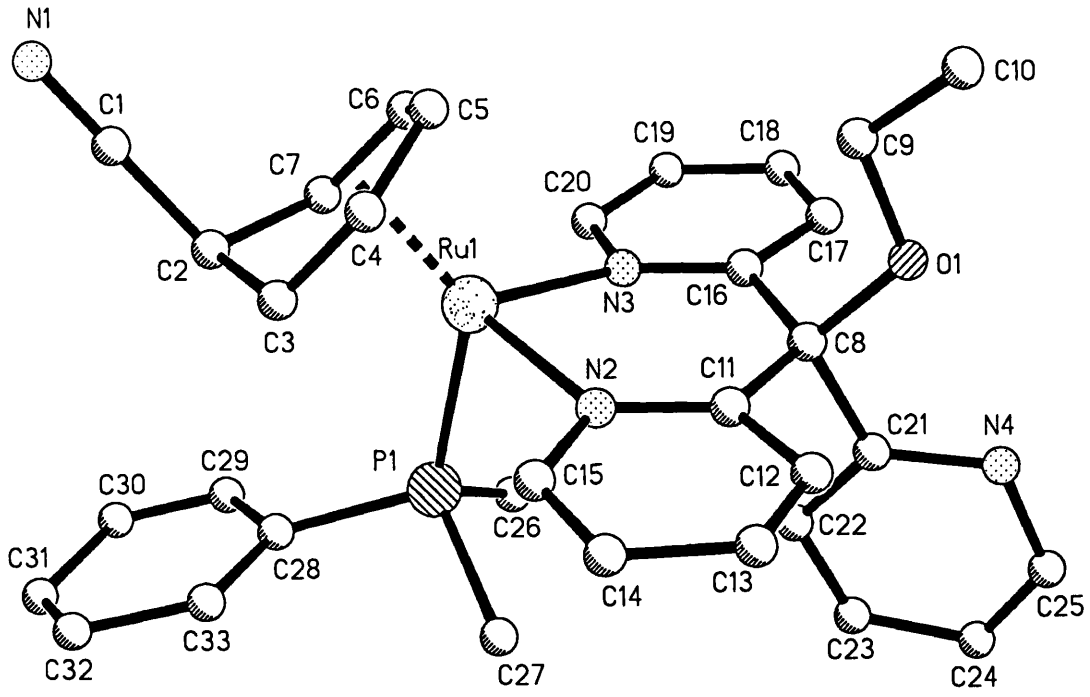
respectively, in **36** the equivalent proton resonances appear as a doublet of doublets and broad multiplet. Similar coupling patterns are also observed for the hydride-derived cyclohexadienyl complexes **37** and **38** formed from **34** and **35** respectively, and may tentatively be ascribed to long range couplings between these protons and the phosphorus nucleus.

Compound **37** was prepared analogously to **36**, by reaction of **34** with $NaBH_4$. Microanalytical data were consistent with the formulation $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$. A fragment observed in the FAB mass spectrum at *m/z* 610 is due to the cation in **37**. As one would expect, except for differences associated with the phosphine ligands, the ^1H NMR spectra of **37** and **36** are closely similar.

Treatment of a suspension of **34** in methanol with KCN, followed by work-up led to the isolation of the cyanide analog of compound **37**, namely $[(\eta^5\text{-}C_6H_6CN)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ **42**. The $\nu(C\text{-}H_{exo})$ band observed in the infrared spectrum of **37** is replaced in **42** by a $\nu(C{\equiv}N)$ band at 2219 cm^{-1}, while in both spectra a $\nu(C\text{-}H_{endo})$ band is present. Furthermore, only four cyclohexadienyl resonances were observed in the ^1H NMR spectrum of **42**, with the absence of the H_{exo} resonance. The ^1H NMR spectra of **37** and **42** are otherwise analogous.

The identity of **42** was conclusively established by X-ray diffraction and the crystal structure of the cation in **42** is shown in Figure 5.6. Bidentate N,N'-coordination of the *tris*(2-pyridyl)ethoxymethane ligand to the Ru(II) ion is

confirmed, while the third pyridyl nitrogen and ethoxy oxygen atoms remain unbound. The metal is bonded to the five sp^2-hybridised carbon atoms of the cyclohexadienyl ring which is bent away from the metal across the C(3)---C(7) axis, resulting in an envelope-type ring conformation. The cyanide exhibits an *exo* stereochemistry in its attachment to the cyclohexadienyl ring. Although the



N(1)-C(1)	1.160(7)	C(1)-C(2)-C(3)	113.8(4)
Ru(1)-C(3)	2.240(4)	C(1)-C(2)-C(7)	113.3(4)
Ru(1)-C(4)	2.196(4)	C(3)-C(2)-C(7)	102.1(3)
Ru(1)-P(1)	2.3739(11)	N(3)-Ru(1)-N(2)	90.09(12)
Ru(1)-N(2)	2.155(3)	N(3)-Ru(1)-P(1)	90.43(9)
Ru(1)-N(3)	2.151(3)	N(2)-Ru(1)-P(1)	89.55(9)
O(1)-C(8)	1.438(4)	N(1)-C(1)-C(2)	177.6(6)

Figure 5.6 Structure of the cation in $[(\eta^5\text{-}C_6H_6CN)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ **(42)** with selected bond lengths (Å) and angles (°)

location of the hydrogen atoms could not be obtained from the X-ray data, examination of the angles around C(2) suggests that C(2) is sp^3-hybridised and therefore that a hydrogen atom is present in the *endo* position. The

tertiary phosphine ligand is orientated in such a manner that its methyl and phenyl substituents are *anti* and *syn*, respectively, to the cyclohexadienyl ring. The phosphorus and two metallated nitrogen atoms occupy three facial sites of an octahedron with the average angle subtended at ruthenium being 90.0(1) °.

The diphenylmethylphosphine analog of **37**, $[(\eta^5\text{-}C_6H_7)Ru(PMePh_2)\{(C_5H_4N)_3COEt\}]PF_6$ **38**, was isolated after work-up of the reaction mixture obtained by treating **35** with $NaBH_4$ in methanol. The monocationic formulation was confirmed by microanalysis. The infrared spectrum of **38** exhibits two bands at 2980 and 2820 cm^{-1} assigned as ν(C-H_{endo}) and ν(C-H_{exo}) respectively. The cation in **38** was observed as a fragment at *m/z* 672 in the FAB mass spectrum.

Unfortunately, attempts to grow 'X-ray quality' crystals of **38** were unsuccessful, although an insight into the structure of **38** was provided by the compound's ^{1}H NMR spectrum, shown in Figure 5.7. As one would expect, a number of analogies can be drawn by comparing the 295 K ^{1}H NMR spectrum of **38** with those of **36** and **37**. For example the broad signals due to the metallated pyridyl rings, phosphine and cyclohexadienyl ligands seen for **36** and **37** are also observed for **38**. However, replacing the tertiary phosphine ligand in **36** or **37** with a diphenylmethylphosphine ligand in **38** does significantly alter the spectrum in other respects. For instance, in the ^{1}H NMR spectrum of **38** the signals at δ 6.39 (d) and 3.41 (m,br) ppm, due to the non-metallated pyridyl ring '3' and cyclohexadienyl ring H_a protons respectively,

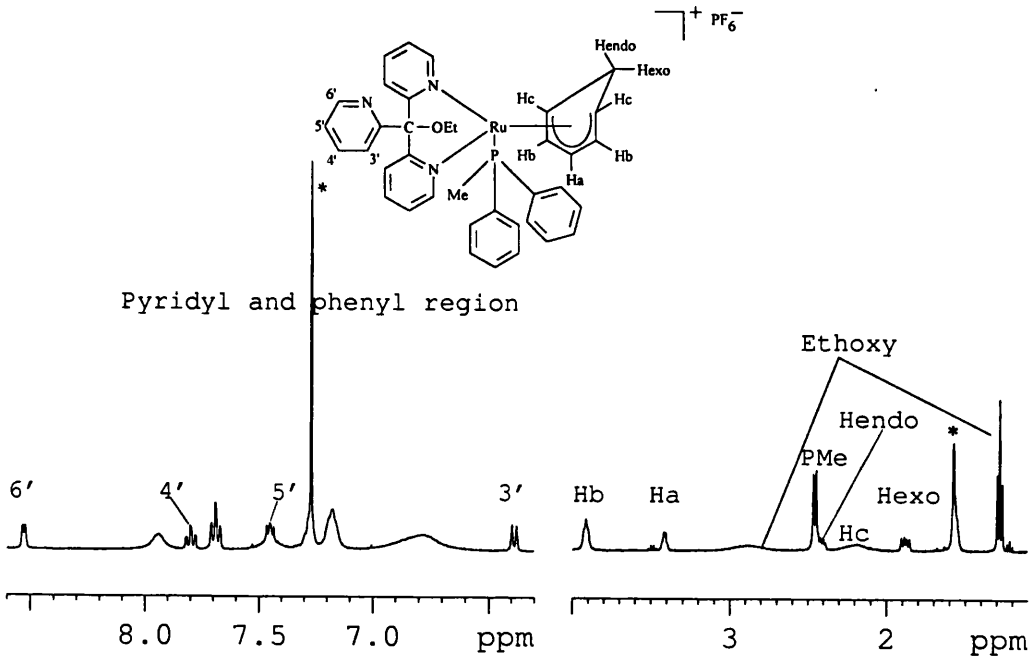


Figure 5.7 ^{1}H NMR spectrum of **38** (* signals due to chloroform and water)

occur at considerably higher fields than the equivalent proton signals of **36** and **37**. This would suggest that the diphenylmethylphosphine ligand in **38** has imposed a geometry upon the structure of **38** that subjects these protons to significantly greater shielding than they experience in **36** and **37**. It should be noted in passing that the Tolman cone angles for diphenylmethylphosphine and triethylphosphine are closely similar, 136 and 137 ° respectively,[140] implying that the observations described above may be due to electronic rather than steric effects. A possible explanation for the shielding will become apparent shortly.

Treatment of a suspension of **34** in methanol with $NaBH_4$, followed by refluxing for 3 hours and work-up of the reaction mixture led to the isolation of compound **40**. While microanalytical and mass spectroscopic data for **40** were consistent with a formulation that was identical to that of compound **37** (the

product of the room temperature reaction between **34** and $NaBH_4$), the ^1H NMR spectrum of **40** suggested that this compound was different to **37**. Investigation shows the quantitative and irreversible conversion of **37** into **40** can be readily achieved by refluxing a solution of **37** in methanol for *ca.* 3 hours. Using shorter reaction times resulted in only a partial conversion, but drew attention to the fact that the transformation is clean i.e. does not proceed *via* any observable intermediate.

Figure 5.8 shows the variable temperature ^1H NMR spectra of **40** in the δ 1.0-4.0 ppm chemical shift range. At 295 K the signals due to the methyl protons of the phosphine ligand, the H_a and H_c protons of the cyclohexadienyl ligand, and the ethoxy-CH_2 protons of the *tris*(2-pyridyl)ethoxymethane ligand (2 signals) are all broad. Increasing the temperature of the NMR probe to 323 K results in the sharpening of many of these resonances and, most notably, the observation of only one set of three signals due to the $P(C\underline{H}_3)_2$, H_c and $CH_3C\underline{H}_2O$-protons. In marked contrast, the same set of signals is observed to split into two sub-sets upon decreasing the temperature from 295 to 233 K (see Figure 5.8). At the same time the H_a proton signal is resolved as a multiplet. At 295 K, in the pyridyl region of the ^1H NMR spectrum of **40** (not shown in Figure 5.8), two sets of pyridyl signals are observed (with integral ratio 2:1). By analogy with the ^1H NMR spectra of **36**, a sharp set of signals is due to the non-metallated pyridyl ring, while a broad set of signals is due to the two metallated pyridyl rings. While increasing the sample temperature from 295 K sharpens the latter set of signals, lowering the temperature from 295 K results in that set of signals splitting into two sub-sets. Thus a fluxional

process must be operating such that at higher temperatures the two metallated pyridyl rings are equivalent, as are the two phosphine-methyl

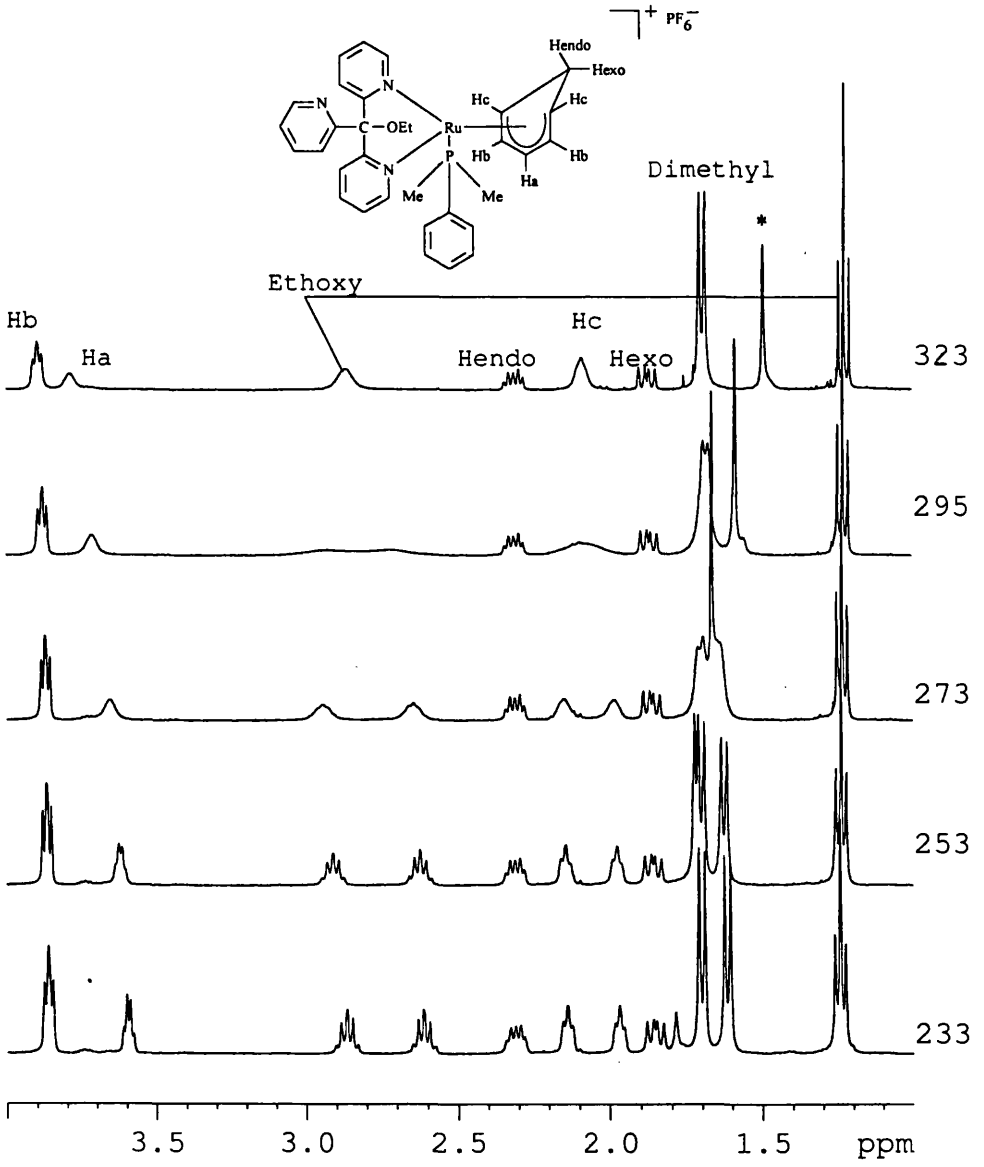


Figure 5.8 Variable temperature (K) ^{1}H NMR spectra of **40** (δ 1.0-4.0 ppm region, * signal due to water)

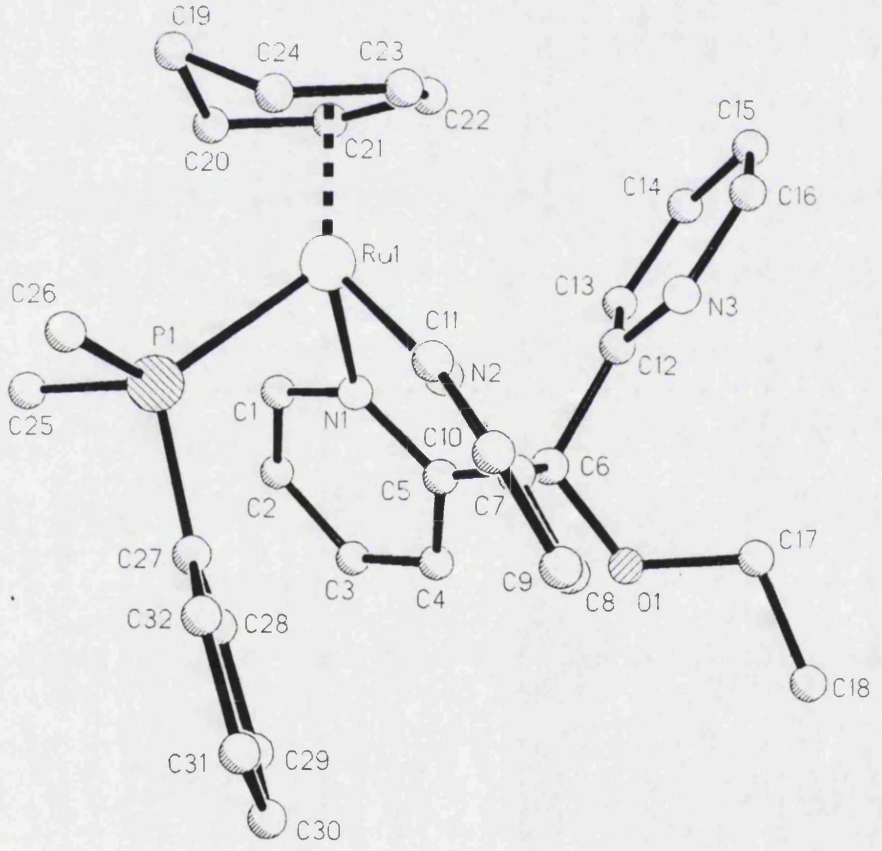
groups, the two cyclohexadienyl-H_c protons, and the two ethoxy-CH_2 protons, while at lower temperatures this equivalence is lost. Hence at 295 K a process involving the rotation of both the cyclohexadienyl and phosphine ligands may

be occurring. This rotation is rapid at higher temperatures resulting in the observation of a single set of signals, whereas at lower temperatures it is clear that restricted rotation of both ligands is observed, as is manifested by the doubling in the number of signals arising from several of the ^{1}H nuclei.

In comparing the ^{1}H NMR spectrum, recorded at 295 K, of **37** with that of **40**, it is immediately apparent that the signals due to the non-metallated pyridyl ring '3' and cyclohexadienyl ring H_a protons, that are found at δ 8.12 and 5.86 ppm in **37**, now appear at δ 6.24 and 3.72 ppm in **40**. Therefore it is deduced that these protons take up more highly shielded positions within the structure of **40** than they do within the structure of **37**. An explanation for these unusual chemical shifts becomes apparent upon examining the X-ray crystal structure of **40**.

The structure of the cation in **40**, as determined by X-ray crystallography, is shown in Figure 5.9. By close analogy with the cationic structure of **42** (Figure 5.6), bidentate N,N'-coordination of the *tris*(2-pyridyl)ethoxymethane ligand to the metal ion is confirmed, as is the presence of phosphine and cyclohexadienyl ligands. However, there are a number of notable differences between the geometries of the two cations, that otherwise only differ in the identity of the group in the *exo* position. For instance, in **40** the tertiary phosphine ligand is orientated such that its methyl and phenyl substituents are *syn* and *anti*, respectively, to the cyclohexadienyl ring, while in **42** the reverse orientation is adopted. Furthermore, in **40** the non-metallated pyridyl ring has, in effect, moved away from the phenyl substituent of the phosphine ligand and

adopted a position in closer proximity to the cyclohexadienyl ring - one might look upon this as the bridgehead carbon atom having inverted its conformation. The phosphorus and two metallated nitrogen atoms occupy three facial sites of what is now a slightly distorted octahedron, with the average angle subtended at ruthenium being 88.22(6) °. The restricted rotation of the phosphine ligand, observed by low temperature ^{1}H NMR spectroscopy of **40**, may be due to greater steric interactions between the coordinated ligands. Examination of Figure 5.9 indicates that the ligands are



Ru(1)-P(1)	2.3550(5)	N(2)-Ru(1)-N(1)	89.57(7)
Ru(1)-N(2)	2.1271(17)	N(1)-Ru(1)-P(1)	89.61(5)
Ru(1)-N(1)	2.1394(17)	N(2)-Ru(1)-P(1)	85.48(5)
O(1)-C(6)	1.429(2)	C(20)-C(19)-C(24)	102.34(17)

Figure 5.9 Structure of the cation in $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ (**40**) with selected bond lengths (Å) and angles (°)

placed such that there is a mutual shielding interaction between the non-metallated pyridyl and cyclohexadienyl rings which is responsible for the low chemical shifts of the signals due to the non-metallated pyridyl ring '3' and cyclohexadienyl ring H_a protons in **40**.

Unfortunately compound **37** was not characterised crystallographically, however, by analogy with **42**, since **37** was prepared at room temperature it is very likely that the structural geometry is analogous to that of the cation in **42**, rather than the cation in **40**. Therefore compounds **37** and **40** are 'kinetic' and 'thermodynamic' isomers respectively, since at ambient temperatures the reaction of **34** with $NaBH_4$ exclusively leads to the monocationic product **37** with a conformation predicted to be closely analogous to that shown in Figure 5.6, while under reflux temperatures the same reaction leads to the monocationic product **40** with the cationic conformation shown in Figure 5.9. As described earlier, refluxing **37** in methanol results in a structural rearrangement of the cation and leads to the formation of the cation **40** which must be considered as the thermodynamically more stable isomer.

The relative stabilities of the cations in compounds **37** and **40** were computationally investigated *via* density functional theory (DFT) calculations (outlined in sub-section 5.2.1). In brief, the atomic co-ordinates of the cations in **42** and **40** were taken from the crystal structures (Figures 5.6 and 5.9 respectively), the only modification being that the cyanide group of **42** was replaced with a hydrogen atom to allow a proper comparison to be made between the two cations. The total molecular bonding energies (the energy of

the cation compared to a zero at which the atoms are removed to infinite separation) were computed for both cations, the result of which was that the cation in **40** was found to be 83.5 kJ/mol more stable than that in **37** (Figure 5.10). Such a conclusion is clearly in accordance with the experimental results described above. With reference to Figure 5.9, one possible contributory factor to the relative stability of **40** may be a C-H----π hydrogen-bonding interaction between H(22) (the hydrogen atom (not shown in Figure 5.9) bound to the cyclohexadienyl C(22) atom) and the π-electron system of the pyridyl ring containing C(12). The distance between H(22) and the pyridyl ring centroid is 2.65 Å and the H(22)-ring centroid-C(12) angle is 97.3 °. These values are comparable to those seen for N-H----π hydrogen-bonds.[141] A possible π-π interaction between the phenyl substituent of the phosphine ligand and the pyridyl ring containing N(2) is unlikely since the ring centroid-ring centroid distance, 3.71 Å, is larger than one would usually associate with such an interaction.

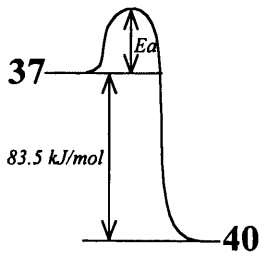


Figure 5.10 Relative stabilities of the cations in **37** and **40**

The deuteride analog of compound **40**, namely [(η^5-C_6H_6D)Ru(PMe_2Ph){($C_5H_4N)_3COEt$}]PF_6 **41**, was isolated following work-up of the reaction between **34** and $NaBD_4$ in refluxing methanol. In comparing the ^1H NMR spectrum, recorded at 295 K, of compound **40** with that of **41**, it is

apparent that the H_{exo} signal in **40** is absent in **41**, and that the H_{endo} multiplet resonance in **40** is replaced by a H_{endo} triplet resonance in **41**. All the other resonances remain essentially unchanged. Furthermore, the ν(C-H_{exo}) band at 2785 cm^{-1} in the infrared spectrum of **40** is replaced in the spectrum of **41** by a ν(C-D_{exo}) band at 2048 cm^{-1} due to the deuterium isotope shift.[124,132] Therefore *exo* addition of a single deuteride nucleophile is confirmed.

The 'thermodynamic' isomer of **36**, compound **39**, was isolated following work-up of the reaction between **33** and $NaBH_4$ in refluxing methanol. By analogy with the relationship between the isomeric compounds **37** and **40**, while microanalytical and mass spectroscopic data could not distinguish between **36** and **39**, ^{1}H NMR data could be used to achieve this. Figure 5.11 shows the ^{1}H NMR spectra, recorded at 215 K, of compounds **36** and **39**. A comparison of the two spectra reveals a number of notable

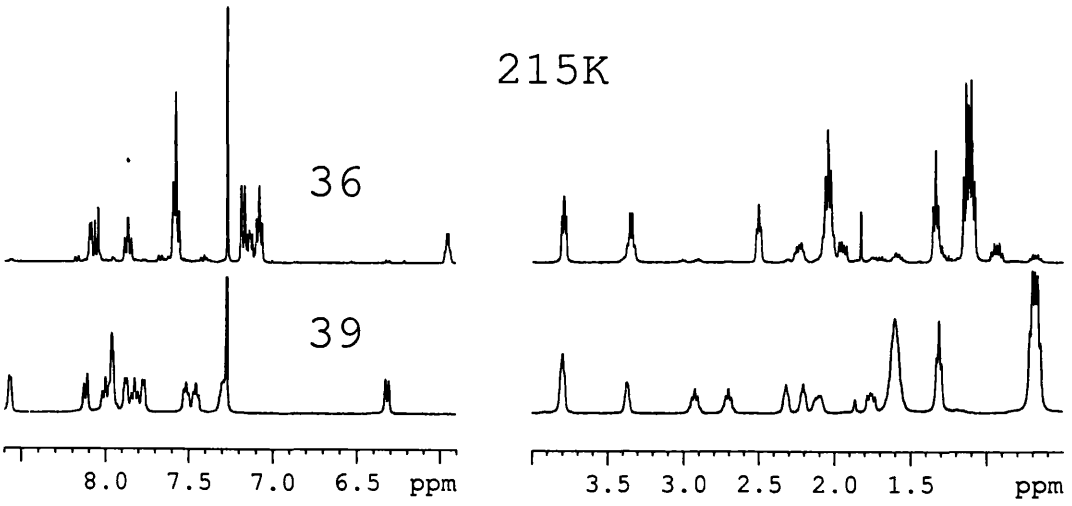


Figure 5.11 ^{1}H NMR spectra of compounds **36** and **39** (215 K)

differences. For instance, in the ^{1}H NMR spectrum of **39**, by analogy with **40**, two sets of signals are observed for the two metallated pyridyl rings, the

cyclohexadienyl H_c (δ 2.20 and 2.32 ppm), and the ethoxy-CH_2 protons (δ 2.70 and 2.92 ppm), while in the ^{1}H NMR spectrum of **36** only one set of signals is observed. Additionally, in the ^{1}H NMR spectrum of **39** the signals due to the non-metallated pyridyl ring '3' and cyclohexadienyl ring H_a protons occur at considerably higher fields than they do in the ^{1}H NMR spectrum of the 'kinetic' isomer **36** (δ 6.32 and 3.37 *vs.* δ 8.06 and 5.95). Thus under the refluxing conditions employed in the synthesis of **39**, it is likely that the cation adopts an orientation analogous to that of the cation in **40**. In the ^{1}H NMR spectrum, recorded at 215 K, of **36**, for reasons discussed earlier, only one sharp set of triethylphosphine signals were observed, however in the corresponding spectrum of **39** the equivalent signals are broad. In the latter case, a fluxional process involving either the rapid or hindered rotation of the phosphine ligand at 215 K is not occurring since one, or potentially three, sharp sets of phosphine-ethyl signals would have been observed respectively. Instead, at 215 K, it is likely that rotation of the phosphine ligand in **39** occurs at a rate comparable to the timescale of the NMR experiment.

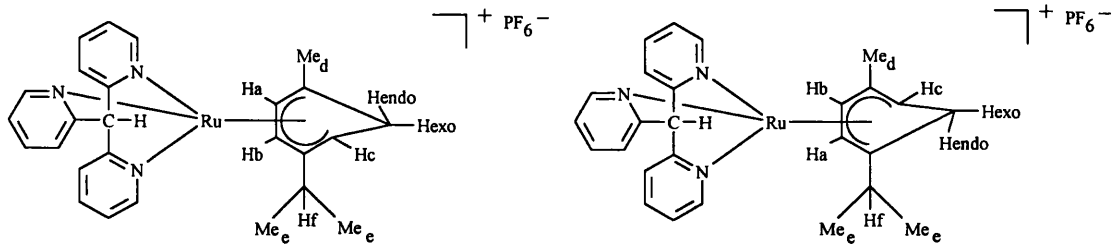
For reasons that were described earlier, the ^{1}H NMR spectrum (Figure 5.7) of compound **38**, formed at room temperature, is analogous to that of **40**. Furthermore the spectroscopic data on compound **38** remains unchanged even when the compound is isolated from refluxing methanol. Therefore it is likely that the cation in **38** adopts an orientation analogous to that seen in **40**. This leads to the conclusion that replacing a methyl group on the phosphine ligand in **37** with a phenyl group significantly reduces the energy barrier between kinetic and thermodynamic isomers such that the latter is isolated

even when the reaction is carried out at ambient temperatures.

5.1.4 The reactions of $[(\eta^6\text{-}MeC_6H_4{}^iPr)Ru\{(C_5H_4N)_3CH\}]\text{-}[PF_6]_2$ (28) with nucleophiles

Treatment of a yellow suspension of complex **28** in THF with $NaBH_4$ immediately resulted in the formation of a dark orange solution, from which a yellow solid, **43**, was isolated following work-up. That product is best formulated as $[(\eta^5\text{-}MeC_6H_5{}^iPr)Ru\{(C_5H_4N)_3CH\}]PF_6$ and a fragment in the FAB mass spectrum at *m/z* 484 was consistent with the cation in **43**. In the infrared spectrum two bands of medium intensity at 2962 and 2797 cm^{-1} were assigned as $\nu(C\text{-}H_{endo})$ and $\nu(C\text{-}H_{exo})$ respectively.

The ^1H NMR spectrum of **43** revealed the presence of two isomers of the types shown in Figure 5.12 (atomic labels used for Experimental section).



A B

Figure 5.12 Two isomeric forms of **43**

Since there are two potential sites for nucleophilic addition on the *para*-cymene ligand of **28**, the observation of two isomers is not surprising i.e. there is one isomer, **A**, in which addition of the hydride nucleophile has occurred at

the site *ortho* to the methyl substituent, and a second isomer, **B**, where addition has occurred at the site *ortho* to the *iso*propyl substituent. The equivalence of the three pyridyl rings of compound **28** is lost following treatment with $NaBH_4$, as reflected by the complexity of the pyridyl region of the ^1H NMR spectrum of **43**. This is due to the formation of two asymmetric cyclohexadienyl products. Due to a high degree of overlap in this region of the spectrum a total of only ten clearly distinguishable signals were observed, although each isomer should exhibit twelve resonances. The two isomers were formed in unequal amounts with isomer **B** being the more prevalent (**A**:**B** *ca.* 1:3, as deduced from the relative integrals of the two sets of cyclohexadienyl signals). Therefore, in contrast to previous studies concerned with similar derivatives containing the [2.2] *para*cyclophane spectator ligand (where hydride addition *ortho* to the methyl was preferred),[128] there is a distinct preference for isomer **B**, where hydride addition has occurred at the site *ortho* to the bulkier of the two ring substituents. Interestingly, when the preparation of **43** is carried out in methanol, rather than in THF, the two isomers are formed in approximately equal amounts. There is no obvious explanation for this difference in behaviour.

In order to try and extend the chemistry described above to other nucleophiles, **28** was reacted with NaOH in methanol. However, work-up of this reaction mixture led to the isolation of a product believed to be $[(\eta^5\text{-}MeC_6H_4CMe_2)Ru\{(C_5H_4N)_3CH\}]PF_6$ **44**. The ^1H NMR spectrum of **44** is shown in Figure 5.13. In contrast to the spectrum of **43**, only one form of the product is observed. The spectrum is also remarkable for its simplicity which indicates

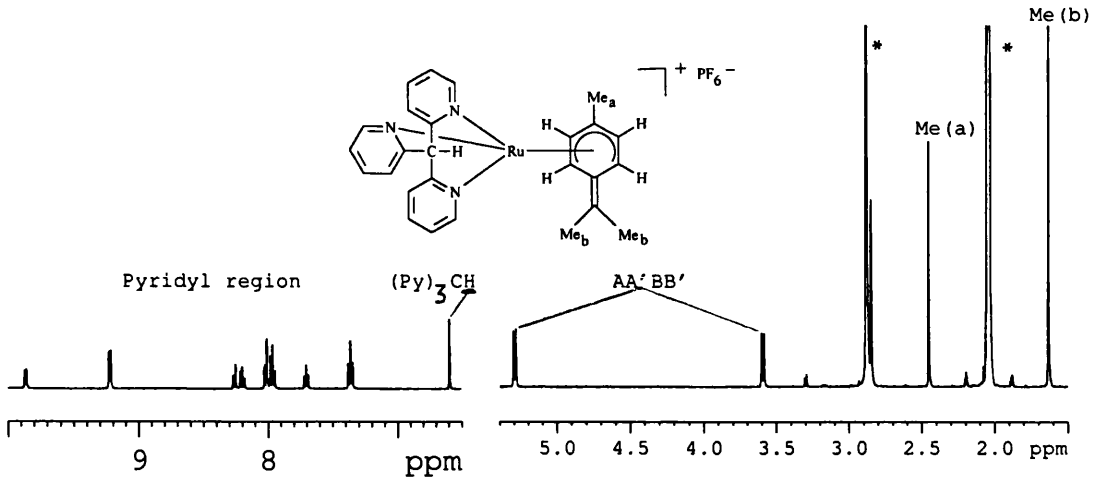


Figure 5.13 ^{1}H NMR spectrum of **44** (* signals due to water and acetone)

that a plane of symmetry is retained in the product. The following observations and deductions were made from the ^{1}H NMR spectrum of **44**, and are consistent with the structural formula shown in Figure 5.13:

i) Of the three metallated pyridyl rings in **44**, two are equivalent and one is unique, suggesting that the cyclohexadienyl ligand is not asymmetric.

ii) The septet resonance in the ^{1}H NMR spectrum of the parent compound **28** is absent in the ^{1}H NMR spectrum of **44**, and correspondingly the doublet resonance (due to the two adjacent methyl groups on the *iso*propyl) is replaced by a singlet resonance. This implies that deprotonation of the *iso*propyl substituent has occurred.

iii) One half of the AA'BB' resonance pattern (due to the cyclohexadienyl ring protons) is considerably more aliphatic in nature than the other, in fact these almost appear as an AX spin system.

On the basis of these observations it is concluded that treatment of **28** with OH^- leads to deprotonation of the *iso*propyl substituent of the *para*-cymene ring and the formation of a cyclohexadienyl product with an *exo*cyclic double bond. Since one of the pyridyl rings is unique it is likely that the

cyclohexadienyl ligand is not rotating rapidly about the M-L axis and perhaps adopts a conformation in which the double bond is in the same plane as one of the pyridyl rings.

Microanalysis was consistent with the formulation **44**•H_2O, and a fragment in the FAB mass spectrum at *m/z* 482 was due to the monocation. The absence of both ν(O-H) and ν(C-H_{endo}) bands in the infrared spectrum of **44** further confirmed that addition of a hydroxide nucleophile to the *para*-cymene ligand of compound **28** had not occurred. Interestingly, treatment of **28** with NaOMe also leads to the formation of compound **44**.

Previous studies have reported that the deprotonation of (η^6-hexamethylbenzene)Ru(II) complexes using such reagents as potassium *tert*-butoxide gives *exo*-methylene-cyclohexadienyl complexes.[129,142,143] However, the deprotonation of (η^6-*para*-cymene)Ru(II) complexes to give cyclohexadienyl products analogous to **44** has not been reported previously as far as can be ascertained. Infact the treatment of (η^6-*para*-cymene)Ru(II) complexes with a variety of nucleophiles (including OH^-) has generally been reported to lead to isomeric mixtures of nucleophilic addition products[19,127-129] similar to those described earlier in this chapter. Therefore the structure of compound **44** was rather unexpected, and furthermore since H^- is a stronger base than OH^- it is unclear why the former species does not also deprotonate **28** to form **44**. Nevertheless the identity of **44** seems secure on both the basis of analytical and spectroscopic data, although it has not been confirmed by X-ray crystallography.

Using an analogous method to the preparation of **44**, treatment of **31**, [(η^6-$MeC_6H_4{}^iPr$)Ru{(3-MeC_5H_3N)(5-MeC_5H_3N)(C_5H_4N)CH}][PF_6]$_2$, with OH^- led to the formation of a product that decomposed extremely rapidly and could not be characterised.

5.1.5 Summary

In contrast to earlier studies on the reactions of nucleophiles with (η^6-arene)Ru(II) complexes containing the [2.2] *para*cyclophane spectator ligand,[127-129,131] the treatment of complexes **24**, **28**, and **33-35** with nucleophiles in either THF or methanol led exclusively to the formation of monocationic cyclohexadienyl products. In all cases, with the exception of compound **44**, single nucleophilic addition to the η^6-bound arene ligand occurred *exo* to the metal, as was generally confirmed by infrared and ^{1}H NMR spectroscopy.

Unlike compound **32** which is unstable, compounds **36-42** are all yellow, air-stable solids, and their stability is undoubtedly attributed to the π-accepting ability of their tertiary phosphine ligands that relieve the build up of electron density associated with nucleophilic addition. Compounds **40** and **42** were further characterised by X-ray crystallography and η^5-coordination of the cyclohexadienyl ligand to the Ru(II) ion was confirmed, as was *exo* addition of the cyanide nucleophile in the latter case.

Compounds **37** and **40** were prepared by the reaction of **34** with H^- in methanol under ambient or refluxing conditions respectively, and were found

to be isomers. Computational investigation into the relative stabilities of the cations in **37** and **40** confirmed that the thermodynamically stable isomer (i.e. the cation in **40**) was the more stable by 83.5 kJ/mol. An isomeric relationship was also found to exist between compounds **36** and **39**, whose ^{1}H NMR spectra suggested that they had structures analogous to those of compounds **37** and **40** respectively.

Reaction of compound **28** with H^- led to the formation of two isomers, single nucleophilic addition having either occurred at the site *ortho* to the methyl or at the site *ortho* to the *iso*propyl substituent of the *para*-cymene ligand. However, treatment of **28** with OH^- led, *via* the deprotonation of the *iso*propyl substituent, to the formation of a single cyclohexadienyl product with an *exo*cyclic double bond.

5.2 Experimental

5.2.1 Instrumentation

As described in sub-section 3.2.1. In addition, DFT calculations were carried out by Dr. Nikolas Kaltsoyannis, using the Amsterdam Density Functional (ADF) program suite.[144,145] An ADF Type IV basis set was used for the Ru atom, i.e. the valence atomic orbitals were represented by uncontracted triple-zeta Slater-type orbitals. All other atoms were modelled with ADF Type III basis sets, which feature double-zeta valence STO's supplemented by a single polarisation function (of p symmetry for H and a d function for C, N, O and P). Non-relativistic frozen cores were employed for C (1s), N (1s), O (1s),

P (2p) and Ru (3d). The local density functional of Vosko, Wilk and Nusair[146] was employed in all calculations. Non-local (gradient) corrections were added using the ADF "postscf" facility in order to obtain improved values for the total molecular bonding energies. The non-local corrections employed were Becke's gradient correction[147] to the exchange part of the potential and the correlation correction due to Perdew.[148] A typical calculation took about 7 hours of CPU time on the EPSRC's "Columbus/Magellan" super-scalar central computing facility.

5.2.2 Materials

All reactions were carried out under a dinitrogen or argon atmosphere in degassed solvents using standard Schlenk line techniques. Methanol and tetrahydrofuran were pre-distilled over calcium hydride and sodium wire respectively. Compounds **23**, **24** and **28** were prepared as described in sub-section 4.2.3. All solvents and other reagents were obtained from the usual commercial sources.

5.2.3 Preparations

[(η^5-C_6H_7)Ru{(C_5H_4N)$_3$COEt}]PF_6, 32

Compound **24** (0.054 g, 0.071 mmol) was suspended in THF (15 cm^3) and treated with $NaBH_4$ (0.050 g, 1.3 mmol), resulting in an immediate colour change of the solution from yellow to dark brown. After stirring for 10 minutes at room temperature, water (15 cm^3) was added to the solution to destroy any remaining $NaBH_4$, and the mixture was extracted with dichloromethane (2 x 50

cm^3). The organic solvent was dried over Na_2SO_4, filtered and then *ca.* 90 % of the solvent was removed *in vacuo*. Addition of diethyl ether (5 cm^3) to the remaining solution led to the precipitation of **32** as a dark yellow solid (with exposure to air, the solid turned green within 2 hours). Satisfactory microanalytical data could not be obtained. MS (FAB): *m/z* 472 [M–PF_6], 443 [M–Et–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 245 K): Cyclohexadienyl ring; δ 2.05 (d, 1H, H_{exo}); δ 2.53 ({d,d}, 2H, H_c); δ 2.88 (m, 1H, H_{endo}); δ 4.69 ({d,d}, 2H, H_b); δ 5.80 (t, 1H, H_a). Metallated pyridyl rings; δ 7.23 ({d,d}, 2H, py-5-H); δ 7.86 ({d,d}, 2H, py-4-H); δ 7.95 (d, 2H, py-3-H); δ 8.70 (d, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.62 ({d,d}, 1H, py-5-H); δ 8.09 (d, 1H, py-3-H); δ 8.18 ({d,d}, 1H, py-4-H); δ 10.37 (d, 1H, py-6-H); δ 1.66 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.87 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C⎓C) 1623, 1463 (m); ν(P-F) 842 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru(PEt_3){(C_5H_4N)$_3$COEt}][PF_6]$_2$, 33

PEt_3 (0.13 cm^3, 0.88 mmol) was added to a solution of **23** (0.10 g, 0.15 mmol) in methanol (50 cm^3). After stirring for 40 minutes at room temperature the mixture was filtered through celite. Addition of a saturated methanolic solution of NH_4PF_6 to the filtrate, followed by removal of *ca.* 50 % of the solvent led to precipitation of **33** as a yellow solid. The solid was filtered, washed with water and diethyl ether, then air-dried. Yield: 0.10 g, 74 % (Yellow crystals of **33**•Me_2CO were grown from acetone prior to microanalysis. Found: C, 42.71; H, 4.87; N, 4.31. Calc. for $C_{30}H_{38}N_3ORuP_3F_{12}$•$Me_2CO$: C, 42.31; H, 4.74; N, 4.49 %). MS (FAB): *m/z* 471 [M–PEt_3–2PF_6], 426 [M–PEt_3–OEt–2PF_6]. ^{1}H NMR (d^6-acetone, 400 MHz, 295 K): δ 6.61 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.53 ({d,d}, 2H, py-5-H); δ 7.72 (d, 2H, py-3-H); δ 8.14 ({d,d}, 2H, py-4-

H); δ 9.09 (d, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.31 ({d,d}, 1H, py-5-H); δ 8.08 ({d,d}, 1H, py-4-H); δ 8.20 (d, 1H, py-6-H); δ 8.31 (d, 1H, py-3-H); δ 1.21 ({d,t}, 9H, $P(CH_2C\underline{H}_3)_3$); δ 2.34 ({d,q}, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.42 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.79 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{alkyl}) 2949 (w); ν(C⁼⁼C) 1603, 1462 (m); ν(P-F) 839 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru(PMe_2Ph){(C_5H_4N)$_3$COEt}][PF_6]$_2$, 34

Using an analogous method to the synthesis of **33**, PMe_2Ph (0.11 cm^3, 0.77 mmol) was reacted with **23** (0.10 g, 0.15 mmol) in a methanol solution to give **34** as a pale yellow solid. Yield: 0.135 g, 98 % (Yellow crystals of **34**•0.5Me_2CO were grown from acetone prior to microanalysis. Found: C, 43.84; H, 3.87; N, 4.58. Calc. for $C_{32}H_{34}N_3ORuP_3F_{12}$•0.5$Me_2CO$: C, 43.37; H, 4.03; N, 4.53 %). MS (FAB): *m/z* 754 [M–PF_6], 610 [M+H–2PF_6], 471 [M–PMe_2Ph–2PF_6], 426 [M–PMe_2Ph–OEt–2PF_6]. ^{1}H NMR (d^6-acetone, 500 MHz, 295 K): δ 6.51 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.22 ({d,d,d}, 2H, py-5-H); δ 7.76 ({d,d}, 2H, py-3-H); δ 8.05 ({d,d,d}, 2H, py-4-H); δ 8.60 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.33 ({d,d,d}, 1H, py-5-H); δ 8.08 ({d,d,d}, 1H, py-4-H, overlapping other signals); δ 8.32 (m, 2H, py-3,6-H); δ 2.27 (d, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 7.40, 7.52, 7.70 (m, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.40 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.79 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-$H_{aromatic}$) 3015 (w); ν(C-H_{alkyl}) 2924 (w); ν(C⁼⁼C) 1585, 1464 (m); ν(P-F) 839 (s, br) cm^{-1}.

[(η^6-C_6H_6)Ru($PMePh_2$){(C_5H_4N)$_3$COEt}][PF_6]$_2$, 35

Using an analogous method to the synthesis of **33**, $PMePh_2$ (0.18 cm^3, 0.96

mmol) was reacted with **23** (0.11 g, 0.17 mmol) in a methanol solution to give **35** as a yellow solid. Yield: 0.14 g, 86 % (Found: C, 46.15; H, 3.70; N, 4.30. Calc. for $C_{37}H_{36}N_3ORuP_3F_{12}$: C, 46.25; H, 3.78; N, 4.37 %). MS (FAB): *m/z* 817 [M+H–PF_6], 671 [M–2PF_6], 471 [M–$PMePh_2$–2PF_6]. ^{1}H NMR (d^6-acetone, 500 MHz, 295 K): δ 6.59 (s, 6H, C_6H_6). Metallated pyridyl rings; δ 7.09 ({d,d,d}, 2H, py-5-H); δ 7.43 ({d,d}, 2H, py-3-H); δ 7.94 ({d,d,d}, 2H, py-4-H); δ 8.63 ({d,d}, 2H, py-6-H). Non-metallated pyridyl ring; approx. δ 7.47 ({d,d,d}, 1H, py-5-H); δ 8.14 ({d,d,d}, 1H, py-4-H); δ 8.24 ({d,d}, 1H, py-3-H); δ 8.57 ({d,d}, 1H, py-6-H); δ 2.45 (d, 3H, $(C_6H_5)_2P(C\underline{H}_3)$); δ 7.52, 7.59, 7.71 (m, 10H, $(C_6\underline{H}_5)_2P(CH_3)$); δ 1.40 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.65 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{alkyl}) 2916 (w); ν(C⋯C) 1602, 1464 (m); ν(P-F) 844 (s, br) cm^{-1}.

[(η^5-C_6H_7)Ru(PEt_3){(C_5H_4N)$_3$COEt}]PF_6, 36

Compound **33** (0.060 g, 0.068 mmol) was suspended in methanol (40 cm^3) and treated with $NaBH_4$ (0.050 g, 1.3 mmol), resulting in an immediate brightening of the yellow solution. After stirring for 30 minutes at room temperature, water (5 cm^3) was added to the solution and the mixture was extracted with dichloromethane (2 x 50 cm^3). The organic solvent was dried over Na_2SO_4, filtered and then evaporated to dryness. The residue was recrystallised from absolute ethanol (5 cm^3), isolated by filtration and washed with diethyl ether to give **36** as a dark yellow solid. Yield: 0.018 g, 36 % (Found: C, 48.56; H, 5.00; N, 5.55. Calc. for $C_{30}H_{39}N_3ORuP_2F_6$: C, 49.04; H, 5.36; N, 5.72 %). MS (FAB): *m/z* 591 [M+H–PF_6], 473 [M+H–PEt_3–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Cyclohexadienyl ring; δ 1.97 (br, 1H, H_{exo}); δ 2.28 (m, 1H, H_{endo}); δ 2.51 (br, 2H, H_c); δ 3.81 (br, 2H, H_b); δ 5.93 (br, 1H, H_a).

Metallated pyridyl rings; δ 7.09 (br, 2H, py-5-H); δ 7.23 (br, 2H, py-3-H); δ 7.58 (br, 2H, py-4-H); δ 7.64 (br, 2H, py-6-H). Non-metallated pyridyl ring; δ 7.11 ({d,d}, 1H, py-5-H, overlapping other signals); δ 7.85 ({d,d}, 1H, py-4-H); δ 8.08 (m, 2H, py-3,6-H); δ 1.16 (br, 9H, $P(CH_2C\underline{H}_3)_3$); δ 2.13 (br, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.33 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.42 (br, 2H, $CH_3C\underline{H}_2O$).

^{1}H NMR ($CDCl_3$, 400 MHz, 215 K): Cyclohexadienyl ring; δ 1.95 ({d,d}, 1H, H_{exo}); δ 2.23 (m, 1H, H_{endo}); δ 2.50 ({d,d}, 2H, H_c); δ 3.79 ({d,d}, 2H, H_b); δ 5.95 ({m,br}, 1H, H_a). Metallated pyridyl rings; δ 7.08 ({d,d}, 2H, py-5-H); δ 7.18 (d, 2H, py-3-H); δ 7.58 (m, 4H, py-4,6-H). Non-metallated pyridyl ring; δ 7.14 ({d,d}, 1H, py-5-H); δ 7.86 ({d,d}, 1H, py-4-H); δ 8.06 (d, 1H, py-3-H); δ 8.09 (d, 1H, py-6-H); δ 1.12 ({d,t}, 9H, $P(CH_2C\underline{H}_3)_3$); δ 2.04 ({d,q}, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.34 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.34 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{endo}) 2939 (m); ν(C-H_{exo}) 2807 (m); ν(C⋯C) 1587, 1463 (m); ν(P-F) 841 (s) cm^{-1}.

[(η^5-C_6H_7)Ru(PMe_2Ph){(C_5H_4N)$_3$COEt}]PF_6, 37

Compound **34** (0.051 g, 0.057 mmol) was suspended in methanol (40 cm^3) and treated with $NaBH_4$ (0.050 g, 1.3 mmol), resulting in an immediate darkening of the yellow solution. After stirring for 30 minutes at room temperature, water (20 cm^3) was added to the solution and the mixture was extracted with dichloromethane (2 x 50 cm^3). The organic solvent was dried over Na_2SO_4, filtered and then *ca.* 90 % of the solvent was removed *in vacuo*. Addition of diethyl ether (5 cm^3) to the remaining solution led to the precipitation of **37** as a yellow solid. Yield: 0.026 g, 61 % (Found: C, 51.10; H, 4.54; N, 5.51. Calc. for $C_{32}H_{35}N_3ORuP_2F_6$: C, 50.92; H, 4.68; N, 5.57 %). MS

(FAB): *m/z* 610 [M–PF_6], 472 [M–PMe_2Ph–PF_6]. ^{1}H NMR ($CDCl_3$, 300 MHz, 295 K): Cyclohexadienyl ring; δ 1.80 ({d,d}, 1H, H_{exo}); δ 2.04 (m, 1H, H_{endo}); δ 2.25 (br, 2H, H_c); δ 3.71 (br, 2H, H_b); δ 5.86 (br, 1H, H_a). Metallated pyridyl rings; δ 6.84 ({(d,d),br}, 2H, py-5-H); δ 7.23 ({m,br}, 4H, py-3,6-H); δ 7.48 ({(d,d),br}, 2H, py-4-H). Non-metallated pyridyl ring; δ 7.14 ({d,d,d}, 1H, py-5-H); δ 7.86 ({d,d,d}, 1H, py-4-H); δ 8.12 ({d,br}, 1H, py-3-H); δ 8.20 ({d,d,d}, 1H, py-6-H); δ 2.11 (d, 6H, $(C_6H_5)P(C\underline{H}_3)_2$, overlapping other signals); δ 7.23 (overlapping other signals), 7.58 ({m,br}, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.31 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.46 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-$H_{aromatic}$) 3021 (w); ν(C-H_{endo}) 2914 (m); ν(C-H_{exo}) 2839 (m); ν(C⁼⁼C) 1583, 1475 (m); ν(P-F) 840 (s,br) cm^{-1}.

[(η^5-C_6H_7)Ru($PMePh_2$){(C_5H_4N)$_3$COEt}]PF_6, 38

Using an analogous method to the synthesis of **37**, compound **35** (0.044 g, 0.046 mmol) was reacted with $NaBH_4$ (0.051 g, 1.3 mmol) in a methanol solution to give **38** as a yellow solid. Yield: 0.014 g, 37 % (Found: C, 53.82; H, 4.64; N, 5.05. Calc. for $C_{37}H_{37}N_3ORuP_2F_6$: C, 54.41; H, 4.58; N, 5.15 %). MS (FAB): *m/z* 672 [M–PF_6], 472 [M–$PMePh_2$–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Cyclohexadienyl ring; δ 1.88 ({d,d}, 1H, H_{exo}); δ 2.18 (br, 2H, H_c); δ 2.42 (m, 1H, H_{endo}); δ 3.41 ({m,br}, 1H, H_a); δ 3.91 (br, 2H, H_b). Non-metallated pyridyl ring; δ 6.39 (d, 1H, py-3-H); δ 7.45 ({m,br}, 1H, py-5-H); δ 7.80 ({d,d}, 1H, py-4-H); δ 8.53 (d, 1H, py-6-H). δ 6.77 (br), 7.18 (br), 7.45 ({m,br}, overlapping other signals), 7.69 (m), 7.94 (br) (18H, metallated pyridyl rings and $(C_6\underline{H}_5)_2P(CH_3)$); δ 2.46 (d, 3H, $(C_6H_5)_2P(C\underline{H}_3)$, overlapping other signals); δ 1.28 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.89 (br, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{endo}) 2980

(m); ν(C-H_{exo}) 2820 (m); ν(C⁼C) approx. 1600, 1463 (m); ν(P-F) 841 (s) cm^{-1}.

[(η^5-C_6H_7)Ru(PEt_3){(C_5H_4N)$_3$COEt}]PF_6, 39

Compound **33** (0.051 g, 0.058 mmol) was suspended in methanol (30 cm^3) and treated with $NaBH_4$ (0.050 g, 1.3 mmol). After stirring for 3 hours at reflux, water (15 cm^3) was added to the bright yellow solution and the mixture was extracted with dichloromethane (2 x 50 cm^3). The organic solvent was dried over Na_2SO_4, filtered and then evaporated to dryness. The residue was recrystallised from absolute ethanol (5 cm^3), isolated by filtration and washed with diethyl ether to give **39** as a dark yellow solid. Yield: 0.020 g, 47 % (Found: C, 48.95; H, 5.06; N, 5.59. Calc. for $C_{30}H_{39}N_3ORuP_2F_6$: C, 49.04; H, 5.36; N, 5.72 %). MS (FAB): *m/z* 590 [M–PF_6], 472 [M–PEt_3–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 330 K): Cyclohexadienyl ring; δ 1.83 ({d,d}, 1H, H_{exo}); δ 2.15 (m, 1H, H_{endo}); δ 2.27 (br, 2H, H_c); δ 3.69 (br, 1H, H_a); δ 3.88 (br, 2H, H_b). Metallated pyridyl rings; δ 7.34 ({(d,d),br}, 2H, py-5-H); δ 7.90 (br, 2H, py-6-H); δ 7.94 ({(d,d),br}, 2H, py-4-H, overlapping other signals); δ 8.09 ({d,br}, 2H, py-3-H). Non-metallated pyridyl ring; δ 6.42 ({d,d}, 1H, py-3-H); δ 7.44 ({d,d,d}, 1H, py-5-H); δ 7.81 ({d,d,d}, 1H, py-4-H); δ 8.52 ({d,d}, 1H, py-6-H); δ 0.82 ({d,t}, 9H, $P(CH_2C\underline{H}_3)_3$); δ 1.68 ({d,q}, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.29 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.98 (q, 2H, $CH_3C\underline{H}_2O$).

^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Cyclohexadienyl ring; δ 1.81 ({d,d}, 1H, H_{exo}); δ 2.14 (m, 1H, H_{endo}); δ 2.28 (br, 2H, H_c); δ 3.56 (br, 1H, H_a); δ 3.84 (br, 2H, H_b). Metallated pyridyl rings; δ 7.35 (br, 2H, py-5-H); δ 7.83 ({m,br}, 2H, py-6-H); δ 7.95 (br, 2H, py-4-H); δ 8.07 (br, 2H, py-3-H). Non-metallated pyridyl

ring; δ 6.37 ({d,br}, 1H, py-3-H); δ 7.46 (br, 1H, py-5-H); δ 7.83 ({m,br}, 1H, py-4-H, overlapping other signals); δ 8.54 (br, 1H, py-6-H); δ 0.77 ({d,t}, 9H, $P(CH_2C\underline{H}_3)_3$); δ 1.66 ({d,q}, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.29 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.94 (br, 2H, $CH_3C\underline{H}_2O$).

^{1}H NMR ($CDCl_3$, 400 MHz, 215 K): Cyclohexadienyl ring; δ 1.76 ({d,d}, 1H, H_{exo}); δ 2.11 (m, 1H, H_{endo}); δ 2.20, 2.32 (br, 2H, H_c); δ 3.37 (br, 1H, H_a); δ 3.80 (br, 2H, H_b). Metallated pyridyl rings; δ 7.46, 7.52 ({d,d}, 2H, py-5-H); δ 7.77, 7.87 (d, 2H, py-6-H); δ 7.96 (br), 8.00 (d,d) (2H, py-4-H); δ 7.96 (br, overlapping other signals), 8.12 (d) (2H, py-3-H). Non-metallated pyridyl ring; δ 6.32 (d, 1H, py-3-H); δ 7.29 (br, 1H, py-5-H, overlapping solvent signal); δ 7.82 ({d,d}, 1H, py-4-H); δ 8.56 (d, 1H, py-6-H); δ 0.68 ({(d,t),br}, 9H, $P(CH_2C\underline{H}_3)_3$); δ 1.60 (br, 6H, $P(C\underline{H}_2CH_3)_3$); δ 1.31 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.70, 2.92 ({d,q}, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-H_{endo}) 2934 (m); ν(C-H_{exo}) 2809 (m); ν(C⋯C) 1583, 1462 (m); ν(P-F) 840 (s) cm^{-1}.

[(η^5-C_6H_7)Ru(PMe_2Ph){($C_5H_4N)_3COEt$}]PF_6, 40

Using an analogous method to the synthesis of **39**, compound **34** (0.086 g, 0.096 mmol) was reacted with $NaBH_4$ (0.050 g, 1.3 mmol) in refluxing methanol to give **40** as a dark yellow solid. Yield: 0.032 g, 44 % (Found: C, 50.91; H, 4.60; N, 5.44. Calc. for $C_{32}H_{35}N_3ORuP_2F_6$: C, 50.92; H, 4.68; N, 5.57 %). MS (FAB): *m/z* 610 [M–PF_6], 472 [M–PMe_2Ph–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 333 K): Cyclohexadienyl ring; δ 1.88 ({d,d}, 1H, H_{exo}); δ 2.09 (br, 2H, H_c); δ 2.32 (m, 1H, H_{endo}); δ 3.82 (br, 1H, H_a); δ 3.91 ({d,d}, 2H, H_b). Metallated pyridyl rings; δ 7.23 ({m,br}, 2H, py-5-H); δ 7.67 (br, 2H, py-6-H); δ 7.86

({(d,d),br}, 2H, py-4-H); δ 7.93 ({d,br}, 2H, py-3-H). Non-metallated pyridyl ring; δ 6.30 ({d,br}, 1H, py-3-H); δ 7.41 ({d,d,d}, 1H, py-5-H); δ 7.75 ({d,d,d}, 1H, py-4-H); δ 8.49 ({d,d,d}, 1H, py-6-H); δ 1.70 (d, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 6.70, 7.11, 7.23 (br, overlapping other signals) (m, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.23 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.88 ({q,br}, 2H, $CH_3C\underline{H}_2O$).

^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Cyclohexadienyl ring; δ 1.87 ({d,d}, 1H, H_{exo}); δ 2.10 (br, 2H, H_c); δ 2.31 (m, 1H, H_{endo}); δ 3.72 (br, 1H, H_a); δ 3.88 ({d,d}, 2H, H_b). Metallated pyridyl rings; δ 7.22 ({m,br}, 2H, py-5-H); δ 7.65 (br, 2H, py-6-H); δ 7.87 (br, 4H, py-3,4-H). Non-metallated pyridyl ring; δ 6.24 (d, 1H, py-3-H); δ 7.42 ({d,d}, 1H, py-5-H); δ 7.74 ({d,d}, 1H, py-4-H); δ 8.49 (d, 1H, py-6-H); δ 1.69 ({d,br}, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 6.63, 7.09, 7.22 (br, overlapping other signals) (m, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.23 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.73, 2.93 (br, 2H, $CH_3C\underline{H}_2O$).

^{1}H NMR ($CDCl_3$, 400 MHz, 233 K): Cyclohexadienyl ring; δ 1.85 ({d,d}, 1H, H_{exo}); δ 1.97, 2.14 ({d,d}, 2H, H_c); δ 2.31 (m,1H, H_{endo}); δ 3.60 ({m,br}, 1H, H_a); δ 3.86 ({d,d}, 2H, H_b). Metallated pyridyl rings; δ 7.20 (m,br), 7.35 (d,d) (2H, py-5-H); δ 7.57, 7.72 (d, 2H, py-6-H); δ 7.81 (d), 7.90 (m) (2H, py-3-H); δ 7.90 (m, 2H, py-4-H, overlapping other signals). Non-metallated pyridyl ring; δ 6.18 (d, 1H, py-3-H); δ 7.45 ({d,d}, 1H, py-5-H); δ 7.75 ({d,d}, 1H, py-4-H, overlapping other signals); δ 8.50 (d, 1H, py-6-H); δ 1.62, 1.70 (d, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 6.54, 7.06, 7.20 (br, overlapping other signals) (m, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.24 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.61, 2.87 ({d,q}, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν($C\text{-}H_{aromatic}$) 3030 (w); ν($C\text{-}H_{endo}$) 2975 (m); ν($C\text{-}H_{exo}$) 2785 (m); ν(C=C) 1582, 1462 (m); ν(P-F) 840 (s) cm^{-1}.

[(η^5-C_6H_6D)Ru(PMe_2Ph){($C_5H_4N)_3COEt$}]PF_6, 41

Using an analogous method to the synthesis of **39**, compound **34** (0.098 g, 0.11 mmol) was reacted with $NaBD_4$ (0.018 g, 0.43 mmol) in refluxing methanol to give **41** as a yellow solid. Yield: 0.040 g, 49 % (Found: C, 50.74; H, 4.17; N, 5.20. Calc. for $C_{32}H_{34}DN_3ORuP_2F_6$: C, 50.85; H, 4.54; N, 5.56 %). MS (FAB): *m/z* 611 [M–PF_6], 473 [M–PMe_2Ph–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Cyclohexadienyl ring; δ 2.06 (br, 2H, H_c); δ 2.29 (t, 1H, H_{endo}); δ 3.70 (br, 1H, H_a); δ 3.88 ({d,d}, 2H, H_b). Metallated pyridyl rings; δ 7.22 ({m,br}, 2H, py-5-H); δ 7.65 (br, 2H, py-6-H); δ 7.86 (br, 4H, py-3,4-H). Non-metallated pyridyl ring; δ 6.24 (d, 1H, py-3-H); δ 7.42 ({d,d}, 1H, py-5-H); δ 7.74 ({d,d}, 1H, py-4-H); δ 8.49 (d, 1H, py-6-H); δ 1.68 ({d,br}, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 6.63, 7.09, 7.22 (br, overlapping other signals) (m, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.23 (t, 3H, $C\underline{H}_3CH_2O$); δ 2.72, 2.92 (br, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-$H_{aromatic}$) 3030 (w); ν(C-H_{endo}) 2975 (m); ν(C-D_{exo}) 2048 (m); ν(C⎓C) 1583, 1463 (m); ν(P-F) 841 (s) cm^{-1}.

[(η^5-C_6H_6CN)Ru(PMe_2Ph){($C_5H_4N)_3COEt$}]PF_6, 42

Compound **34** (0.051 g, 0.057 mmol) was suspended in methanol (40 cm^3) and treated with KCN (0.049 g, 0.75 mmol). After stirring for 40 minutes at room temperature, the yellow solution was filtered through celite. The volume of the filtrate was reduced *in vacuo* until **42** precipitated out as a yellow solid. Yield: 0.026 g, 59 % (Found: C, 51.11; H, 4.33; N, 7.19. Calc. for $C_{33}H_{34}N_4ORuP_2F_6$: C, 50.83; H, 4.40; N, 7.19 %). MS (FAB): *m/z* 635 [M–PF_6], 497 [M–PMe_2Ph–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz, 295 K): Cyclohexadienyl ring; δ 2.69 (br, 2H, H_c); δ 2.89 (br, 1H, H_{endo}); δ 4.18 (br, 2H,

H_b); δ 6.39 (br, 1H, H_a). Metallated pyridyl rings; δ 6.99 ({(d,d),br}, 2H, py-5-H); δ 7.48 ({d,br}, 2H, py-3-H); δ 7.61 ({d,br}, 2H, py-6-H); δ 7.74 ({(d,d),br}, 2H, py-4-H). Non-metallated pyridyl ring; δ 7.26 ({d,d,d}, 1H, py-5-H); δ 8.01 ({d,d,d}, 1H, py-4-H); δ 8.23 ({d,br}, 1H, py-3-H); δ 8.31 ({d,d,d}, 1H, py-6-H); δ 2.16 (d, 6H, $(C_6H_5)P(C\underline{H}_3)_2$); δ 7.39, 7.89 ({m,br}, 5H, $(C_6\underline{H}_5)P(CH_3)_2$); δ 1.30 (t, 3H, $C\underline{H}_3CH_2O$); δ 3.61 (q, 2H, $CH_3C\underline{H}_2O$). IR (KBr): ν(C-$H_{aromatic}$) 3037 (w); ν(C-H_{endo}) 2940 (m); ν(C≡N) 2219 (m); ν(C⁻⁻C) 1587, 1478 (m); ν(P-F) 838 (s) cm^{-1}.

[(η^5-$MeC_6H_5{}^iPr$)Ru{$(C_5H_4N)_3CH$}]PF_6, 43

Compound **28** (0.055 g, 0.071 mmol) was suspended in THF (20 cm^3) and treated with $NaBH_4$ (0.043 g, 1.1 mmol), resulting in an immediate colour change of the solution from yellow to dark orange. After stirring for 15 minutes at room temperature, water (10 cm^3) was added to the solution and the mixture was extracted with dichloromethane (2 x 50 cm^3). The organic solvent was dried over Na_2SO_4, filtered and then *ca.* 90 % of the solvent was removed *in vacuo*. Addition of diethyl ether (5 cm^3) to the remaining solution led to precipitation of **43** as a yellow solid. Yield: 0.013 g, 29 % (Found: C, 50.67; H, 4.70; N, 7.72. Calc. for $C_{26}H_{28}N_3RuPF_6$: C, 49.67; H, 4.50; N, 6.69 %).* MS (FAB): *m/z* 484 [M–PF_6], 405 [M–H–py–PF_6]. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K): Isomer **A**, cyclohexadienyl ring; δ 1.08 (s, 3H, H_d); δ 1.29, 1.37 (d, 6H, H_e); δ 1.94 (d, 1H, H_c); δ 2.23 (d, 1H, H_{exo}); δ 2.41 (sept, 1H, H_f); δ 2.72 ({d,d}, 1H, H_{endo}); δ 4.40 (d, 1H, H_a); δ 5.75 (d, 1H, H_b). Isomer **B**, cyclohexadienyl ring; δ

* Microanalytical data were consistent with **43** being contaminated by *ca.* 10 % *tris*(2-pyridyl)methane. Very weak signals due to the contaminant were observed in the ^{1}H NMR spectrum.

0.14, 0.87 (d, 6H, H_e); δ 1.83 (sept, 1H, H_f); δ 1.97 (d, 1H, H_c); δ 2.17 (s, 3H, H_d); δ 2.30 (d, 1H, H_{exo}); δ 2.61 ({d,d}, 1H, H_{endo}); δ 4.40 (d, 1H, H_a, overlapping other signals); δ 5.74 (d, 1H, H_b, overlapping other signals). Isomers **A** and **B**; δ 7.07 (m), 7.51 (m), 7.71 (d,d), 8.02 (m), 8.11 (d), 8.34 (d,d), 8.44 (d), 8.60 (d), 8.90 (m), 10.05 (m) (pyridyl ring protons). Isomer **A**; δ 6.41 (s, 1H, CH). Isomer **B**; δ 6.42 (s, 1H, CH). IR (KBr): ν(C-H_{endo}) 2962 (m); ν(C-H_{exo}) 2797 (m); ν(C=C) 1602, 1471 (m); ν(P-F) 843 (s) cm^{-1}.

[(η^5-$MeC_6H_4CMe_2$)Ru{$(C_5H_4N)_3CH$}]PF_6, 44

Compound **28** (0.085 g, 0.11 mmol) was suspended in methanol (50 cm^3) and treated with NaOH (0.062 g, 1.6 mmol), resulting in an immediate darkening of the yellow solution. After stirring for 15 minutes at room temperature, the solution was filtered through celite and the filtrate was evaporated to dryness. Acetone (30 cm^3) was added to the residue and the resulting solution was filtered through celite and the filtrate was then evaporated to dryness. The residue was recrystallised from absolute ethanol (5 cm^3) and diethyl ether (2 cm^3), isolated by filtration and washed with diethyl ether to give **44**•H_2O as an orange solid. Yield: 0.014 g, 20 % (Found: C, 48.49; H, 3.88; N, 6.33. Calc. for $C_{26}H_{26}N_3RuPF_6 \bullet H_2O$: C, 48.44; H, 4.39; N, 6.52 %). MS (FAB): *m/z* 482 [M–PF_6]. ^{1}H NMR (d^6-acetone, 300 MHz, 295 K): δ 1.63 (s, 6H, $(CH_3)C_6H_4C(C\underline{H}_3)_2$); δ 2.45 (s, 3H, $(C\underline{H}_3)C_6H_4C(CH_3)_2$); δ 3.59 & 5.29 (AA'BB', 4H, $(CH_3)C_6\underline{H}_4C(CH_3)_2$). Equivalent metallated pyridyl rings; δ 7.36 ({d,d,d}, 2H, py-5-H); δ 7.96 ({d,d,d}, 2H, py-4-H); δ 8.02 ({d,d}, 2H, py-3-H); δ 9.22 ({d,d}, 2H, py-6-H). Unique metallated pyridyl ring; δ 7.70 ({d,d,d}, 1H, py-5-H);

δ 8.20 ({d,d,d}, 1H, py-4-H); δ 8.26 ({d,d}, 1H, py-3-H); δ 9.86 ({d,d}, 1H, py-6-H); δ 6.59 (s, 1H, CH). IR (KBr): ν(C-H_{alkyl}) 2924 (w); ν(C⁼⁼C) 1615, 1467 (m); ν(P-F) 840 (s) cm^{-1}.

Crystallographic characterisation of $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ (40)

Table 5.1 **Crystal data and structure refinement for 40.**

Formula	$C_{32}H_{35}F_6N_3OP_2Ru$	
Formula weight	754.71	
Temperature	100(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.8855(3) Å	α= 90°.
	b = 14.5479(4) Å	β= 106.3500(10)°.
	c = 17.6662(4) Å	γ= 90°.
Volume	3177.73(14) $Å^3$	
Z	4	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	0.661 mm^{-1}	
F(000)	1536	
Crystal size	0.30 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.50 to 27.50°.	
Index ranges	-16<=h<=15, -18<=k<=17, -22<=l<=22	
Reflections collected	35645	
Independent reflections	7280 [R(int) = 0.0360]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Scalepack	
Max. and min. transmission	0.9369 and 0.8264	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7280 / 0 / 446	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0675	
R indices (all data)	R1 = 0.0420, wR2 = 0.0712	
Extinction coefficient	0.0021(2)	
Largest diff. peak and hole	0.502 and -0.781 $e.Å^{-3}$	

Table 5.2 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for 40.**

	x	y	z	U(eq)
Ru(1)	6332(1)	8984(1)	2270(1)	11(1)
P(1)	6403(1)	8188(1)	3445(1)	13(1)
F(1)	12427(1)	9304(1)	4948(1)	34(1)
O(1)	9727(1)	8235(1)	1879(1)	17(1)
N(1)	6954(1)	7794(1)	1836(1)	13(1)
C(1)	6281(2)	7065(2)	1616(1)	15(1)
P(2)	13144(1)	8436(1)	4836(1)	20(1)
F(2)	13857(1)	7583(1)	4725(1)	49(1)
N(2)	7940(1)	9401(1)	2855(1)	13(1)
C(2)	6614(2)	6211(2)	1431(1)	17(1)
F(3)	14041(7)	8781(7)	5553(6)	100(5)
N(3)	8425(2)	10137(1)	1463(1)	17(1)
C(3)	7699(2)	6089(2)	1488(1)	18(1)
F(4)	12667(7)	7793(5)	5350(5)	66(2)
C(4)	8392(2)	6835(2)	1676(1)	17(1)
F(5)	12178(6)	8092(5)	4100(3)	62(3)
C(5)	7995(2)	7687(1)	1824(1)	13(1)
F(6)	13540(6)	9033(5)	4242(5)	84(3)
C(6)	8698(2)	8548(2)	1930(1)	14(1)
C(7)	8831(2)	9023(1)	2725(1)	13(1)
C(8)	9851(2)	9134(2)	3258(1)	19(1)
C(9)	9975(2)	9732(2)	3889(1)	23(1)
C(10)	9082(2)	10193(2)	3975(1)	21(1)
C(11)	8080(2)	9993(2)	3466(1)	16(1)
C(12)	8216(2)	9251(2)	1267(1)	14(1)
C(13)	7693(2)	8964(2)	505(1)	17(1)
C(14)	7352(2)	9626(2)	-79(1)	20(1)
C(15)	7544(2)	10547(2)	117(1)	21(1)
C(16)	8078(2)	10768(2)	893(1)	20(1)
C(17)	10427(2)	8893(2)	1658(1)	20(1)
C(18)	11526(2)	8441(2)	1811(2)	30(1)
C(19)	4301(2)	9582(2)	2304(1)	18(1)
C(20)	4552(2)	8837(2)	1785(1)	17(1)
C(21)	5024(2)	9088(2)	1188(1)	19(1)
C(22)	5648(2)	9907(2)	1260(1)	18(1)
C(23)	5860(2)	10387(2)	1993(1)	18(1)
C(24)	5362(2)	10098(2)	2569(1)	17(1)
C(25)	5490(2)	7216(2)	3355(1)	22(1)
C(26)	6077(2)	8838(2)	4228(1)	21(1)
C(27)	7720(2)	7681(2)	3936(1)	15(1)
C(28)	8086(2)	6921(2)	3602(1)	18(1)
C(29)	9115(2)	6566(2)	3935(1)	23(1)
C(30)	9790(2)	6963(2)	4608(1)	24(1)
C(31)	9433(2)	7708(2)	4951(1)	22(1)
C(32)	8410(2)	8073(2)	4617(1)	18(1)
F(3A)	14207(6)	8943(9)	5263(7)	97(4)
F(4A)	13098(12)	8104(8)	5679(6)	147(6)
F(5A)	12097(6)	7947(6)	4434(8)	133(5)
F(6A)	13238(8)	8833(7)	4053(4)	93(4)

Table 5.3 **Bond lengths [Å] and angles [°] for 40.**

Ru(1)-N(2)	2.1271(17)	N(3)-C(12)	1.342(3)
Ru(1)-N(1)	2.1394(17)	N(3)-C(16)	1.342(3)
Ru(1)-C(23)	2.147(2)	C(3)-C(4)	1.385(3)
Ru(1)-C(21)	2.169(2)	C(4)-C(5)	1.393(3)
Ru(1)-C(24)	2.199(2)	C(5)-C(6)	1.527(3)
Ru(1)-C(22)	2.209(2)	C(6)-C(7)	1.532(3)
Ru(1)-C(20)	2.221(2)	C(6)-C(12)	1.547(3)
Ru(1)-P(1)	2.3550(5)	C(7)-C(8)	1.394(3)
P(1)-C(25)	1.818(2)	C(8)-C(9)	1.388(3)
P(1)-C(26)	1.819(2)	C(9)-C(10)	1.376(3)
P(1)-C(27)	1.830(2)	C(10)-C(11)	1.381(3)
F(1)-P(2)	1.6083(15)	C(12)-C(13)	1.388(3)
O(1)-C(6)	1.429(2)	C(13)-C(14)	1.389(3)
O(1)-C(17)	1.442(3)	C(14)-C(15)	1.389(3)
N(1)-C(1)	1.355(3)	C(15)-C(16)	1.387(3)
N(1)-C(5)	1.356(3)	C(17)-C(18)	1.515(3)
C(1)-C(2)	1.383(3)	C(19)-C(20)	1.512(3)
P(2)-F(5A)	1.513(6)	C(19)-C(24)	1.514(3)
P(2)-F(6A)	1.536(6)	C(20)-C(21)	1.406(3)
P(2)-F(3)	1.539(9)	C(21)-C(22)	1.423(3)
P(2)-F(4)	1.547(7)	C(22)-C(23)	1.428(3)
P(2)-F(3A)	1.551(9)	C(23)-C(24)	1.411(3)
P(2)-F(6)	1.556(6)	C(27)-C(28)	1.397(3)
P(2)-F(4A)	1.582(8)	C(27)-C(32)	1.400(3)
P(2)-F(2)	1.5896(17)	C(28)-C(29)	1.390(3)
P(2)-F(5)	1.606(5)	C(29)-C(30)	1.386(3)
N(2)-C(7)	1.350(3)	C(30)-C(31)	1.383(3)
N(2)-C(11)	1.352(3)	C(31)-C(32)	1.389(3)
C(2)-C(3)	1.385(3)		

N(2)-Ru(1)-N(1)	89.57(7)	C(20)-Ru(1)-P(1)	94.20(6)
N(2)-Ru(1)-C(23)	90.81(8)	C(25)-P(1)-C(26)	100.87(11)
N(1)-Ru(1)-C(23)	142.95(7)	C(25)-P(1)-C(27)	102.63(10)
N(2)-Ru(1)-C(21)	144.77(8)	C(26)-P(1)-C(27)	103.35(10)
N(1)-Ru(1)-C(21)	90.95(7)	C(25)-P(1)-Ru(1)	116.19(8)
C(23)-Ru(1)-C(21)	68.45(8)	C(26)-P(1)-Ru(1)	117.02(8)
N(2)-Ru(1)-C(24)	102.42(7)	C(27)-P(1)-Ru(1)	114.64(7)
N(1)-Ru(1)-C(24)	167.99(7)	C(6)-O(1)-C(17)	117.87(16)
C(23)-Ru(1)-C(24)	37.86(8)	C(1)-N(1)-C(5)	117.50(18)
C(21)-Ru(1)-C(24)	78.89(8)	C(1)-N(1)-Ru(1)	117.45(13)
N(2)-Ru(1)-C(22)	109.33(7)	C(5)-N(1)-Ru(1)	124.82(14)
N(1)-Ru(1)-C(22)	107.85(7)	N(1)-C(1)-C(2)	123.7(2)
C(23)-Ru(1)-C(22)	38.23(8)	F(5A)-P(2)-F(6A)	92.3(6)
C(21)-Ru(1)-C(22)	37.93(9)	F(3)-P(2)-F(4)	92.5(6)
C(24)-Ru(1)-C(22)	67.74(8)	F(5A)-P(2)-F(3A)	178.8(6)
N(2)-Ru(1)-C(20)	166.88(7)	F(6A)-P(2)-F(3A)	88.6(6)
N(1)-Ru(1)-C(20)	103.55(7)	F(3)-P(2)-F(6)	93.5(6)
C(23)-Ru(1)-C(20)	78.93(8)	F(5A)-P(2)-F(4A)	92.0(7)
C(21)-Ru(1)-C(20)	37.34(8)	F(6A)-P(2)-F(4A)	175.1(7)
C(24)-Ru(1)-C(20)	64.46(8)	F(3A)-P(2)-F(4A)	87.1(7)
C(22)-Ru(1)-C(20)	67.23(8)	F(5A)-P(2)-F(2)	92.5(3)
N(2)-Ru(1)-P(1)	85.48(5)	F(6A)-P(2)-F(2)	89.2(4)
N(1)-Ru(1)-P(1)	89.61(5)	F(3)-P(2)-F(2)	91.7(3)
C(23)-Ru(1)-P(1)	127.35(6)	F(4)-P(2)-F(2)	86.5(3)
C(21)-Ru(1)-P(1)	129.74(6)	F(3A)-P(2)-F(2)	88.2(4)
C(24)-Ru(1)-P(1)	92.00(6)	F(6)-P(2)-F(2)	92.3(3)
C(22)-Ru(1)-P(1)	156.70(6)	F(4A)-P(2)-F(2)	93.1(3)

Table 5.3 **cont.**

F(3)-P(2)-F(5)	178.1(5)	C(10)-C(9)-C(8)	118.9(2)
F(4)-P(2)-F(5)	86.7(4)	C(9)-C(10)-C(11)	118.9(2)
F(6)-P(2)-F(5)	87.4(4)	N(2)-C(11)-C(10)	123.0(2)
F(2)-P(2)-F(5)	89.9(3)	N(3)-C(12)-C(13)	123.10(19)
F(5A)-P(2)-F(1)	87.7(3)	N(3)-C(12)-C(6)	115.52(17)
F(6A)-P(2)-F(1)	90.6(3)	C(13)-C(12)-C(6)	121.11(19)
F(3)-P(2)-F(1)	88.2(3)	C(12)-C(13)-C(14)	118.5(2)
F(4)-P(2)-F(1)	93.8(3)	C(15)-C(14)-C(13)	119.2(2)
F(3A)-P(2)-F(1)	91.5(4)	C(16)-C(15)-C(14)	118.2(2)
F(6)-P(2)-F(1)	87.4(3)	N(3)-C(16)-C(15)	123.4(2)
F(4A)-P(2)-F(1)	87.1(3)	O(1)-C(17)-C(18)	106.77(19)
F(2)-P(2)-F(1)	179.67(11)	C(20)-C(19)-C(24)	102.34(17)
F(5)-P(2)-F(1)	90.2(3)	C(21)-C(20)-C(19)	118.7(2)
C(7)-N(2)-C(11)	117.78(18)	C(21)-C(20)-Ru(1)	69.35(12)
C(7)-N(2)-Ru(1)	124.12(14)	C(19)-C(20)-Ru(1)	94.07(13)
C(11)-N(2)-Ru(1)	117.51(14)	C(20)-C(21)-C(22)	120.2(2)
C(1)-C(2)-C(3)	118.2(2)	C(20)-C(21)-Ru(1)	73.31(12)
C(12)-N(3)-C(16)	117.59(19)	C(22)-C(21)-Ru(1)	72.55(12)
C(4)-C(3)-C(2)	119.1(2)	C(21)-C(22)-C(23)	116.75(19)
C(3)-C(4)-C(5)	119.8(2)	C(21)-C(22)-Ru(1)	69.52(12)
N(1)-C(5)-C(4)	121.45(19)	C(23)-C(22)-Ru(1)	68.53(12)
N(1)-C(5)-C(6)	117.32(18)	C(24)-C(23)-C(22)	119.9(2)
C(4)-C(5)-C(6)	121.13(18)	C(24)-C(23)-Ru(1)	73.07(12)
O(1)-C(6)-C(5)	105.04(16)	C(22)-C(23)-Ru(1)	73.24(12)
O(1)-C(6)-C(7)	109.62(16)	C(23)-C(24)-C(19)	118.64(19)
C(5)-C(6)-C(7)	113.08(16)	C(23)-C(24)-Ru(1)	69.07(12)
O(1)-C(6)-C(12)	110.20(16)	C(19)-C(24)-Ru(1)	94.89(13)
C(5)-C(6)-C(12)	110.59(16)	C(28)-C(27)-C(32)	118.5(2)
C(7)-C(6)-C(12)	108.28(17)	C(28)-C(27)-P(1)	119.83(16)
N(2)-C(7)-C(8)	121.58(19)	C(32)-C(27)-P(1)	121.57(17)
N(2)-C(7)-C(6)	117.30(17)	C(29)-C(28)-C(27)	120.7(2)
C(8)-C(7)-C(6)	120.84(19)	C(30)-C(29)-C(28)	120.1(2)
C(9)-C(8)-C(7)	119.2(2)	C(31)-C(30)-C(29)	119.8(2)
		C(30)-C(31)-C(32)	120.4(2)
		C(31)-C(32)-C(27)	120.4(2)

Crystallographic characterisation of $[(\eta^5\text{-}C_6H_6CN)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$ (42)

Table 5.4 **Crystal data and structure refinement for 42.**

Formula	$C_{33}H_{34}F_6N_4OP_2Ru$	
Formula weight	779.72	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.129(2) Å b = 12.596(3) Å c = 13.980(3) Å	α = 112.34(3) °. β = 92.84(3) °. γ = 99.37(3) °.
Volume	1775.1(7) $Å^3$	
Z	2	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	0.595 mm^{-1}	
F(000)	792	
Crystal size	0.78 x 0.34 x 0.22 mm	
Theta range for data collection	2.52 to 26.06 °.	
Index ranges	0<=h<=13, -15<=k<=15, -17<=l<=17	
Reflections collected	7355	
Independent reflections	6977 [R(int) = 0.0721]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6968 / 0 / 424	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1173	
R indices (all data)	R1 = 0.0571, wR2 = 0.1341	
Largest diff. peak and hole	0.877 and -1.028 $e.Å^{-3}$	

Table 5.5 **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for 42.**

	x	y	z	U(eq)
Ru(1)	2764(1)	68(1)	7000(1)	31(1)
P(1)	2596(1)	666(1)	8808(1)	39(1)
O(1)	1988(3)	-3979(2)	5381(2)	47(1)
N(1)	3912(5)	3769(4)	6194(5)	85(2)
N(2)	3785(3)	-1217(3)	7078(2)	37(1)
N(3)	1081(3)	-1197(3)	6639(2)	34(1)
N(4)	1389(5)	-4757(4)	6916(4)	79(1)
C(1)	3685(4)	3200(4)	6672(4)	60(1)
C(2)	3368(4)	2422(4)	7249(4)	47(1)
C(3)	4240(3)	1585(4)	7160(3)	43(1)
C(4)	4198(4)	651(4)	6184(3)	47(1)
C(5)	3093(4)	188(4)	5470(3)	52(1)
C(6)	2027(4)	650(4)	5843(3)	49(1)
C(7)	2121(4)	1578(4)	6820(4)	47(1)
C(8)	2017(4)	-3013(3)	6359(3)	40(1)
C(9)	2341(6)	-3616(4)	4536(4)	62(1)
C(10)	2561(7)	-4659(5)	3648(5)	91(2)
C(11)	3380(4)	-2383(3)	6743(3)	41(1)
C(12)	4189(5)	-3131(4)	6751(4)	60(1)
C(13)	5412(5)	-2692(5)	7099(5)	68(1)
C(14)	5843(4)	-1481(4)	7462(4)	54(1)
C(15)	5014(4)	-789(4)	7440(3)	46(1)
C(16)	967(4)	-2372(3)	6261(3)	39(1)
C(17)	-184(4)	-3117(4)	5813(4)	53(1)
C(18)	-1232(4)	-2669(4)	5771(4)	54(1)
C(19)	-1122(4)	-1459(4)	6205(3)	48(1)
C(20)	27(3)	-761(4)	6627(3)	42(1)
C(21)	1625(4)	-3552(4)	7165(3)	44(1)
C(22)	1530(5)	-2758(4)	8099(3)	52(1)
C(23)	1191(7)	-3143(6)	8845(4)	83(2)
C(24)	938(7)	-4316(6)	8677(5)	86(2)
C(25)	1030(6)	-5131(5)	7713(5)	77(2)
C(26)	1062(4)	295(5)	9165(4)	59(1)
C(27)	3475(5)	0(5)	9499(4)	66(1)
C(28)	3081(4)	2242(4)	9625(3)	51(1)
C(29)	2233(6)	2989(5)	9846(5)	78(2)
C(30)	2635(9)	4191(6)	10472(6)	108(3)
C(31)	3828(10)	4643(7)	10887(6)	116(3)
C(32)	4672(8)	3924(7)	10659(6)	107(3)
C(33)	4314(5)	2720(5)	10033(4)	76(2)
P(2)	1849(1)	7930(1)	2114(1)	51(1)
F(1)	2808(4)	7755(4)	1276(3)	104(1)
F(2)	920(3)	8148(4)	2973(3)	104(1)
F(3)	1202(6)	8629(7)	1599(4)	184(3)
F(4)	2722(5)	9102(4)	2861(3)	141(2)
F(5)	2529(7)	7314(7)	2652(5)	202(4)
F(6)	994(6)	6807(5)	1333(5)	203(4)

Table 5.6 **Bond lengths [Å] and angles [°] for 42.**

Ru(1)-N(3)	2.151(3)	C(8)-C(11)	1.557(6)
Ru(1)-N(2)	2.155(3)	C(8)-C(21)	1.566(5)
Ru(1)-C(6)	2.189(4)	C(9)-C(10)	1.491(7)
Ru(1)-C(4)	2.196(4)	C(11)-C(12)	1.408(6)
Ru(1)-C(7)	2.232(4)	C(12)-C(13)	1.370(7)
Ru(1)-C(3)	2.240(4)	C(13)-C(14)	1.402(7)
Ru(1)-C(5)	2.245(4)	C(14)-C(15)	1.375(6)
Ru(1)-P(1)	2.3739(11)	C(16)-C(17)	1.413(6)
P(1)-C(27)	1.839(5)	C(17)-C(18)	1.384(6)
P(1)-C(26)	1.840(4)	C(18)-C(19)	1.391(6)
P(1)-C(28)	1.845(5)	C(19)-C(20)	1.386(6)
O(1)-C(8)	1.438(4)	C(21)-C(22)	1.330(6)
O(1)-C(9)	1.468(5)	C(22)-C(23)	1.353(7)
N(1)-C(1)	1.160(7)	C(23)-C(24)	1.382(9)
N(2)-C(11)	1.349(5)	C(24)-C(25)	1.369(9)
N(2)-C(15)	1.379(5)	C(28)-C(33)	1.401(7)
N(3)-C(16)	1.350(5)	C(28)-C(29)	1.404(7)
N(3)-C(20)	1.375(5)	C(29)-C(30)	1.411(9)
N(4)-C(21)	1.398(6)	C(30)-C(31)	1.360(12)
N(4)-C(25)	1.416(7)	C(31)-C(32)	1.375(12)
C(1)-C(2)	1.501(6)	C(32)-C(33)	1.408(9)
C(2)-C(3)	1.522(6)	P(2)-F(5)	1.523(5)
C(2)-C(7)	1.538(6)	P(2)-F(6)	1.544(5)
C(3)-C(4)	1.415(6)	P(2)-F(3)	1.565(5)
C(4)-C(5)	1.433(6)	P(2)-F(4)	1.573(4)
C(5)-C(6)	1.440(6)	P(2)-F(2)	1.597(3)
C(6)-C(7)	1.405(6)	P(2)-F(1)	1.601(4)
C(8)-C(16)	1.553(5)		

N(3)-Ru(1)-N(2)	90.09(12)	C(27)-P(1)-C(26)	99.7(3)
N(3)-Ru(1)-C(6)	87.75(14)	C(27)-P(1)-C(28)	102.3(2)
N(2)-Ru(1)-C(6)	139.3(2)	C(26)-P(1)-C(28)	103.2(2)
N(3)-Ru(1)-C(4)	138.94(14)	C(27)-P(1)-Ru(1)	115.8(2)
N(2)-Ru(1)-C(4)	88.68(14)	C(26)-P(1)-Ru(1)	116.5(2)
C(6)-Ru(1)-C(4)	67.6(2)	C(28)-P(1)-Ru(1)	116.92(14)
N(3)-Ru(1)-C(7)	102.02(13)	C(8)-O(1)-C(9)	113.5(3)
N(2)-Ru(1)-C(7)	166.40(13)	C(11)-N(2)-C(15)	117.4(3)
C(6)-Ru(1)-C(7)	37.0(2)	C(11)-N(2)-Ru(1)	127.5(2)
C(4)-Ru(1)-C(7)	78.1(2)	C(15)-N(2)-Ru(1)	114.9(3)
N(3)-Ru(1)-C(3)	165.44(13)	C(16)-N(3)-C(20)	117.5(3)
N(2)-Ru(1)-C(3)	103.00(13)	C(16)-N(3)-Ru(1)	126.3(2)
C(6)-Ru(1)-C(3)	78.2(2)	C(20)-N(3)-Ru(1)	115.1(2)
C(4)-Ru(1)-C(3)	37.2(2)	C(21)-N(4)-C(25)	117.1(5)
C(7)-Ru(1)-C(3)	64.3(2)	N(1)-C(1)-C(2)	177.6(6)
N(3)-Ru(1)-C(5)	103.93(14)	C(1)-C(2)-C(3)	113.8(4)
N(2)-Ru(1)-C(5)	104.3(2)	C(1)-C(2)-C(7)	113.3(4)
C(6)-Ru(1)-C(5)	37.9(2)	C(3)-C(2)-C(7)	102.1(3)
C(4)-Ru(1)-C(5)	37.6(2)	C(4)-C(3)-C(2)	117.9(4)
C(7)-Ru(1)-C(5)	67.0(2)	C(4)-C(3)-Ru(1)	69.7(2)
C(3)-Ru(1)-C(5)	66.9(2)	C(2)-C(3)-Ru(1)	94.8(2)
N(3)-Ru(1)-P(1)	90.43(9)	C(3)-C(4)-C(5)	120.6(4)
N(2)-Ru(1)-P(1)	89.55(9)	C(3)-C(4)-Ru(1)	73.1(2)
C(6)-Ru(1)-P(1)	131.08(13)	C(5)-C(4)-Ru(1)	73.1(2)
C(4)-Ru(1)-P(1)	130.59(12)	C(4)-C(5)-C(6)	116.2(4)
C(7)-Ru(1)-P(1)	96.45(13)	C(4)-C(5)-Ru(1)	69.3(2)
C(3)-Ru(1)-P(1)	95.96(11)	C(6)-C(5)-Ru(1)	69.0(2)
C(5)-Ru(1)-P(1)	159.80(12)	C(7)-C(6)-C(5)	120.5(4)

Table 5.6 **cont.**

C(7)-C(6)-Ru(1)	73.1(2)	C(22)-C(21)-C(8)	113.8(4)
C(5)-C(6)-Ru(1)	73.2(2)	N(4)-C(21)-C(8)	122.7(4)
C(6)-C(7)-C(2)	117.9(4)	C(21)-C(22)-C(23)	117.9(5)
C(6)-C(7)-Ru(1)	69.8(2)	C(22)-C(23)-C(24)	123.0(5)
C(2)-C(7)-Ru(1)	94.7(2)	C(25)-C(24)-C(23)	118.9(5)
O(1)-C(8)-C(16)	108.5(3)	C(24)-C(25)-N(4)	119.5(5)
O(1)-C(8)-C(11)	107.7(3)	C(33)-C(28)-C(29)	118.5(5)
C(16)-C(8)-C(11)	123.5(3)	C(33)-C(28)-P(1)	120.4(4)
O(1)-C(8)-C(21)	106.8(3)	C(29)-C(28)-P(1)	121.1(4)
C(16)-C(8)-C(21)	103.9(3)	C(28)-C(29)-C(30)	119.6(6)
C(11)-C(8)-C(21)	105.3(3)	C(31)-C(30)-C(29)	121.5(7)
O(1)-C(9)-C(10)	108.4(4)	C(30)-C(31)-C(32)	119.4(7)
N(2)-C(11)-C(12)	121.0(4)	C(31)-C(32)-C(33)	121.1(7)
N(2)-C(11)-C(8)	124.6(3)	C(28)-C(33)-C(32)	119.9(7)
C(12)-C(11)-C(8)	114.4(4)	F(5)-P(2)-F(3)	176.8(5)
C(13)-C(12)-C(11)	120.8(4)	F(6)-P(2)-F(3)	87.5(5)
C(12)-C(13)-C(14)	118.9(4)	F(5)-P(2)-F(4)	86.9(4)
C(15)-C(14)-C(13)	118.0(4)	F(6)-P(2)-F(4)	176.8(4)
C(14)-C(15)-N(2)	123.9(4)	F(3)-P(2)-F(4)	89.8(4)
N(3)-C(16)-C(17)	120.8(4)	F(5)-P(2)-F(2)	89.7(3)
N(3)-C(16)-C(8)	124.4(3)	F(6)-P(2)-F(2)	93.5(3)
C(17)-C(16)-C(8)	114.6(3)	F(3)-P(2)-F(2)	90.4(3)
C(18)-C(17)-C(16)	121.2(4)	F(4)-P(2)-F(2)	88.3(2)
C(17)-C(18)-C(19)	117.9(4)	F(5)-P(2)-F(1)	90.5(3)
C(20)-C(19)-C(18)	118.9(4)	F(6)-P(2)-F(1)	88.4(3)
N(3)-C(20)-C(19)	123.6(4)	F(3)-P(2)-F(1)	89.3(3)
C(22)-C(21)-N(4)	123.5(4)	F(4)-P(2)-F(1)	89.7(2)
		F(2)-P(2)-F(1)	178.0(3)

Appendix I

List of compound numbers

1. *Tris*(2-pyridyl)methanol

2. *Tris*(2-pyridyl)chloromethane

3. *Tris*(2-pyridyl)ethoxymethane

4. *Tris*(2-pyridyl)methane

5. (5-Methyl-2-pyridyl)*bis*(2-pyridyl)methanol

6. (6-Methyl-2-pyridyl)*bis*(2-pyridyl)methanol

7. (6-Methyl-2-pyridyl)*bis*(2-pyridyl)chloromethane

8. (6-Methyl-2-pyridyl)*bis*(2-pyridyl)ethoxymethane

9. (3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methanol

10. (3-Methyl-2-pyridyl)(5-methyl-2-pyridyl)(2-pyridyl)methane

11. $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}]PF_6$

12. $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COH\}][PF_6]_2$

13. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(C_5H_4N)_3CO\}]PF_6$

14. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(C_5H_4N)_3COH\}][PF_6]_2$

15. $[\{(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}\}_2Ag][PF_6]_3$

16. $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3CO\}PdCl_2]PF_6$

17. $[(\eta^6\text{-}C_6H_6)Ru\{(5\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}][PF_6]_2$

18. $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2COH\}][PF_6]_2$

19. $[(\eta^6\text{-}C_6H_6)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$

20. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CO\}]PF_6$

21. $[(\eta^6\text{-}C_6H_6)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)COH\}][PF_6]_2$

22. $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3CCl\}]PF_6$

23. $[(\eta^6\text{-}C_6H_6)RuCl\{(C_5H_4N)_3COEt\}]PF_6$

24. $[(\eta^6\text{-}C_6H_6)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$

25. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)RuCl\{(C_5H_4N)_3COEt\}]PF_6$

26. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(C_5H_4N)_3COEt\}][PF_6]_2$

27. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)RuCl\{(C_5H_4N)_3CH\}]PF_6$

28. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(C_5H_4N)_3CH\}][PF_6]_2$

29. $[(\eta^6\text{-}C_6H_6)RuCl\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2CCl\}]PF_6$

30. $[(\eta^6\text{-}C_6H_6)RuCl\{(6\text{-}MeC_5H_3N)(C_5H_4N)_2COEt\}]PF_6$

31. $[(\eta^6\text{-}MeC_6H_4{}^{i}Pr)Ru\{(3\text{-}MeC_5H_3N)(5\text{-}MeC_5H_3N)(C_5H_4N)CH\}][PF_6]_2$

32. $[(\eta^5\text{-}C_6H_7)Ru\{(C_5H_4N)_3COEt\}]PF_6$

33. $[(\eta^6\text{-}C_6H_6)Ru(PEt_3)\{(C_5H_4N)_3COEt\}][PF_6]_2$

34. $[(\eta^6\text{-}C_6H_6)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}][PF_6]_2$

35. $[(\eta^6\text{-}C_6H_6)Ru(PMePh_2)\{(C_5H_4N)_3COEt\}][PF_6]_2$

36. $[(\eta^5\text{-}C_6H_7)Ru(PEt_3)\{(C_5H_4N)_3COEt\}]PF_6$

37. $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$

38. $[(\eta^5\text{-}C_6H_7)Ru(PMePh_2)\{(C_5H_4N)_3COEt\}]PF_6$

39. $[(\eta^5\text{-}C_6H_7)Ru(PEt_3)\{(C_5H_4N)_3COEt\}]PF_6$

40. $[(\eta^5\text{-}C_6H_7)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$

41. $[(\eta^5\text{-}C_6H_6D)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$

42. $[(\eta^5\text{-}C_6H_6CN)Ru(PMe_2Ph)\{(C_5H_4N)_3COEt\}]PF_6$

43. $[(\eta^5\text{-}MeC_6H_5{}^{i}Pr)Ru\{(C_5H_4N)_3CH\}]PF_6$

44. $[(\eta^5\text{-}MeC_6H_4CMe_2)Ru\{(C_5H_4N)_3CH\}]PF_6$

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