Thiophene Complexes of Ruthenium and Osmium

A thesis presented to the University of London in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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To my mother and father, for all their labours.

"The pictures I contemplate painting would constitute a halfway state and an attempt to point out the direction of the future, without arriving there completely"

- Jackson Pollock

ABSTRACT

This thesis describes the synthesis, characterisation and reactivity of a series η^5-coordinated thiophene complexes of ruthenium and osmium metal centres. Chapter 1 reviews the background to this chemistry and includes a discussion on the motivation behind this research. The coordination chemistry relating to mononuclear transition metal complexes of thiophenes are reviewed, along with an extensive examination of the synthesis and reactivity of mononuclear ruthenium and osmium complexes containing thiophenes.

Chapter 2 describes an examination of the coordination chemistry of the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ dimer. The synthesis and characterisation of a series of novel complexes of η^5-tetramethylthiophene-ruthenium(II) containing mono-, bi- and tri-dentate coligands are described. The compounds $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$, $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)][PF_6]_2$, $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ and $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ were characterised crystallographically.

Chapter 3 reports an investigation into the nucleophilic reactivity of a series of tetramethylthiophene complexes, $[Ru(\eta^5\text{-}C_4Me_4S)(L_3)]^{2+}$ (L_3 = $HC(Pz)_3$, $[9]aneS_3$, [2.2]-*para*cyclophane). In general these complexes undergo nucleophilic addition reactions, in which *exo*-attack occurs at the carbon of the '2' position forming an η^4-thiopheneyl complex of the type $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}Nuc)(L_3)]^+$. The crystal structures of $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)([9]aneS_3)][PF_6]$ and $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)([9]aneS_3)][PF_6]$ are presented.

Chapter 4 describes the synthesis and reactivity of a series of mixed sandwich compounds of the type $[Os(\eta^5\text{-}Th)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ (Th = C_4H_4S, 2,5-$Me_2C_4H_2S$, C_4Me_4S). These compounds were found not to react cleanly with nucleophiles, but did react via base hydrolysis to give acyl-thiolate complexes of the type $[Os(\sigma,\eta^3\text{-}SC_3R_3C(O)R)(\eta^6\text{-}p\text{-cymene})]$. The compound $[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ was characterised crystallographically.

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TABLE OF CONTENTS

ABBREVIATIONS

HDS	Hydrodesulfurisation
DBT	Dibenzothiophene
BT	Benzothiophene
dppe	1,2-*bis*(diphenylphosphino)ethane
(S,S)-Chiraphos	(2S, 3S)-*bis*(diphenylphosphanyl)butane
Me	Methyl (CH_3)
Et	Ethyl (CH_2CH_3)
Ph	Phenyl (C_6H_5)
Cp	Cyclopentadiene ($C_5H_5^-$)
Cp*	Pentamethylcyclopentadienyl ($C_5Me_5^-$)
THF	Tetrahydrofuran (C_4H_8O)
Th	Generic symbol for thiophenes (unless otherwise stated)
DMT	Dimethylthiophene (2,5-$Me_2C_4H_2S$)
TMT	Tetramethylthiophene (2,3,4,5-Me_4C_4S)
p-cymene	1-methyl-4-iso-propyl-benzene ($C_{10}H_{14}$)
Tth	2,2':5',2"-terthiophene
Qth	2,2':5',2":5",2"'-quaterthiophene
Me_2Tth	5,5"-dimethyl-2,2':5',2"-terthiophene
Bipy	2,2'-bipyridyl ($C_{10}H_8N_2$)
Pz	Pyrazolyl ($C_3N_2H_3$)
Pz*	3,5-dimethylpyrazolyl ($C_3N_2H_7$)
[9]aneS_3	1,4,7-trithiacyclononane ($C_6H_{12}S_3$)
[9]aneS_2N	1-aza-4,7-dithiacyclononane ($C_6H_{13}S_2N$)

[2.2]-*para*cyclophane	Tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene ($C_{16}H_{16}$)
Nuc	Nucleophile
h	Hour/s
min	Minutes
NMR	Nuclear magnetic resonance
COSY	Correlated spectroscopy
DEPT	Distortionless enhancement by polarisation transfer
HETCOR	Heteronuclear shift correlation
ppm	Parts per million
br	Broad
m	Multiplet
s	Singlet
d	Doublet
t	Triplet
q	Quartet
dd	Doublet of doublets
sept	Septet
IR	Infrared
s	Strong
m	Medium
w	Weak
MS	Mass spectroscopy
FAB	Fast atom bombardment
EI	Electron impact

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

This thesis is being written at a time when mankind is becoming increasingly concerned with the effects of industrialisation on the world's ecology. A plethora of environmental issues are currently affecting the biosphere: photochemical smog, depletion of the ozone layer, acid rain, the greenhouse effect. These are just some of the consequences associated with the technological advances made by humanity. Governments throughout the world are continuing to act to minimise the effects of environmental pollutants through legislative processes.

The petrochemical industry has been confronted with stringent directives to produce more environmentally sound fuels; in particular there is a requirement to reduce the sulfur and nitrogen content of fuels.[1,2] These heteroatom impurities are generally found as constituents of organic compounds in crude oil. If these contaminants are not removed, combustion will generate the environmentally damaging oxides of sulfur and nitrogen responsible for some of the phenomena listed above. These heteroatom contaminants also act as catalyst poisons; several steps of petrochemical refining depend heavily on catalysts, and damaging them causes major economic and processing problems.[3]

1.2 THE HYDRODESULFURISATION PROCESS

The process by which sulfur atom contaminants are removed from their parent organic compounds is termed hydrodesulfurisation (HDS). The industrial process is achieved by treatment of the feedstocks with hydrogen gas (up to

200 atm pressure) over a sulfided transition metal catalyst at temperatures in the region of 300-450 °C (Equation 1.1).[1,4] This reaction produces a range of

$$\text{ORGANOSULFUR COMPOUNDS} \xrightarrow[\substack{H_2\ (200\ ATM)\\ 300\text{-}450\ ^{o}C}]{\text{CATALYST}} \text{HYDROCARBONS} + H_2S$$

Equation 1.1

useful hydrocarbons and H_2S gas,[4] which can then be removed as elemental sulfur *via* the Claus process.[5] The scale of petrochemical operations, (26 million barrels of feedstock are processed per day world-wide - 1995 figures),[6] makes the HDS process one of the most important chemical reactions currently being performed.[1,7]

The catalyst generally used in the HDS of petroleum feedstocks consists of molybdenum disulfide, promoted with the addition of either cobalt or nickel, supported on Al_2O_3. Other metals (osmium, ruthenium, iridium and rhodium) are known to be better catalysts, although due to the availability and low cost of molybdenum it is the catalyst of choice in an industrial context.[7,8]

The role of the catalyst support should not be ignored, as it also plays a conspicuous role in HDS activity and selectivity. For example ruthenium supported on alumina[9,10] is found to have different HDS properties than ruthenium supported on carbon (supports impregnated using $RuCl_3.3H_2O$).[11] A recent communication combined the high activity of ruthenium and the unique properties of a new support, magnesium fluoride, to develop a novel catalyst, (Ru/MgF_2 1.61 %wt; impregnated using $Ru_3(CO)_{12}$), which showed unprecedented activity and selectivity toward HDS.[12]

The general types of organosulfur compounds commonly found in crude oil are shown in Figure 1.1.[1] These compounds are present as mixtures and there are

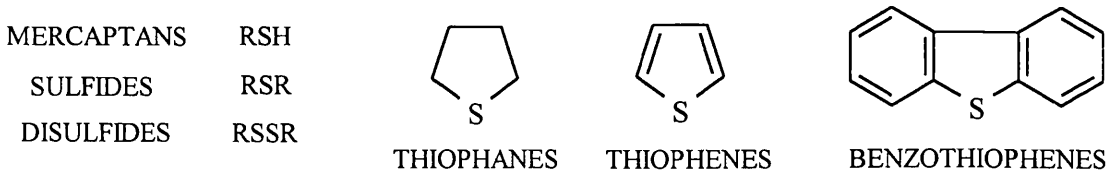


Figure 1.1: Classes of organosulfur compounds in crude oil.

varying degrees of carbon side chain substitution (*i.e.* thiophene, methylthiophene, dimethylthiophene, tetramethylthiophene *etc*...), and the precise composition is a function of the source of the crude oil.[3]

Current HDS technology can adequately desulfurise aliphatic and acyclic sulfur components. However thiophenes and benzothiophenes require more strenuous conditions of HDS, due to the stability imparted to them by their aromaticity.[8,13] For this reason, and to address the more demanding recent clean air regulations, it is thiophenes and related molecules that have been the focus of most HDS studies.[13]

1.3 THE COORDINATION CHEMISTRY OF THIOPHENES

Work relating to the HDS process has primarily been concentrated in modelling thiophenic substrates. Numerous studies have been conducted both on metal surfaces and on discrete organometallic compounds in order to elucidate mechanistic details of the HDS process. Many of the aspects of this chemistry have been reviewed in a number of papers.[1,3,7,8,14-17] The following discussion will primarily focus on the organometallic chemistry of mononuclear thiophene complexes and no direct attempt will be made to discuss the chemistry

associated with complexes of benzothiophenes or dibenzothiophenes; nor will the discussion consider the cluster chemistry allied to thiophenes.

The transition metal coordination chemistry of thiophenes has received considerable attention in recent years; such that six distinct binding modes have been established (Figure 1.2). These will be discussed in sections A to F below: -

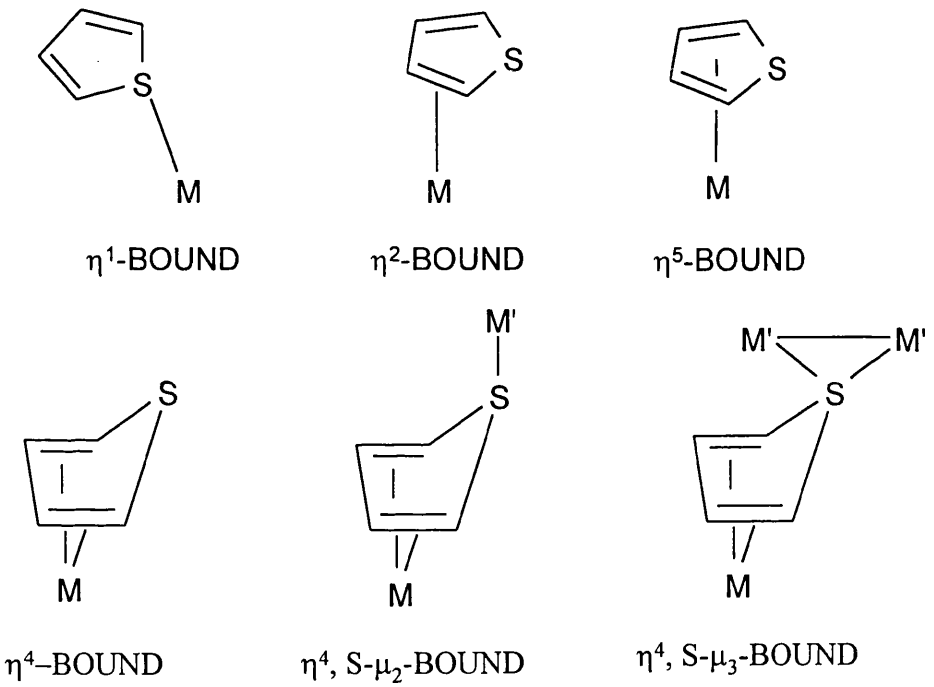


Figure 1.2: Known types of thiophene binding to metals.

A) η^1-BOUND THIOPHENE COMPLEXES

When compared to sulfides (dialkyl, aryl-alkyl) or even tetrahydrothiophene complexes, relatively few well-characterised S-bound thiophene complexes are known.[14] The reason for this lies with the poor donor ability of the thiophene sulfur atom, indeed many research groups have noted that η^1-thiophenes are very weakly coordinating as ligands, and many attempts to prepare such

complexes have failed.[15] Even for the complexes that have been prepared the thiophene may be easily displaced by coordinating solvents such as CH_3NO_2.[18-20]

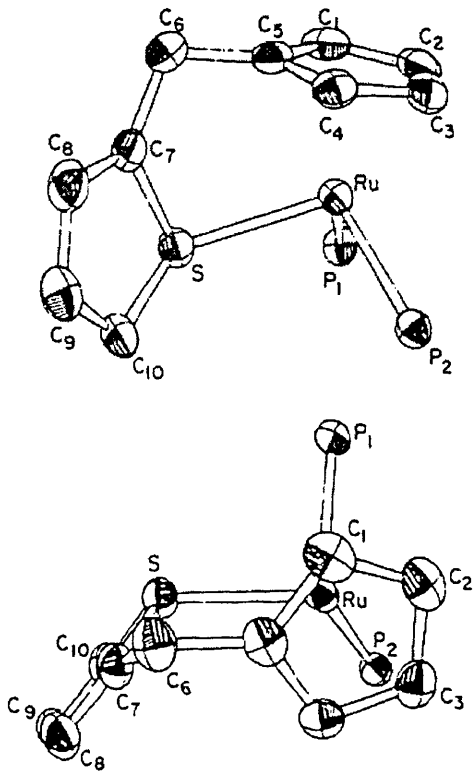


Figure 1.3: Two views of the cation in [Ru(η^5,η^1-$C_5H_4CH_2C_4H_3S$)(PPh_3)$_2$][BPh_4] 1 phenyl rings have been omitted for clarity.[21]

The first structurally characterised compound of this type was [Ru(η^5,η^1-$C_5H_4CH_2C_4H_3S$)(PPh_3)$_2$][BPh_4] **1** (Figure 1.3).[21] In **1** the thiophene is bound to the ruthenium metal centre *via* the sulfur atom although this adduct is stabilised by linking the thiophene ring to an η^5-coordinated cyclopentadienyl ring through a methylene functionally. The X-ray structure was important because it definitively established that the ruthenium is located outside the thiophene ring plane, such that the sulfur is pyramidal (see Figure 1.3).[21]

All structurally characterised η^1-thiophene complexes (including η^1-BT and η^1-DBT complexes) share this bonding characteristic, of a trigonal pyramidal sulfur

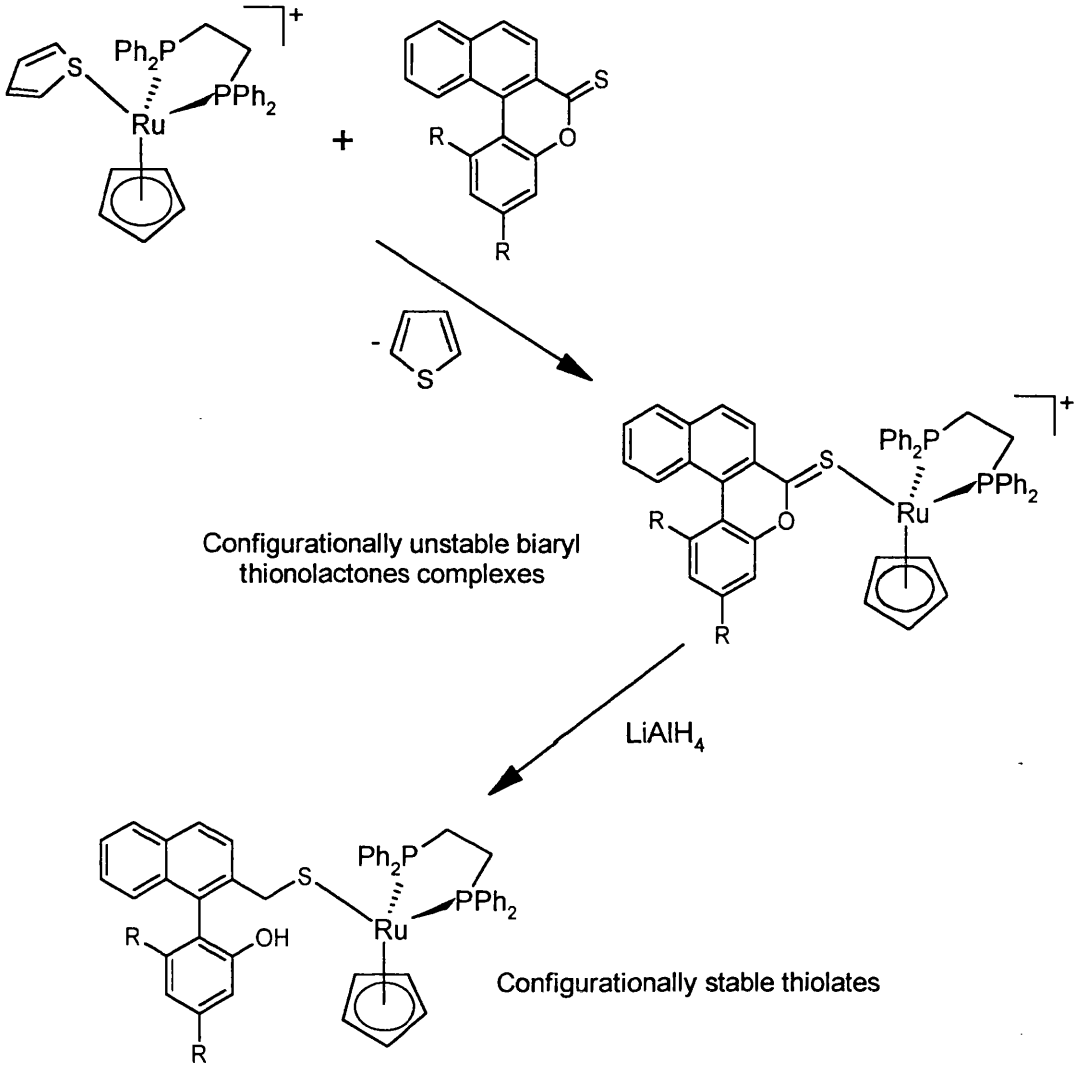
that is approximately sp^3 hybridised.[15] This is clearly illustrated by examining the tilt angle, the angle between the metal-sulfur-ring plane vector. This angle would be 180 ° if the metal-thiophene plane were perpendicular, but as can be seen from Table 1.1, the tilt angles for all structurally characterised η^1-thiophenes are considerably smaller than this.[15]

Table 1.1: Tilt angles for η^1-thiophene complexes.

COMPOUND	TILT ANGLE (°)	REFERENCE
$[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(CO)_2]$	140.4	22
$[Ru(\eta^5,\eta^1\text{-}C_5H_4CH_2C_4H_3S)(PPh_3)_2][BPh_4]$	126	21
$[Ru(6\text{-}(2\text{-thienyl})\text{-}2,2'\text{-bipyridine})_2Cl][BF_4].CH_2Cl_2$	123.6	23,24
$[Ru(\eta^1\text{-}2\text{-}MeC_4H_3S)(\eta^5\text{-}C_5H_5)(CO)(PPh_3)][BF_4]$	119.1	25
$[Re(\eta^1\text{-}3\text{-}MeBT)(\eta^5\text{-}C_5Me_5)(CO)_2]$	131	26
$[Ir(\eta^1\text{-}DBT)(\eta^5\text{-}C_5Me_5)Cl_2]$	128	27
$[Fe(\eta^1\text{-}DBT)(\eta^5\text{-}C_5H_5)(CO)_2][BF_4]$	119.4	18

There are a number of examples in which η^1-thiophene complexes react to yield a new complex where the thiophene has adopted a different binding mode (*vide infra*). The substitutional lability of η^1-thiophene complexes greatly limits the study of their reactivity,[15] but the lability has nevertheless been utilised in organic synthesis. For example (Scheme 1.1) biaryl-thionolactones can easily be introduced as a ligand into $[Ru(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)(dppe)][BF_4]$ **2** by the displacement of the thiophene ligand, consequently allowing the metal mediated double nucleophilic addition of hydride to the coordinated thionolactone, converting it into an axially chiral racemic thiolate (Scheme 1.1).[28] This work was further extended to enantioselective organic synthesis

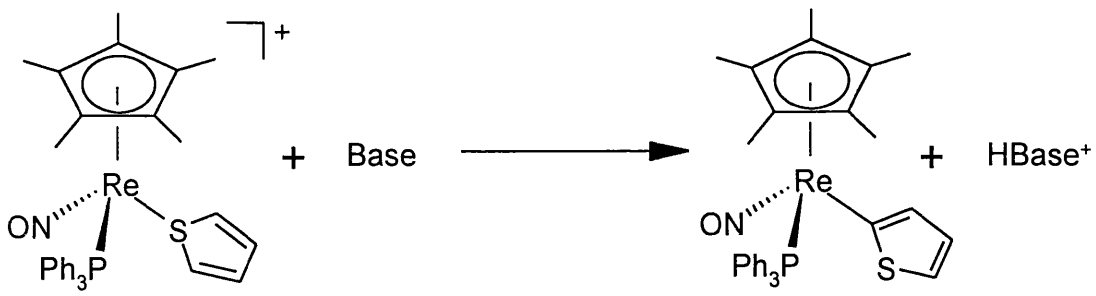
using chiral transition metal complexes synthesised from $[Ru(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)\{(S,S)\text{-Chiraphos}\}][BF_4]$ **3**.[29]



Scheme 1.1: Coordination and ring opening of biaryl thionolactones.

The reaction of $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(PPh_3)(NO)][BF_4]$ **4** with base (Equation 1.2) is of possible relevance to HDS catalysis. This model reaction, the base removal of the 2-proton from the η^1-thiophene ligand suggests a mechanism for the exchange of the α-protons with deuterium during the HDS of thiophenes on heterogeneous catalysts.[15,30,31] Another interesting reaction of η^1-thiophenes was observed when $[Ir(\eta^1\text{-}C_4H_4S)_2(PPh_3)_2(H)_2][PF_6]$ **5** was heated to 80 °C, resulting in the migration of a hydride ligand to the α-carbon of

the thiophene to give an η^4-hydrothiopheneyl complex, $[Ir(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)(PPh_3)_2(H)][PF_6]$ **6**.[32]



(Where Base = OH^-, Et_3N)

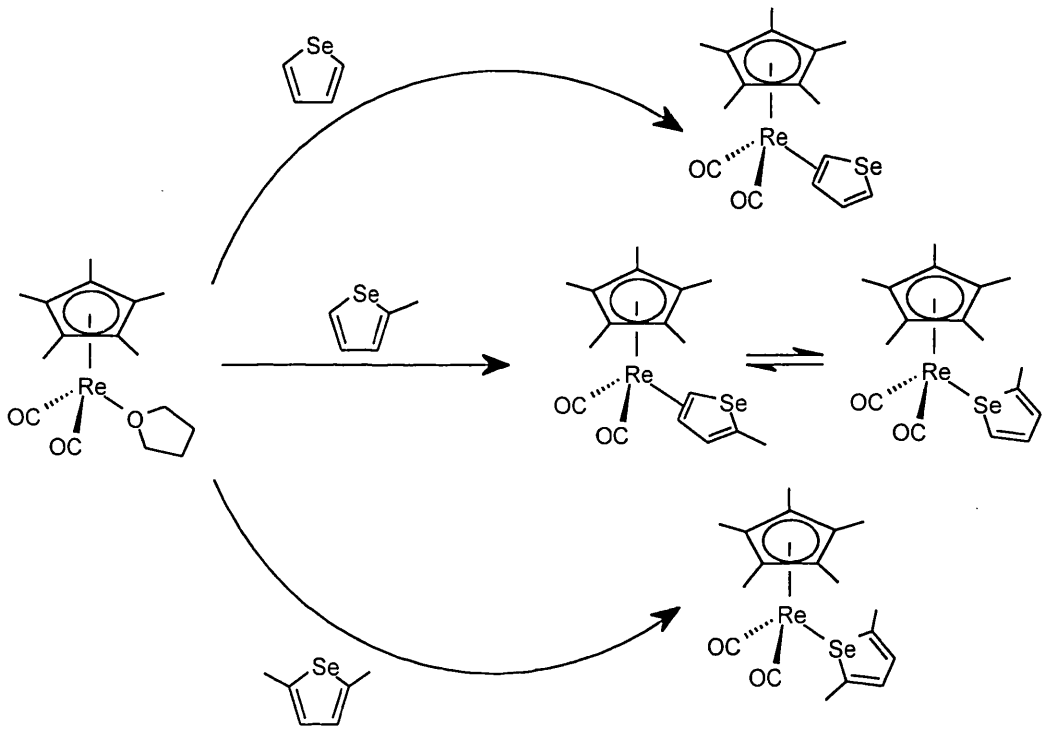
Equation 1.2

B) η^2-BOUND THIOPHENE COMPLEXES

There are no X-ray determined structures of η^2-thiophenes, although a series of osmium complexes of the type $[Os(2,3\text{-}\eta^2\text{-}Th)(NH_3)_5]^{2+}$, (where Th is a generic symbol for thiophenes) have been fully characterised spectroscopically.[33-35] These complexes will be discussed in Section 1.5.

Selenophene (the selenium analogue of thiophene) forms an η^2-coordinated species in the compound $[Re(2,3\text{-}\eta^2\text{-}C_4H_4Se)(\eta^5\text{-}C_5Me_5)(CO)_2]$ **7** (Scheme 1.2). In **7** the metal was found to be situated above the selenophene plane,[15,36,37] an observation which contrasts with the thiophene derivative, $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(CO)_2]$ **8**, in which the sulfur is η^1-bound.[22] Thiophene and selenophene are known to have very similar organic chemistry,[38] thus it is quite noteworthy that their coordination modes differed in the '$Re(\eta^5\text{-}C_5Me_5)(CO)_2$' fragment. It can only be concluded that the olefin constituent in selenophene is a better π-accepting ligand than in thiophene.[15]

The coordination mode adopted by selenophenes is influenced by the number of methyl substituents on the ring. For example in [Re(η^1-2,5-$Me_2C_4H_2Se$)(η^5-C_5Me_5)$(CO)_2$] **9** is coordinated in an η^1 fashion through the selenium (Scheme 1.2), whereas the 2-methylselenophene complex [Re(2-MeC_4H_3Se)(η^5-C_5Me_5)$(CO)_2$] **10** exists as a mixture of η^2 and η^1 isomers (Scheme 1.2).[15,37]



Scheme 1.2: Coordination modes of selenophenes with 'Re(η^5-C_5Me_5)$(CO)_2$'.

The balance between η^2 and η^1 coordination in complexes **7**, **9** and **10** is a function of the level of methylation, and can be explained in terms of the steric and electron donating properties of the methyl groups. The electron density provided by the methyl groups makes the selenium atom in selenophene a better σ-donor to the metal, thus favouring η^1-coordination. The methyl groups also cause the olefin component to be a poorer π-acceptor, as well as making the metal centre sterically less accessible. All of these effects reduce the

coordinating ability of the olefin to η^2-binding, and bolsters the η^1-coordination mode as the number of methyl groups in the selenophene ligand increases.[15,37]

The equilibrium between the two isomers is also affected by the electron-donating ability of the cyclopentadienyl ligand in the rhenium complex. The η^2 isomer is slightly favoured in complex **10** with the very strongly donating Cp* functionally providing substantial electron density to the rhenium, which back-bonds and stabilises the η^2-coordination mode. However in $[Re(\eta^5\text{-}C_5H_5)(2\text{-}MeC_4H_3Se)(CO)_2]$ **11,** the Cp ligand is less electron-donating and so the η^2-coordination mode is less stabilised. The rhenium is therefore better able to accept electron density from the selenium atom, thereby making the η^1-coordinated isomer more favourable. High electron density on the metal centre leads to a preference for η^2 over η^1 coordination.[15,37]

C) η^5-BOUND THIOPHENE COMPLEXES

The most prevalent form of thiophene bonding to transition metal centres is the η^5 coordination mode. This mode has been clearly authenticated in Cr, Mn, Fe, Ru, Rh and Ir metal systems, with the vast majority of these complexes having a d^6 electron count.[15] Almost all known η^5-thiophene complexes have related η^6-arene analogues;[15] this relationship can be understood by examining the '$M(\eta^6\text{-}C_6H_6)$' and '$M(\eta^5\text{-}C_4H_4S)$' fragments.[16] Both these fragments can be viewed as nido cages, a perspective consistent with the isoelectronic nature of the C=C bond and S atom with regard to cage structures.[16] In general η^5-thiophene complexes are more kinetically labile than their η^6-arene brethren.[16]

The first reported η^5-thiophene complex was $[Cr(\eta^5\text{-}C_4H_4S)(CO)_3]$ **12**, obtained in low yield from the carbonyl displacement reaction of thiophene with $[Cr(CO)_6]$ **13**.[39,40] The X-ray structure of this compound was seriously disordered such that no accurate bond lengths were obtained, although the structure did confirm the presence of the η^5-thiophene, which is formally a 6 electron donor occupying three facial coordination sites on the Cr(0) atom.[41]

The treatment of **12** with butyl lithium results in the deprotonation of the thiophene at the 2 and the 5 positions, forming a highly reactive dilithio species $[Cr(\eta^5\text{-}2,5\text{-}Li_2H_2C_4S)(CO)_3]$ **14**.[42] Quenching compound **14** with D_2O results in the formation of $[Cr(\eta^5\text{-}2,5\text{-}D_2H_2C_4S)(CO)_3]$ **15** which undergoes H/D exchange if it is subsequently treated with H_2O. This result clearly indicates that coordinated thiophene is sufficiently acidic to undergo deprotonation with aqueous base at these positions adjacent to the sulfur atom. Depending on the conditions utilised it is possible to control the level of lithiation, thus the treatment of the monolithiated or dilitiated species with Me_3SiCl will yield the appropriately substituted complex $[Cr\{(Me_3Si)_nC_4H_{4-n}S\}(CO)_3]$ (n = 1 or 2).[16,42] Despite the existence of chromium η^5-thiophene compounds, numerous attempts to prepare η^5-thiophene complexes of molybdenum and tungsten have failed, this being noteworthy as these metals are put to use in industrial HDS catalysts.[15]

The isoelectronic relationship between '$Cr(CO)_3$' and '$Mn(CO)_3^{+}$' fragments was first exploited by Singer in the synthesis of a range π-thiophene complexes, $[Mn(\eta^5\text{-}Th)(CO)_3]^+$ (Th = C_4H_4S, 2-MeC_4H_3S, 2,5-$Me_2C_4H_2S$, C_4Me_4S).[16,43,44] This methodology utilises the reaction of $[Mn(CO)_5Cl]$ **16** with an appropriate

thiophene in the presence of $AlCl_3$ to yield the desired π-complexed thiophene compound.[43,44] It has been suggested that the synthesis of these π-thiophenes proceeds *via* an S-bound thiophene intermediate.[16] The use of the labile triflate complex $[Mn(CO)_5(CF_3SO_3)]$ **17** results in greater yields, *ca.* 70 %, of these complex cations $[Mn(\eta^5\text{-Th})(CO)_3]^+$.[45] The thiophene ligand in $[Mn(\eta^5\text{-Th})(CO)_3]^+$ can be easily displaced by polar solvents such as acetonitrile and water to yield the solvento complexes of the type $[Mn(solvent)_3(CO)_3]^+$.[45]

The reactions of a variety of nucleophiles with the thiophene ring in $[Mn(\eta^5\text{-Th})(CO)_3]^+$ have been explored.[16,45] For example the reaction of $[Mn(\eta^5\text{-}C_4H_4S)(CO)_3][CF_3SO_3]$ **18** with aqueous KCN gives the neutral addition compound $[Mn(\eta^4\text{-}C_4H_4S\text{-2-CN})(CO)_3]$ **19**, which was characterised by X-ray crystallography (Figure 1.4).[45] The structure demonstrated that the CN^- had

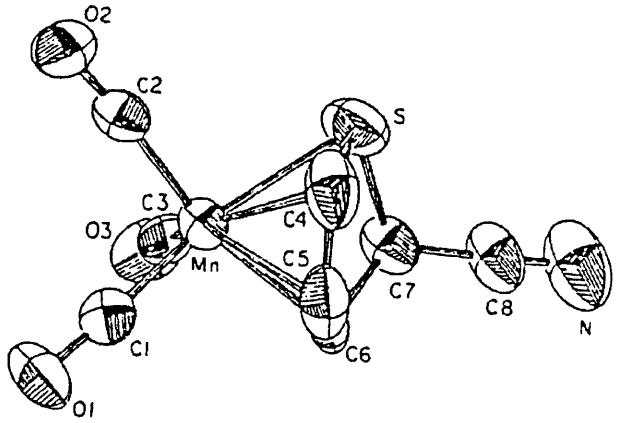
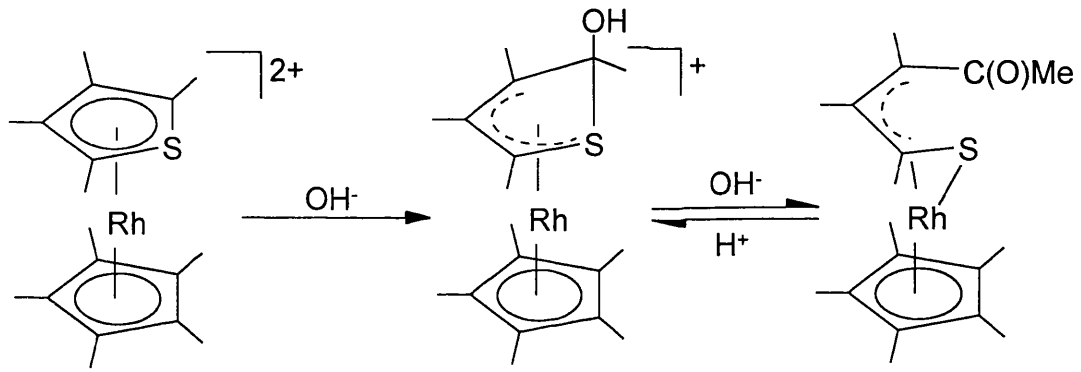


Figure 1.4: Structure of $[Mn(\eta^4\text{-}C_4H_4S\text{-2-CN})(CO)_3]$ 19.[45]

added *exo* to the α-carbon of the thiophene leaving a thiopheneyl ligand, η^4-bound through three carbons atoms and the sulfur atom.[45] Complex **18** also reacts with hydride sources (*e.g.* $HFe(CO)_4^-$, $HW(CO)_5^-$ and $NaBH_4$) to give $[Mn(\eta^4\text{-}C_4H_4S\text{-2-H})(CO)_3]$ **20**.[45,46] Since free thiophene does not react with any of these hydride sources it is clear that η^5-coordination is vital in promoting this

reaction[15]; presumably the metal withdraws electron density from the thiophene thus making it more susceptible to attack by nucleophiles.

In a similar fashion nucleophilic attack of two equivalents of hydroxide on $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]_2$ **21,** gives the neutral acylthiolate compound $[Rh(\sigma,\eta^3\text{-}SC_3Me_3C(O)Me)(\eta^5\text{-}C_5Me_5)]$ **22** (Scheme 1.3).[47,48] Attack



Scheme 1.3

of the OH^- occurs initially at the sulfur atom of the thiophene and the OH group subsequently migrates to the 2 position, where C-S bond cleavage occurs upon deprotonation of $[Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OH)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]$ **23,** to give the acylthiolato complex **22.**[48] A similar reactivity has been shown to occur in ruthenium η^5-thiophene complexes (see Section 1.5).

There are a number of iron derivatives of π-thiophenes that are cationic analogues of ferrocene.[16] For example the mildly air-sensitive compound $[Fe(\eta^5\text{-}C_4Me_4S)_2][PF_6]_2$ **24** was synthesised from a Friedel-Crafts like reaction of TMT, $FeCl_2$ and $AlCl_3$, followed by aqueous workup and anion metathesis.[49] The cation in **24** was subjected to hydride attack by reaction with $NaBH_4$ in THF, which gave a brown solid that "appears to be a hydride adduct."[49]

Ferrocenes generally undergo ring exchange reactions with alkylthiophenes in $AlBr_3$ promoted reactions, to give mixed-ring compounds.[16] For example, the reaction of ferrocene, $AlBr_3$, and powdered aluminium in neat TMT at 130 °C for 8 hours gives (after anion metathesis) $[Fe(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5H_5)][PF_6]$ **25**.[50] The same compound can be synthesised under milder reaction conditions; $[Fe(\eta^5\text{-}C_6H_5Cl)(\eta^5\text{-}C_5H_5)][PF_6]$ **26** undergoes photochemical exchange of its weakly basic chlorobenzene ligand in the presence of an excess of alkylthiophene.[51]

In 1978 Maitlis and co-workers published a comprehensive report on TMT complexes of the platinum group metals.[52] Their study was prompted by the observation that thiophenes severely poisoned hydrogenation catalysts generated *in situ* from the $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ **27** dimer. Thiophenes do not react directly with the rhodium dimer, thus it was hypothesised that the thiophene must have been interacting directly with the catalytic species.[16] In order to simulate the catalytic species **27** was converted into $[Rh(\eta^5\text{-}C_5Me_5)(CH_3CN)_3][PF_6]_2$ **28**, which reacted rapidly with TMT to give $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][PF_6]_2$ **29**. This synthetic strategy was applied to give the analogous iridium complex and $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$ **30**.[52]

Maitlis's group reported the preparation of a series of cations of the general formulation of $[Rh(diene)(\eta^5\text{-}Th)]^+$ (Th = 2,5-$Me_2C_4H_2S$, C_4Me_4S), by the reaction of these thiophenes with $[Rh(diene)(acetone)_2]^+$.[52] This investigation was further extended to the preparation of $[M(\eta^5\text{-}C_4H_4S)(PPh_3)_2]^+$ cations (M = Rh, Ir), which were synthesised by the hydrogenation of $[M(norbornadiene)(PPh_3)_2]^+$ in the presence of thiophene.[53] This synthesis was

ingenious in that the metal complex catalysed the hydrogenation of the norbonadiene, thereby depriving itself of a donor ligand, so that the thiophene molecule is consequently adopted by the metal complex. These complexes appear to be the only examples of non-d^6 metal centres of η^5-complexed thiophenes.[16]

D) η^4-BOUND THIOPHENE COMPLEXES

Thus far in the discussion of the coordination modes of thiophenes the complexes have in the main been constructed by the reaction of a precursor complex and the free thiophene. It is almost a prerequisite of η^4-coordination that the thiophene-metal ligation is already present, as in most cases η^4-thiophene complexes are formed from the chemical reduction of η^5-thiophenes. Previous studies on η^6-arene systems showed that a 2-electron reduction results in a change of hapticity of the ligand, an observation that has been echoed in thiophene complexes.[16]

The first documented example of η^4-thiophene complexes came from the work of Angelici's group who observed that $[Ir(\eta^5\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)][PF_6]_2$ **31** was reduced with 2 mol equivalents of $NaBHEt_3$.[54] Subsequent work using cobaltocene as reductant lead to a series of iridium complexes $[Ir(\eta^4\text{-}Th)(\eta^5\text{-}C_5Me_5)]$[55,56] as well as $[Rh(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)]$ **32**.[57,58] The η^5-thiophene precursor complexes have 18 valence electrons, thus the addition of 2 electrons will bring the electron count to 20, therefore the sulfur moves out of bonding range of the metal in order to re-establish the 18 electron count.[15]

The electrochemical reduction of the parent η^5-complexes occurs in two well-defined steps. The reduction of the iridium complexes are electrochemically irreversible while the cyclic voltammetric data for $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]_2$ **33** shows two reversible reduction waves at –250 and –350 mV versus the Ag/AgCl couple.[57] The authors commented that the average of these potentials was *ca.* 300 mV more anodic than the reduction of the analogous arene compound $[Rh(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_5Me_5)]^{2+}$, which implied that the TMT ligand stabilises Rh(I) more effectively than does hexamethylbenzene.[16,57]

The X-ray crystal structure of $[Ir(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^5\text{-}C_5Me_5)]$ **34** was obtained and is shown in Figure 1.5. The η^4-thiophene ligand is no longer planar, with the sulfur being displaced out of the plane of the four carbon atoms.[55] The Ir-S distance in the complex is 2.968(4) Å, significantly longer than the typical Ir-S bond distances (*ca.* 2.350 Å).[55,59] A noteworthy feature in the crystal data is that the C-S bond distances in the η^4-thiophene are longer than those in free thiophene, indicating that there is a weakening of these bonds in the coordinated ligand.[55] This observation may account for the high reactivity of η^4-coordinated thiophenes.

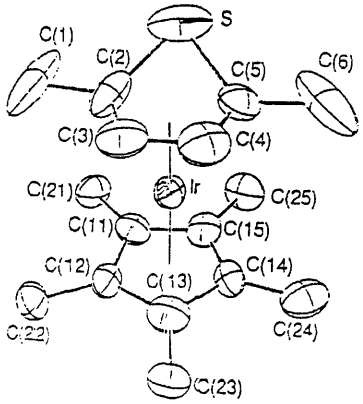
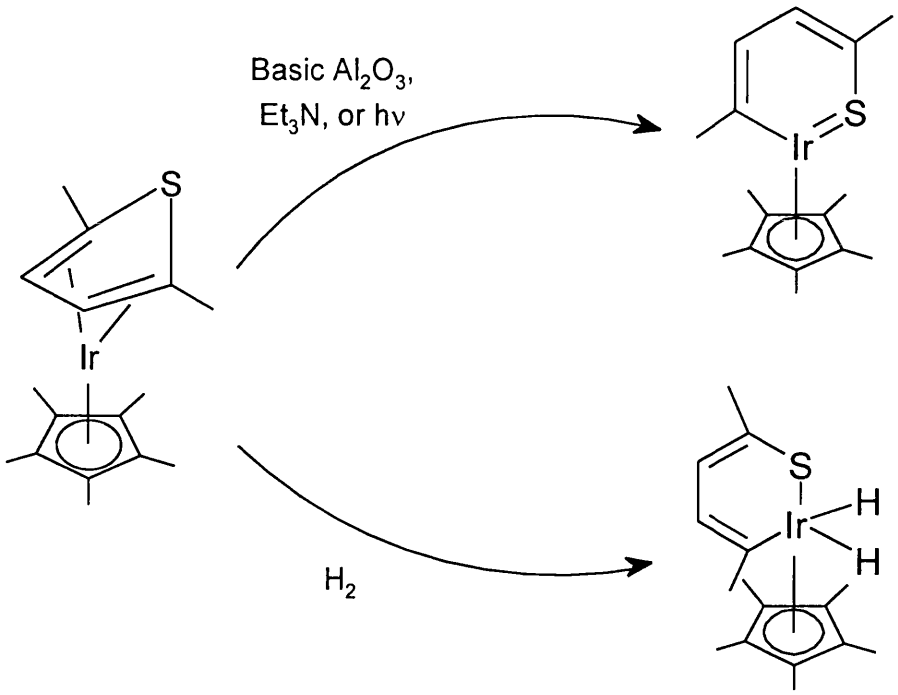


Figure 1.5: Structure of $[Ir(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^5\text{-}C_5Me_5)]$ 34.[55]

Complex **34** undergoes isomerisation by the insertion of the iridium into the C-S bond of the η^4-thiophene (Scheme 1.4).[56] This reaction is catalysed by basic sites on Al_2O_3 and moreover is also catalysed more slowly by the action of Et_3N or ultra-violet light.[56,60] Complex **34** reacts with molecular hydrogen to yield a dihydride complex (Scheme 1.4). Attempts to bring about the migration of the hydride ligands to the thiophene were unsuccessful in that only unidentifiable products were recovered.[61] Compound **34** can be converted back to the starting η^5-thiophene complex by treatment with two equivalents of the ferrocenium cation, which performs a two electron oxidation.[56] The occurrence of the η^4 versus η^5 coordination modes is clearly governed by the oxidation state of the metal, thus it can be envisaged that this same type of control can influenced by the HDS catalysts.[15]



Scheme 1.4: Reactions of [Ir(η^4-2,5-$Me_2C_4H_2S$)(η^5-C_5Me_5)] 34.

In general the sulfur atom of an η^4-thiophene ligand is an excellent donor in its own right and readily coordinates to various Lewis acids. This results in the formation of η^4,S-μ^2 and η^4,S-μ^3 transition metal thiophene complexes.

E) η^4,S-μ^2-BOUND THIOPHENE COMPLEXES

These complexes are in the main formed from precursor complexes that already contain η^1 or η^4-thiophene ligands. For instance the thiophene in $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(CO)_2]$ **35** reacts with $Fe_2(CO)_9$ to give $[\{Re(\eta^5\text{-}C_5Me_5)(CO)_2\}(\eta^1,\eta^4\text{-}C_4H_4S)\{Fe(CO)_3\}]$ **36**.[62] The η^1-thiophene promotes the reaction by disturbing the aromaticity of the ligands leaving the diene portion vulnerable to attack by $Fe_2(CO)_9$. Compound **36** was characterised by X-ray crystallographic analysis (Figure 1.6) which showed the thiophene acting as a bridging ligand, η^4-bound to '$Fe(CO)_3$' through the diene, and S-bound to the '$Re(\eta^5\text{-}C_5Me_5)(CO)_2$' fragment. The complexation of the '$Fe(CO)_3$' fragment to the thiophene lowers the absorption frequencies of the rhenium ν(CO) bands. This is attributed to the sulfur atom in the thiophene ligand of **36** being a better σ-donor than in **35** due to reduced aromaticity of the thiophene **36**.[16,62]

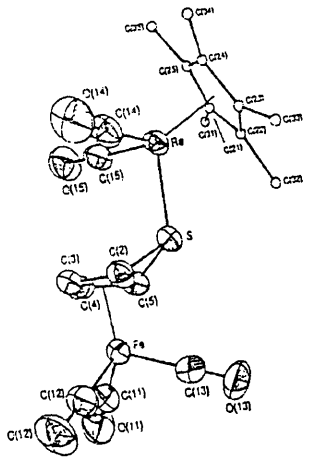


Figure 1.6: Structure of $[\{Re(\eta^5\text{-}C_5Me_5)(CO)_2\}(\eta^1,\eta^4\text{-}C_4H_4S)\{Fe(CO)_3\}]$ 36.[62]

The greater basicity of the sulfur atom in η^4-thiophenes complexes means that these ligands are perfectly set up to undergo complexation to other metals. Indeed iron carbonyls react with compounds **32**[58] and **34**[63] to give axially coordinated '$Fe(CO)_4$' adducts. A noteworthy feature of the geometries of η^4 and η^4-μ^2-thiophene ligands is that they are all quite similar, despite the fact that the known examples are bound to several different metals and have a wide range of co-ligands.[16]

F) η^4,S-μ^3-BOUND THIOPHENE COMPLEXES

Compounds exhibiting this mode of coordination contain bridging thiophene ligands, which are S-bound to two metal centres and η^4-coordinated through the diene to third metal centre. As with the η^4,-μ^2-adducts the driving force for the formation of these complexes is the strong donor ability of the sulfur in the activated thiophene.[14] Two such compounds are assembled from the reaction of $[Ir(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^5\text{-}C_5Me_5)]$ **34** with $[(\eta^5\text{-}C_5H_5)(CO)_2Mo{=}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **37** or iron carbonyls. Both $[\{Ir(\eta^5\text{-}C_5Me_5)\}(\eta^4\text{-}S\text{-}\mu^3\text{-}2,5\text{-}Me_2C_4H_2S)\{Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2\}]$ **38**[64] (Figure 1.7) and $[\{Ir(\eta^5\text{-}C_5Me_5)\}(\eta^4\text{-}S\text{-}\mu^3\text{-}2,5\text{-}Me_2C_4H_2S)\{Fe_2(CO)_7\}]$ **39**[63] have been characterised crystallographically and both structures contain a binuclear unit, which is bridged by a sulfur that has an approximately tetrahedral geometry. The coordination of the metals to the sulfur atom results in very little change in the geometry of the η^4-thiophene from that in the precursor complex **34**. These crystal structures again illustrate that the generic structure of the η^4-thiophene remains unperturbed by the composition and the number of metal fragments coordinated to it.[14]

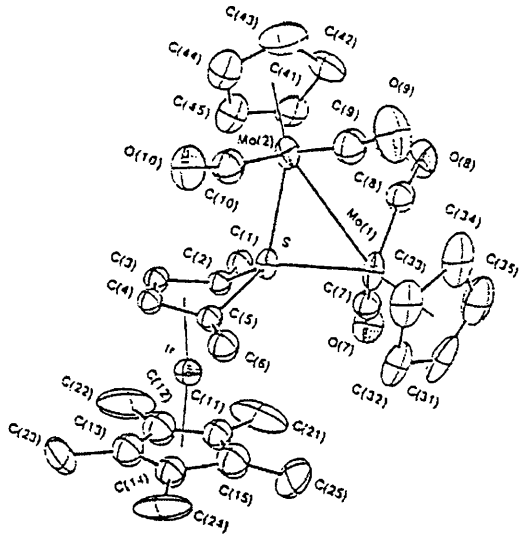
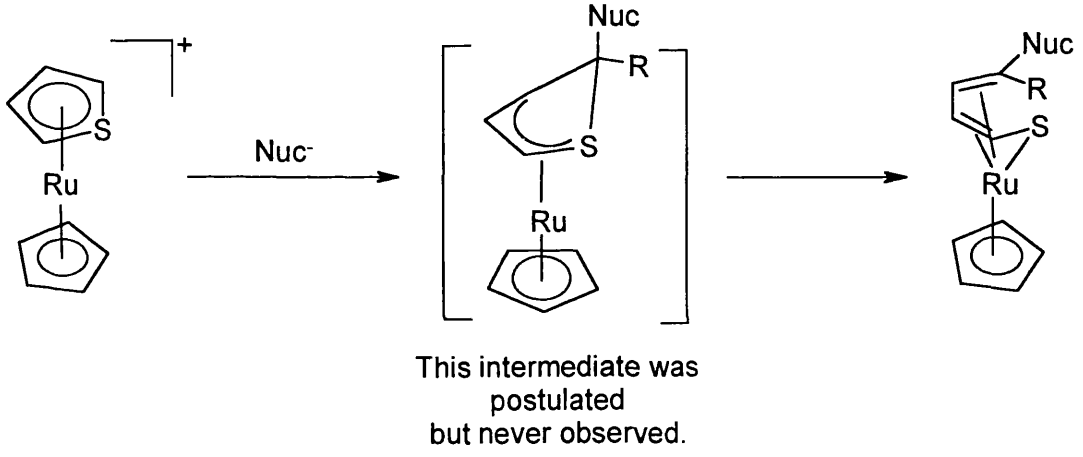


Figure 1.7: Crystal structure of compound 38.[64]

1.4 THE CHEMISTRY OF RUTHENIUM-THIOPHENE COMPLEXES

The first reported thiophene complex of ruthenium came from the work by Maitlis and co-workers in 1978.[52] The synthesis of $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$ **30** was accomplished by the reaction of $[\{Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$ **40** with TMT in the presence of $Ag[PF_6]$ in acetone solution.[52] Angelici and co-workers developed the area with the synthesis of a series of ruthenium-cyclopentadienyl mixed-sandwich complexes of the type $[Ru(\eta^5\text{-}Th)(\eta^5\text{-}C_5H_5)]^+$.[65-67] The initial route to these complexes was merely an extension of the methodology utilised by Singer in the synthesis of $[Mn(\eta^5\text{-}Th)(CO)_3]^+$, namely the reaction of thiophene with $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ and $Ag[BF_4]$, to give an air-stable salt $[Ru(\eta^5\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)][BF_4]$ **41**.[65] A superior route to these compounds utilised the chemistry of $[Ru(\eta^5\text{-}C_5H_5)(CH_3CN)_3][BF_4]$ **42**. Refluxing **42** in dichloromethane in the presence of a thiophene (thiophene, methylthiophene, DMT, TMT) leads to the displacement of the acetonitrile ligands and the complexation of the heterocyclic ligand.[66]

The compounds $[Ru(\eta^5\text{-Th})(\eta^5\text{-}C_5H_5)]^+$ (Th = C_4H_4S, 2-MeC_4H_3S, 2,5-$Me_2C_4H_2S$) were found to be attacked by a variety of nucleophiles (H^-, MeO^-, MeS^-, EtS^-, *i*-PrS^-, and $CH(CO_2Me)_2^-$). This results not only in the addition of the nucleophile to the carbon adjacent to the sulfur, but also causes C-S bond cleavage to yield a butadienethiolate ligand. It was postulated that this reaction proceeded *via* an η^4-thiopheneyl intermediate (Scheme 1.5).[68-70] It is still unclear as to why C-S bond cleavage occurs in the ruthenium compounds, yet in related studies on manganese carbonyls the heterocyclic ring remains intact.



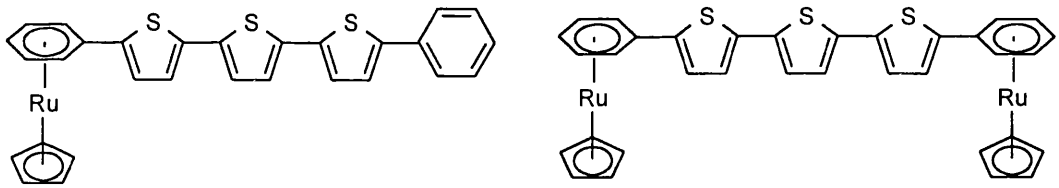
Scheme 1.5: Nucleophilic attack of the $[Ru(\eta^5\text{-Th})(\eta^5\text{-}C_5H_5)]^+$ cation.

Compound **41** undergoes selective base catalysed H/D exchange at the 2,5 position in a solution of KOH and CD_3OD. This has been suggested as an important model of deuterium exchange on catalytic surfaces.[65,66] Furthermore in acetone solutions complex **41** undergoes ligand exchange with substituted thiophenes.[67]

The chemistries of $[Ru(\eta^5\text{-}C_5H_5)(CH_3CN)_3][BF_4]$ **42** and $[Ru(\eta^5\text{-}C_5Me_5)(CH_3CN)_3][PF_6]$ **43** have been utilised in the synthesis of a series of mono and binuclear ruthenium oligothiophene complexes (Figure 1.8).[71-74]

These oligothiophene complexes are proposed as model compounds providing insights into the unique properties of polythiophenes, which are used as conducting polymers and as novel materials in organic transistors and light emitting devices.[71] In the non-phenyl derivatised oligothiophene complexes ruthenium binds in a η^5 fashion to the outermost thiophene of the chain, while in the phenyl derivatised oligothiophene the ruthenium preferentially binds to the pendant phenyl group. The η^6-arene bound systems were found to be stable with respect to decomplexation. However in contrast thiophene bound systems are only stable in the solid state or in dichloromethane solutions. When placed in acetone solutions these complexes convert to an equilibrium mixture of free oligothiophene, mono and binuclear species.[71-73]

(n = 1), 2,2':5',2"-terthiophene (Tth) Complexes.
(n = 2), 2,2':5',2":5",2'"-quaterthiophene (Qth) Complexes.

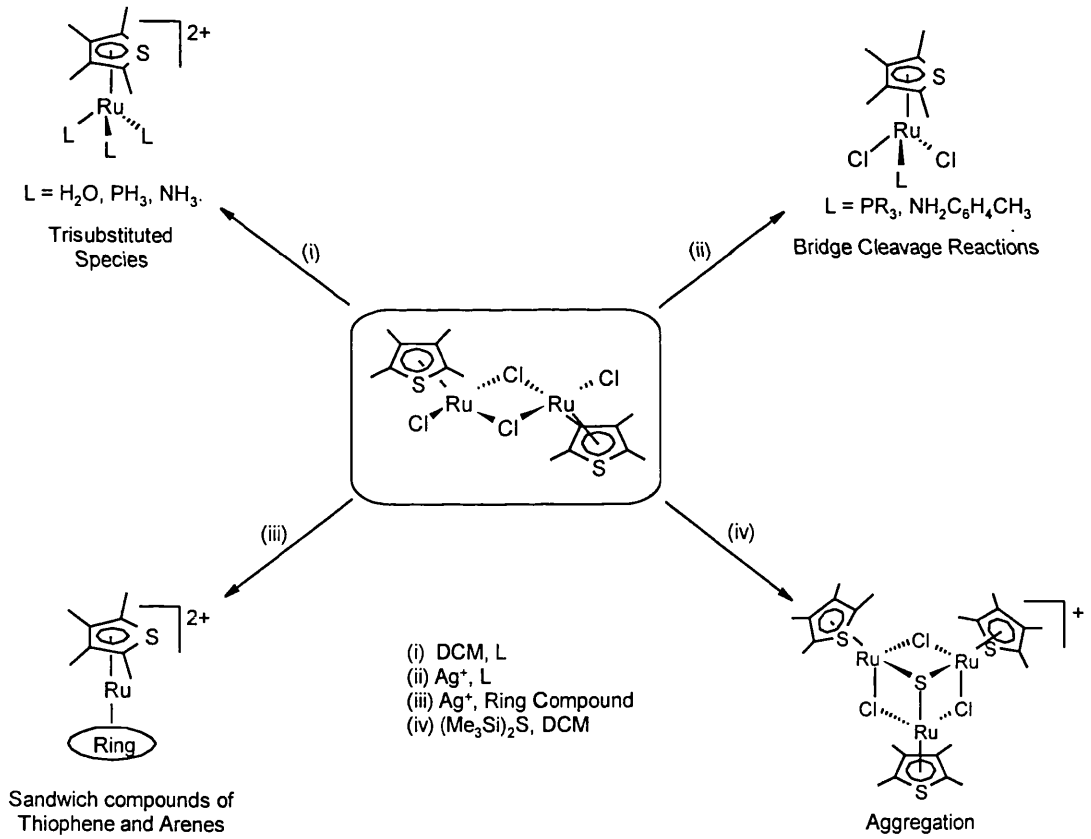


5,5"-diphenyl-2,2':5',2"-terthiophene (Ph_2Tth) Complexes.

Figure 1.8: Selected examples of ruthenium-oligothiophene complexes.

Over a decade ago Rauchfuss and co-workers reported the preparation of a groundbreaking compound, namely $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44**.[75,76] This dimeric species was described as "a versatile synthetic intermediate and represents an unusual example of a thiophene complex with replaceable co-

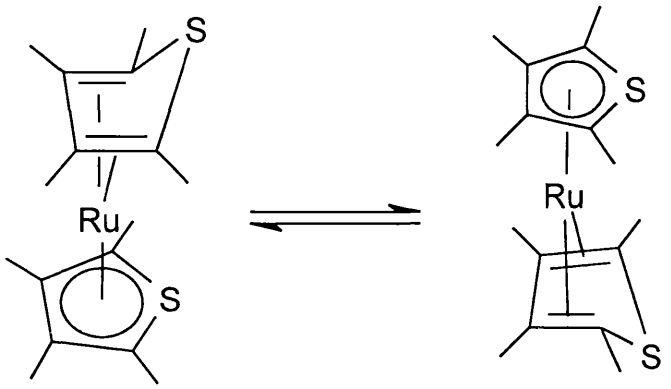
ligands."[16] Compound **44** was prepared by thermal arene exchange of **40** with TMT, and required there to be an excess of TMT and reaction temperatures of 210 °C (*i.e.* greater than that of the boiling point of *p*-cymene).[76] Unsuccessful attempts have been made to prepare analogous Os and Fe compounds and attempts to exchange the *p*-cymene ligand in **40** with DMT also proved unsuccessful.[76] The coordination chemistry of **44** was described by Rauchfuss's group in a series of papers (Scheme 1.6),[75,76] but this chemistry remains relatively unexplored when compared to that of [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] compounds.[77]



Scheme 1.6: Reactivity of the tetramethylthiophene-ruthenium dimer

Compound **44** reacts with a variety of phosphine ligands to give the bridge-cleaved adducts [Ru(η^5-C_4Me_4S)Cl_2(PR_3)] (R = Ph, Me, *n*-Bu, *p*-C_6H_4Me) as does *p*-toluidine.[75] The treatment of **44** with silver salts in the presence of a

variety of ligands results in the formation of a series of *tris* substituted complexes $[Ru(\eta^5\text{-}C_4Me_4S)L_3]^{2+}$ (L = H_2O, D_2O, PH_3, NH_3).[75,76] The reaction of **44** with an excess of $(Me_3Si)_2S$ gives the rather unique and unexpected cluster $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl\}_3(\mu^3\text{-}S)][PF_6]$ **45** (Scheme 1.6),[75] which is the only example of a metal sulfide cluster with a thiophene co-ligand and is a rare example of an η^5-thiophene complex for which there is no direct η^6-arene anologue.[16] Compound **44** reacts with TMT in the presence of $Ag[BF_4]$ in acetone to give the robust air stable homoleptic sandwich compound $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46**.[75] X-ray crystallographic analysis of **46** showed the complex possesses a psuedo-octahedral geometry with the two sulfur atoms being *cis* oriented to each other.[75] Cyclic voltammetric studies on **46** revealed two reversible one-electron reductions[75] and the chemical reduction of the cation was accomplished with cobaltocene.[78] The resulting neutral complex $[Ru(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_4Me_4S)]$ **47** was found to be unstable at room temperature ($t_{1/2} \approx$ 10 mins) and a variable temperature NMR study showed the complex to be fluxional as a result of the interconversion of η^5-TMT and η^4-TMT ligands (Scheme 1.7).[78] The treatment of **47** with $[Fe(CO)_5]$ and Me_3NO results in the formation of the '$Fe(CO)_4$' adduct, $[\{Ru(\eta^5\text{-}C_4Me_4S)\}(\eta^4\text{-}\mu^2\text{-}C_4Me_4S)\{Fe(CO)_4\}]$



Scheme 1.7: Fluxional process for $[Ru(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_4Me_4S)]$ 47.

48, which is thermally stable and conclusively identified by an X-ray crystallographic study (Figure 1.9).[78]

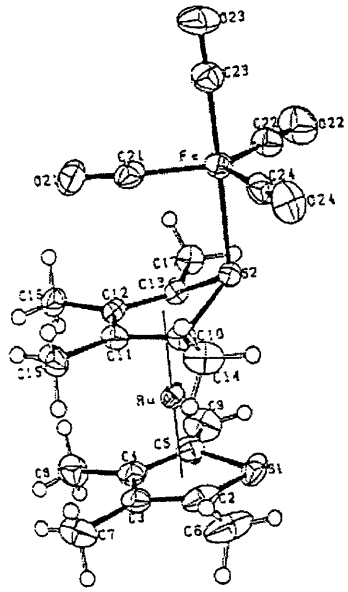


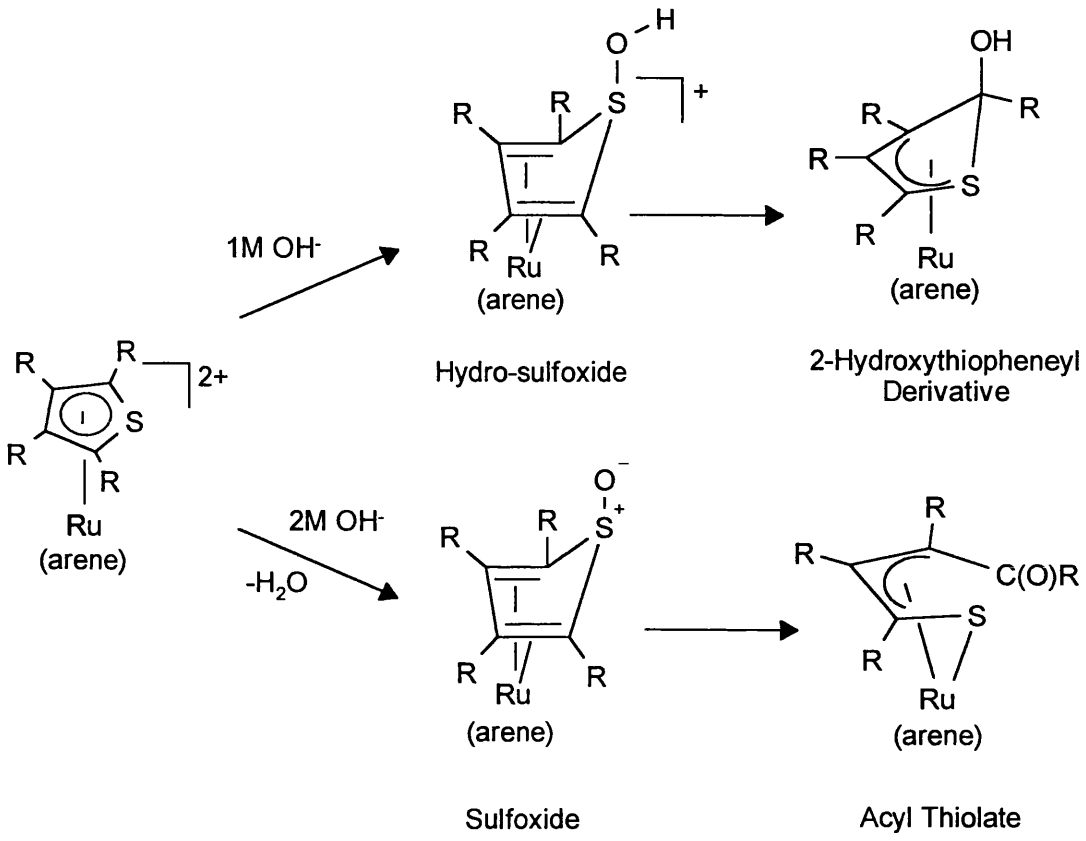
Figure 1.9: Structure of [{Ru(η^5-C_4Me_4S)}(η^4-μ^2-C_4Me_4S){Fe(CO)$_4$}] 48.[78]

The reaction of **44** with Ag[CF_3SO_3] in dichloromethane gives the synthetically versatile [Ru(η^5-C_4Me_4S)(CF_3SO_3)$_2$]$_n$ **49** although it should be noted that the exact nature of this material has not been established.[76] Spectroscopic studies suggest that compound **49** does not have a simple structure, due to the ability of triflate ligands to bind covalently to one or more metals in a variety of ways. This complex was found to be a highly reactive electrophilic reagent and acts as a supplier of the 'Ru(η^5-C_4Me_4S)' moiety in many synthetic procedures.[76] The related species [Ru(η^6-*p*-cymene)(CF_3SO_3)$_2$]$_n$ **50** and [Ru(η^6-C_6Me_6)(CF_3SO_3)$_2$]$_n$ **51** were also prepared and these together with **49** were employed as a synthons for a series of closely related complex ions [Ru(η^5-Th)(η^6-arene)]$^{2+}$ [76,79] and [Ru(η^5-Th)(η^5-C_4Me_4S)]$^{2+}$ [76] (Th = C_4H_4S, 2,5-$Me_2C_4H_2S$, C_4Me_4S). The synthesis of one of these typically involves placing

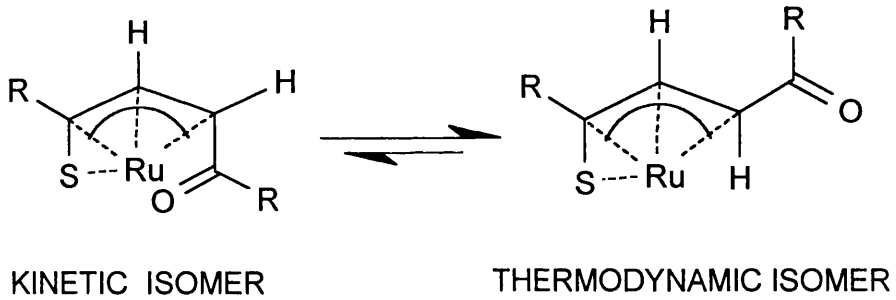
the "triflate polymer" in a dichloromethane solution with a slight excess of the thiophene; stirring at room temperature then results in the precipitation of the desired product. The organometallic chemistry of these π-thiophene systems has been extensively explored.[76, 78-84]

As noted earlier (Section 1.2 C) the complex ions $[Ru(\eta^5\text{-Th})(\eta^6\text{-arene})]^{2+}$ (Th = 2,5-$Me_2C_4H_2S$, C_4Me_4S; arene = *p*-cymene, C_6Me_6) undergo base hydrolysis (Scheme 1.8) with attack of OH^- occuring initially on the sulfur to give $[Ru(\eta^4\text{-}C_4R_4S\text{-1-OH})(\eta^6\text{-arene})]^+$ cations.[82] This species subsequently displays two forms of reactivity: 1) rearrangement to give the 2-hydroxythiopheneyl derivative $[Ru(\eta^4\text{-}C_4R_4S\text{-2-OH})(\eta^6\text{-arene})]^+$; 2) upon further addition of one equivalent of OH^- produces the sulfoxide derivative $[Ru(\eta^4\text{-}C_4R_4S\text{-1-O})(\eta^6\text{-arene})]$.[82] The sulfoxide derivative undergoes a rearrangement process to give the acyl thiolate complexes $[Ru(\sigma,\eta^3\text{-}SC_3R_3C(O)R)(\eta^6\text{-arene})]$.[82] In $[Ru(\sigma,\eta^3\text{-}SC_3RH_2C(O)R)(\eta^6\text{-}p\text{-cymene})]$ (R = H, Me) the acyl thiolate exists in two isomeric forms. Initially a kinetic isomer is formed which converts into a thermodynamic isomer over time. These isomers differ in the relative orientation of the carbonyl functionality with respect to the sulfur atom (Scheme 1.9).[82]

When the compounds $[Ru(\eta^5\text{-Th})(\eta^6\text{-arene})]^{2+}$ (Th = C_4H_4S, 2-MeC_4H_3S, DMT; arene = *p*-cymene, C_6Me_6) are treated with ammonia, C-S bond cleavage is observed to occur and gives iminium-thiolate derivatives $[Ru(\sigma,\eta^3\text{-}SC_4R_4NH_2)(\eta^6\text{-arene})]$.[83] In the case of the DMT derivatives kinetic isomers are initially isolated which slowly isomerise to give thermodynamic isomers, in all



Scheme 1.8: Base hydrolysis of [Ru(η⁵-Th)(η⁶-arene)]²⁺.



R = H, Me.
p-cymene group omitted for clarity

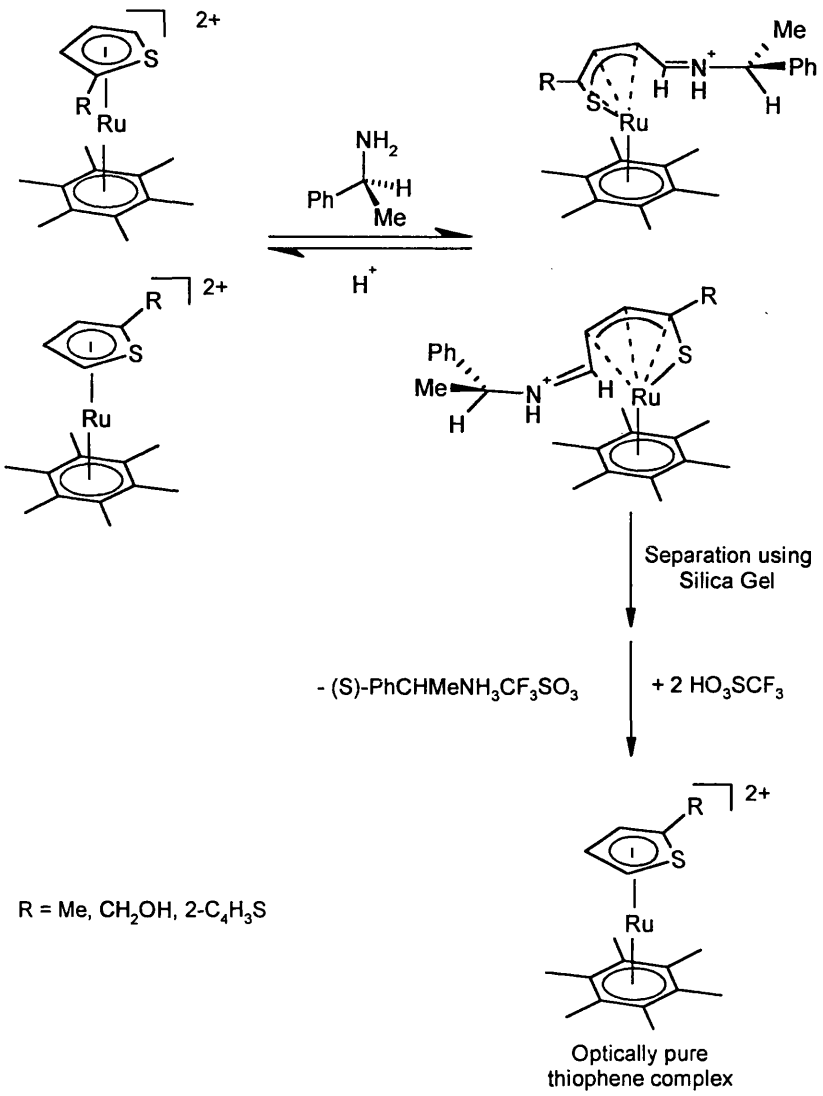
Scheme 1.9: Isomerisation of [Ru(σ,η³-SC₃RH₂C(O)R)(η⁶-p-cymene)].

other cases only one isomer was observed. In the case of the 2-methylthiophene complexes C-S bond cleavage occurs regiospecifically at the S-CH linkage giving only one isomer. In contrast the reaction of ammonia with $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$ **30** results in the formation of $[Ru(\eta^4\text{-}$

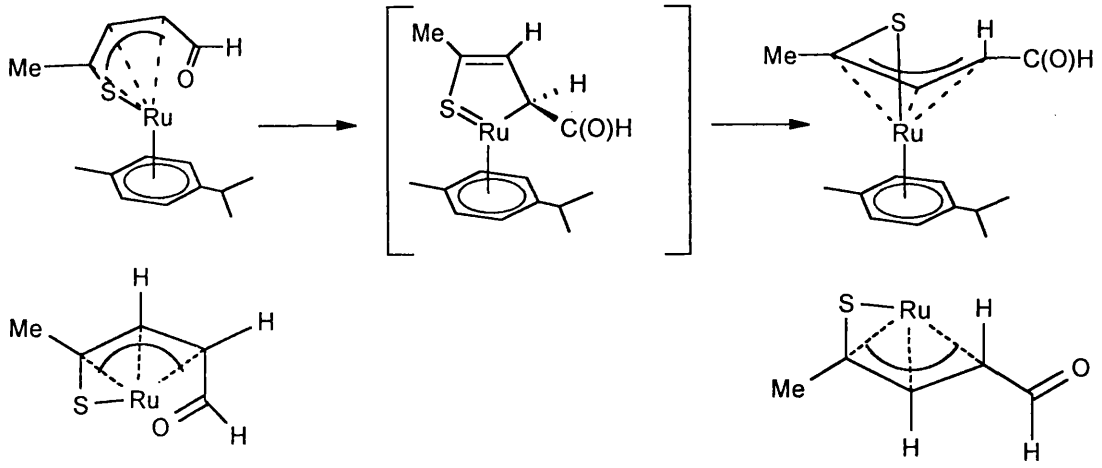
C_4Me_4S-2-NH_2)(η^6-*p*-cymene)][PF_6] **52** in which there has been no C-S bond cleavage.[83]

An extension of this chemistry was used in the optical resolution of some π-thiophene complexes that exhibited the phenomenon of "planar chirality". Diastereomeric imimium-thiolato complexes were synthesised from the reaction of S(-)-α-methylbenzylamine with [Ru(η^5-C_4H_3S-2-R)(η^6-C_6Me_6)]$^{2+}$ (R = Me, CH_2OH, 2-C_4H_3S). Each of the diastereomeric complexes were isolated by chromatography and the optically pure thiophene complex released by treatment with acid (Scheme 1.10).[84] Optically pure (-)-[Ru(η^5-2-MeC_4H_3S)(η^6-C_6Me_6)][CF_3SO_3]$_2$ **53** was used to probe the mechanism for base hydrolysis of η^5-thiophenes. It was hypothesised that the initial product isomerises *via* an intramolecular pathway which involves an η^3-η^1 conversion of the allyl group (Scheme 1.11).[82,84] If this mechanism operates then the isomerisation should proceed with inversion of the stereochemistry at the metal. Base hydrolysis of **53** confirmed that the isomerisation of the acyl thiolato complex inverts the configuration at the ruthenium metal centre, thus suggesting that this mechanism is indeed in operation.[84]

The chemical reduction of [Ru(η^5-Th)(η^6-C_6Me_6)][CF_3SO_3]$_2$ (Th = C_4H_4S, 2,5-$Me_2C_4H_2S$, C_4Me_4S) was accomplished using cobaltocene, with the thiophene ligand being reduced in preference to the arene ligand. The products [Ru(η^4-Th)(η^6-C_6Me_6)], were only stable when DMT or TMT were present intially.[79] The electrochemical reduction of [Ru(η^5-C_4Me_4S)(η^6-C_6Me_6)][CF_3SO_3]$_2$ **54** occurs in two one electron steps (-442 and –607 mV versus Ag/AgCl).[79] These

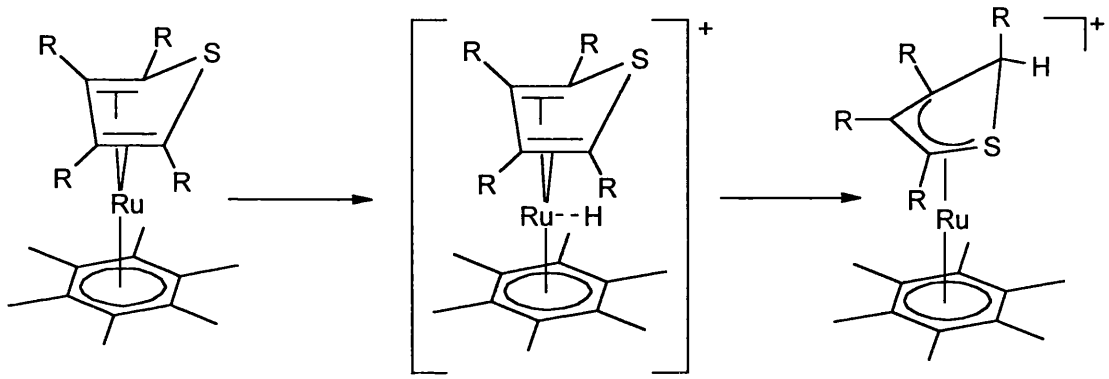


Scheme 1.10: Formation of optically pure thiophene complexes

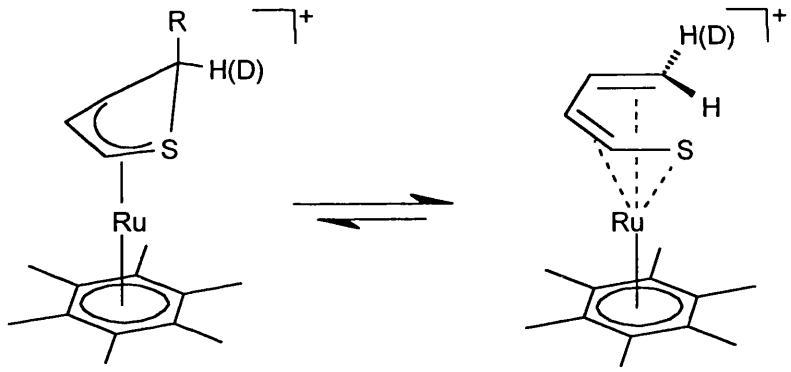


Scheme 1.11: Mechanism of isomerisation in acyl-thiolato complexes.

potentials are comparable to the ones reported for $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46**, but are 400 mV more anodic than those observed for the $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$ cation, consistent with the thiophene being a better electron acceptor than the arene.[79] Each of the ruthenium(0) complexes $[Ru(\eta^4\text{-Th})(\eta^6\text{-}C_6Me_6)]$ (Th =



Scheme 1.12: Mechanism for protonation of $[Ru(\eta^4\text{-Th})(\eta^6\text{-}C_6Me_6)]$.



Equation 1.3

C_4H_4S, 2,5-$Me_2C_4H_2S$, C_4Me_4S) are highly basic, and can be protonated using NH_4PF_6 (pKa ≈ 9.24). The products exhibit *endo* addition of the proton to the 2 position of the η^4-thiophene ligand (Figure 1.10). This mode of attack suggests that the proton arrives at the carbon *via* the initial protonation at the metal followed by migration (Scheme 1.12).[79] Studies of $[Ru(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)(\eta^6\text{-}C_6Me_6)][PF_6]$ **55** showed that the initially formed hydrothiopheneyl complex underwent spontaneously C-S bond cleavage to give the ring opened isomer

(Equation 1.3).[80] Deuterium isotopic labelling studies demonstrated that ring opening occurs stereospecifically.[80]

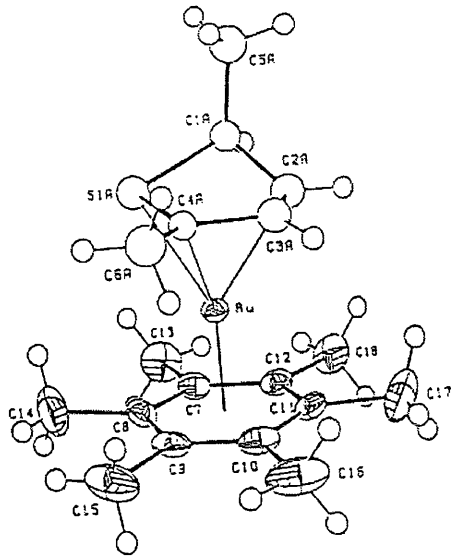


Figure 1.10: Structure of [Ru(η^4-2,5-Me$_2$C$_4$H$_2$S-2-H)(η^6-C$_6$Me$_6$)][PF$_6$] 88.[79]

The compound [Ru(η^4-C$_4$Me$_4$S)(η^6-C$_6$Me$_6$)] **56** was found to have intriguing thermal chemistry, in that heating of **56** in a hydrocarbon solution affords the trinuclear product [Ru$_3$(η^4-μ^2-C$_4$Me$_4$S)$_2$(η^6-C$_6$Me$_6$)$_3$] **57** (Figure 1.11).[81] This molecule contains two 'Ru(η^4-C$_4$Me$_4$S)(η^6-C$_6$Me$_6$)' moieties coordinated thorough the sulfur atom in the η^4-thiophene to a central 'Ru(η^6-C$_6$Me$_6$)' unit. Furthermore when the thermolysis was conducted in aromatic solvents (benzene or toluene), the products observed had undergone arene exchange and took the form [Ru$_3$(η^4-μ^2-C$_4$Me$_4$S)$_2$(η^6-Solvent)(η^6-C$_6$Me$_6$)$_2$].[81] These compounds differed only in the nature of the central unit *i.e.* in the aromatic solvent the central unit is the 'Ru(η^6-Solvent)' moiety rather than a 'Ru(η^6-C$_6$Me$_6$)' unit, as observed in the hydrocarbon solvent.[81] The arene exchange reaction was found to occur competitively with either the hexamethylbenzene or

the solvent coordinating to the unique ruthenium; this process was found to be dependant on the concentration of **56** (Scheme 1.13).[81]

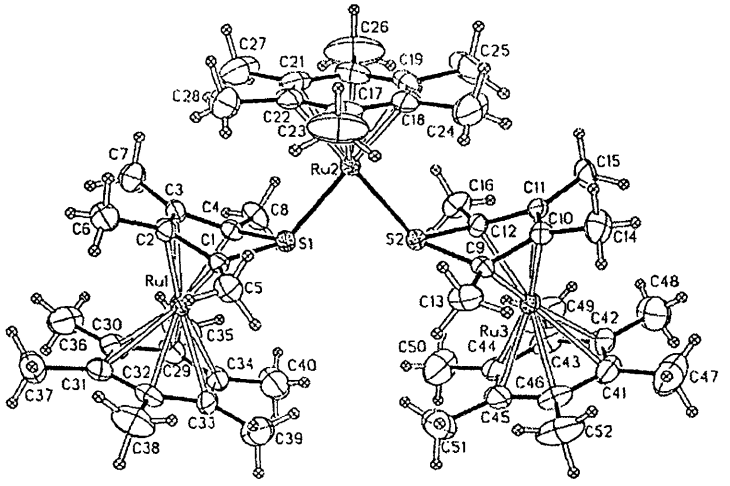
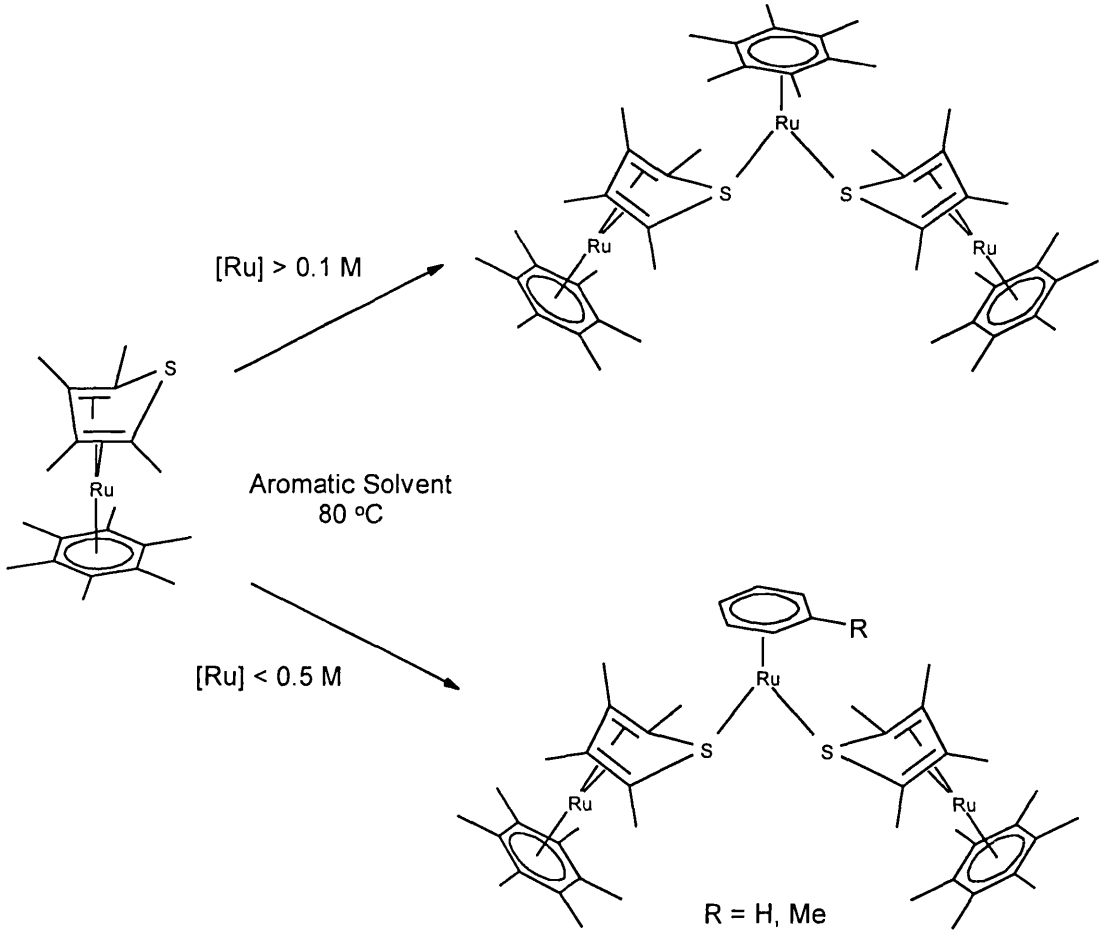


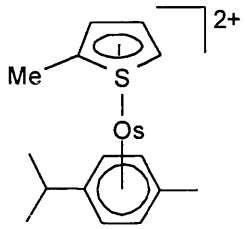
Figure 1.11: Structure of [Ru$_3$(η^4-μ^2-C$_4$Me$_4$S)$_2$(η^6-C$_6$Me$_6$)$_3$] 57.[81]



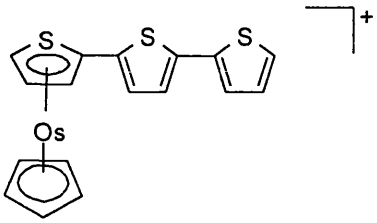
Scheme 1.13: Thermal reactions of [Ru(η^4-C$_4$Me$_4$S)(η^6-C$_6$Me$_6$)] 56.

1.5 THE CHEMISTRY OF OSMIUM-THIOPHENE COMPLEXES

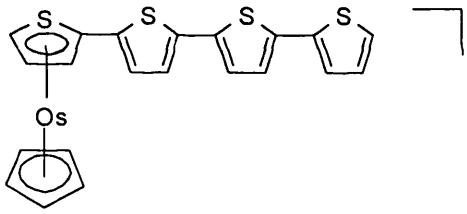
In contrast to the chemistry of ruthenium the chemistry associated with non-cluster osmium-thiophene systems remains largely unexplored. This is illustrated by the fact that there are no reported X-ray crystallographic determinations of any non-cluster osmium-thiophene system, furthermore there are only four reported η^5-thiophene complexes of mononuclear osmium (Figure 1.12).



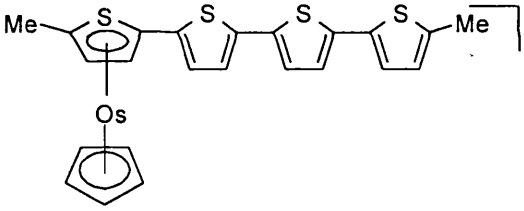
$[Os(\eta^5\text{-}2\text{-}MeC_4H_3S)(\eta^6\text{-}p\text{-cymene})]^{2+}$



$[Os(\eta^5\text{-Tth})(\eta^5\text{-}C_5H_5)]^+$



$[Os(\eta^5\text{-Qth})(\eta^5\text{-}C_5H_5)]^+$



$[Os(\eta^5\text{-}Me_2Qth)(\eta^5\text{-}C_5H_5)]^+$

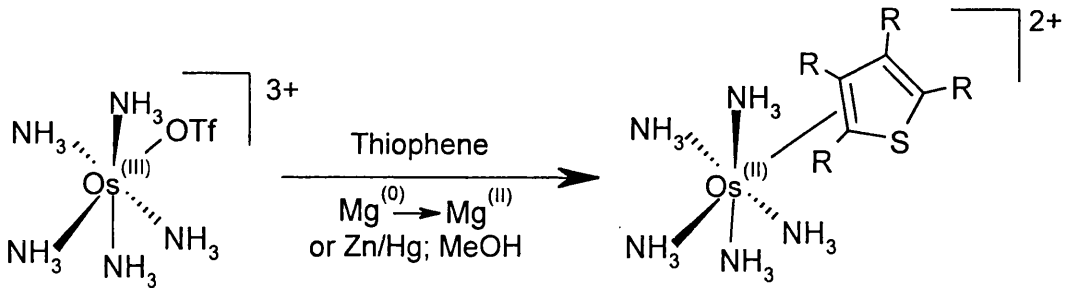
Figure 1.12: Structures of known η^5-thiophenes of osmium.

Rauchfuss *et. al.* synthesised $[Os(\eta^5\text{-}2\text{-}MeC_4H_3S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ **58** in an attempt to exploit the optical resolution methodology which they had so successfully applied to ruthenium systems (Section 1.4).[84] This proved fruitless as the resulting iminium thiolato complex was configurationally unstable, the complex rapidly isomerised and then decomposed.[84]

Mann and co-workers reported an electrochemical investigation on a series of osmium-oligothiophene complexes of 2,2':5',2"-terthiophene (Tth),

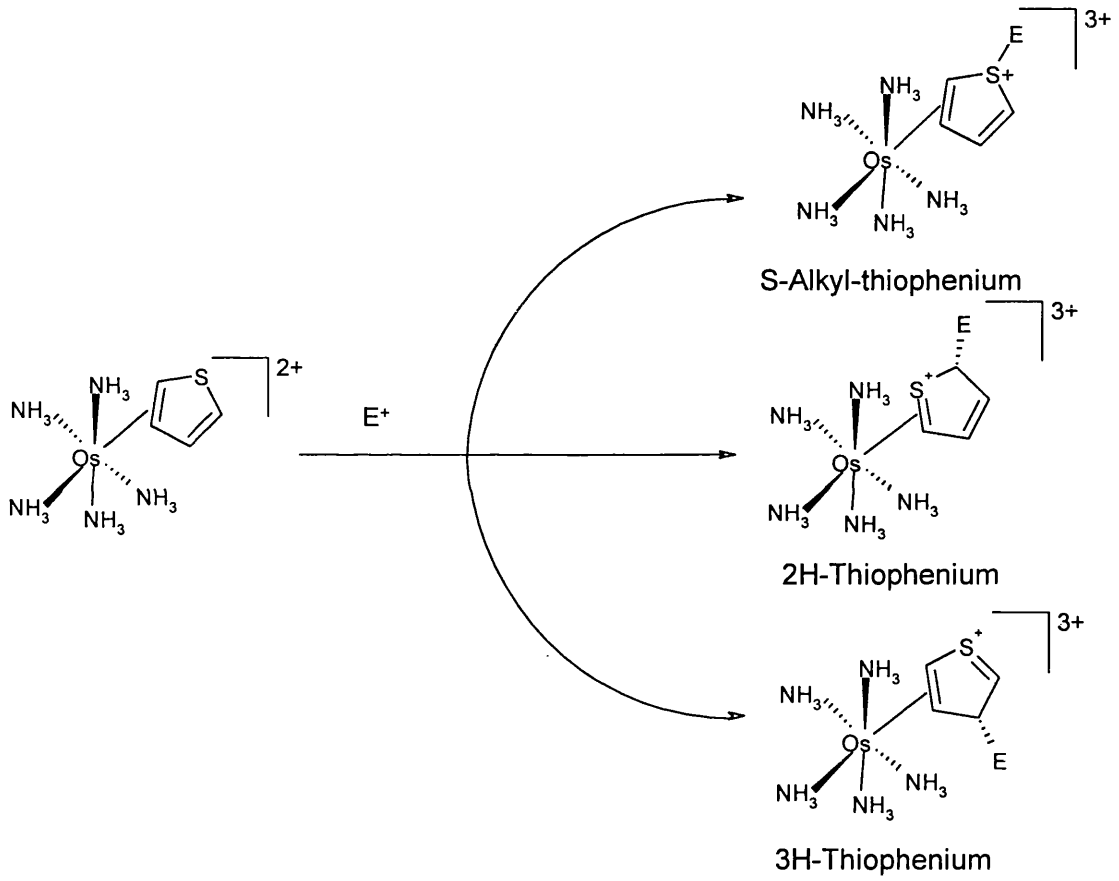
2,2':5',2":5",2"'-quaterthiophene (Qth), and 5,5"-dimethyl-2,2':5',2"-terthiophene (Me_2Tth).[71-73] These complexes were synthesised by the thermal displacement of the acetonitrile ligands in $[Os(\eta^5\text{-}C_5H_5)(CH_3CN)_3]^+$ cation, to give complexes of the general formulation $[Os(\eta^5\text{-}C_5H_5)(\eta^5\text{-oligothiophene})][PF_6]$ (Figure 1.12).[71-73] These osmium complexes were found to be more kinetically stable, with respect to decomplexation and scrambling reactions, than their ruthenium analogs.[71-73]

The only comprehensive study of osmium-thiophene complexes was an investigation into η^2-thiophene binding utilising the chemistry of pentaammineosmium complexes.[33-35] These complexes were prepared by the chemical reduction of the osmium(III) precursor $[Os(NH_3)_5(CF_3SO_3)][CF_3SO_3]_2$ **59** in the presence of an excess of the desired thiophene and results in the isolation of the η^2-thiophene complexes, $[Os(4,5\text{-}\eta^2\text{-Th})(NH_3)_5][CF_3SO_3]_2$, in high yield (Equation 1.4).[33-35] Although no X-ray diffraction studies were conducted, these complexes have been well characterised spectroscopically. It was argued that it is the strong π-back bonding from osmium to the π^* orbitals of the coordinated olefin that stabilises η^2-olefin rather than η^1-sulfur coordination of the thiophene in these complexes.[34]



Equation 1.4

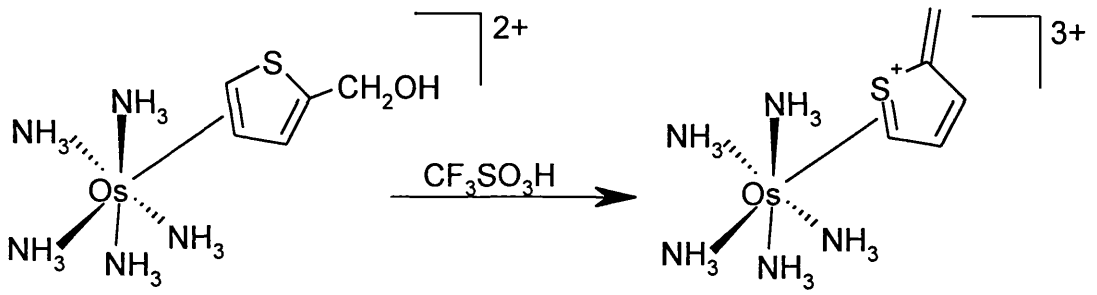
The complexes were found to be highly reactive in a variety of electrophilic reactions (protonation or alkylation).[34-35] Depending on the electrophile and the substitution pattern of the coordinated thiophene it is possible to control the manner of addition such that the electrophile can add either to the sulfur, the 2-carbon, or the 3-carbon of the thiophene ring, affording thiophenium complexes in the process (Scheme 1.14).[35] Pentaammineosmium complexes of formyl



Scheme 1.14: Electrophilic addition reactions of η^2- thiophene complexes.

and acetyl-thiophenes, as well as their alcohol derivatives, are readily converted into novel thiafulvenium complexes by treatment with the appropriate electrophiles.[35] For example, the treatment of $[Os(4,5\text{-}\eta^2\text{-}C_4H_3S\text{-}2\text{-}CH_2OH)(NH_3)_5]^{2+}$ with triflic acid results in the protonation of the hydroxy group, which after the elimination of water, gives a 1,2-η^2-thiafulvenium species (Equation 1.5).[35] It is believed that the π-basic nature of the

pentaammineosmium(II) metal centre helps to stabilise the electron deficient products of these reactions (*i.e.* thiophenium, S-alkylthiophenium, and thiafulvenium), such that there is an inhibition of the re-aromatisation reaction.[35]



Equation 1.5

1.6 AIM OF THESIS

As has been described above the chemistry associated with the non-cluster transition metal coordination chemistry of thiophenes has been and still is the subject of intensive investigation. Complexes containing thiophene show extensive organometallic reactivity and in many cases the reactivity is analogous to that observed in related arene complexes. However thiophene complexes do show some very unique and surprising reactivity and thus should not be regarded as simply some sort of a moderately perturbed aromatic system. Thus it was with the basic aim of further developing the chemistry of π-thiophene complexes of ruthenium and osmium that this project was undertaken.

Given the synthetic utility and the increasing recognition of the catalytic activity demonstrated by the isoelectronic and isostructural series of compounds $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ there is clear and considerable scope for the further

development of the coordination chemistry of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44**. With that goal in mind the coordination chemistry of **44** was extensively explored with mono-, bi-, and tridentate ligands (Chapter 2). The reactivity of some of these novel complexes towards nucleophiles were investigated, and comparisons drawn with work already in the literature (Chapter 3). As mentioned earlier, (Section 1.5) osmium-thiophene compounds remain largely unexplored compared to those of ruthenium. As a step to extending this area several sandwich compounds of osmium have been prepared and their reactivity was examined (Chapter 4).

CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF η^5-TETRAMETHYLTHIOPHENE COMPLEXES OF RUTHENIUM (II)

2.1 INTRODUCTION

This chapter reports an investigation into the coordination chemistry of the [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] **44** dimer. As previously noted **44** is isostructural and isoelectronic with the [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] series of compounds. Since their discovery in 1967 [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] compounds have increasingly been used as the starting point for much of the known arene-ruthenium chemistry, such that they are now established as important synthons for the 'Ru(η^6-arene)' fragments.[77, 85-89] A great deal is known about their reactivity, indeed the chemistry associated with these dimeric species has been extensively reviewed in a number of papers.[77, 85-89] While it is not the intention to extensively review this chemistry, a brief summary of some of the more salient features of the chemistry of [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] compounds is now presented in order to illustrate the synthetic utility of such species.

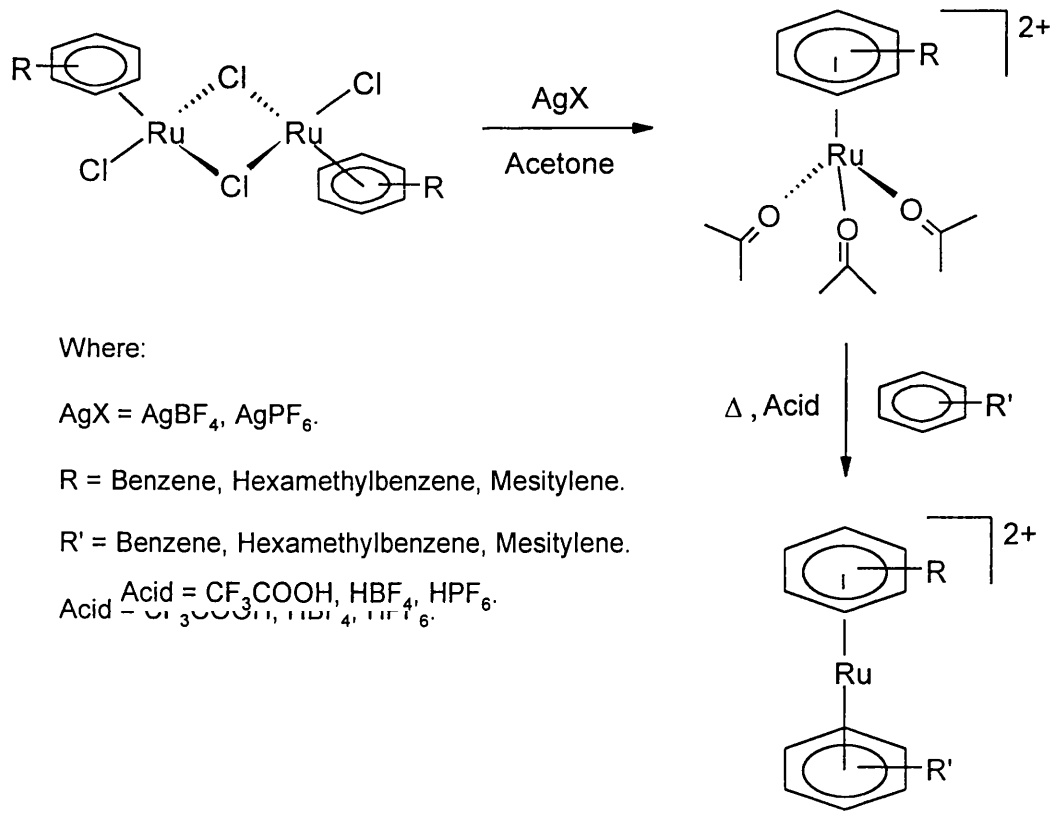
The [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] dimers were initially formed from the reaction of cyclohexadiene derivatives with ethanolic solutions of $RuCl_3.xH_2O$.[90-95] While these complexes were initially believed to be polymeric in nature they are now accepted as being binuclear, following the work of Bennett and co-workers on the molecular weight of the [{Ru(η^6-*p*-cymene)Cl(μ-Cl)}$_2$] **40** complex by osmometry.[94] The [{Ru(η^6-*p*-cymene)Cl(μ-Cl)}$_2$] **40** dimer is a particularly useful starting material in that the *p*-cymene ligand can be easily displaced by other arenes simply by heating the complex in either a neat solution or a melt of the desired arene; this procedure has been utilised in the production of a range of dimers not accessible *via* the cyclohexadiene methodology.[95,96] The chloride ligands in [{Ru(η^6-arene)Cl(μ-Cl)}$_2$] compounds can be exchanged for bromide,

iodide or thiocyanate, either by the metathesis of the chloride dimer with the respective sodium salts or by starting with the appropriate ruthenium trihalide.[91,92,94] An interesting reaction of $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ dimers is the formation of the $[Ru_2(\eta^6\text{-arene})_2(\mu\text{-}Cl)_3]^+$ cations. These triply chloro-bridged complexes were formed by dissolution of the appropriate dimer in hot water, and were isolated from the aqueous solution by anion metathesis.[94] It was subsequently found that these binuclear compounds could be prepared in better yields by the reaction of the dimers with an excess of NH_4PF_6 in methanol.[96-98] A series of these triply bridged compounds have been synthesised with a variety of bridging ligands; examples include hydride, hydroxide, alkoxide (OMe^-, OEt^-, OPh^-), and thiolate (SEt^-) bridges.[99-101]

The chloride bridges in $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ can be cleaved by a large variety of two-electron donor ligands (for example L = phosphines[91,92,94] phosphites[91,92], arsines[91,92], stibines[91,92], pyridines[91,92], isonitriles[102], carbon monoxide[103], dimethyl sulfoxide[104], *etc...*) to give mononuclear complexes of the type $[Ru(\eta^6\text{-arene})Cl_2L]$.[87] Bidentate ligands L_2 (L_2 = $Ph_2AsC_2H_4AsPh_2$, $Ph_2P(CH_2)_nPPh_2$ (n = 2,3,4))[91,92,105] also react with $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ to cleave the chloride bridges, producing binuclear complexes of the type $[\{Ru(\eta^6\text{-arene})Cl_2\}_2(\mu\text{-}L_2)]$.[87] In polar solvents two basic ligands can be added per ruthenium to afford cationic compounds of the general type $[Ru(\eta^6\text{-arene})Cl(L)_2]^+$ (for example $(L)_2$ = $(PR_3)_2$,[106,107] $(P(OR)_3)_2$,[106,107] diphosphines,[105] diarsines[105], bipyridines,[108] pyrazoles[109] *etc...*).[87]

The reaction of $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ with hydrazine hydrate in methanol yields the $[Ru(\eta^6\text{-arene})(N_2H_4)_3]^{2+}$ series of cations which are isolated as their

tetraphenylborate salts. The subsequent treatment of these complexes with pyridine in acetone gives a range of *tris*-pyridyl complexes of the general formulation $[Ru(\eta^6\text{-arene})(C_5R_5N)_3][BPh_4]_2$.[110] A more effective way of synthesising *tris*-substituted arene ruthenium complexes is to treat $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ with an excess of silver salts in coordinating solvents, which gives rise to the formation of *tris*-solvento complexes of the type $[Ru(\eta^6\text{-arene})(Solvent)_3]^{2+}$ (Solvent = acetonitrile, acetone, methanol *etc...*).[87,94,111,112] These solvento complexes are highly useful synthetic intermediates in that they are easy to produce and are relatively stable with respect to decomposition. Further to this the solvent ligands in these complexes can be easily displaced by other ligands; for example a wide variety of symmetric and asymmetric *bis*-arene complexes have been synthesised using the $[Ru(\eta^6\text{-arene})(acetone)_3]^{2+}$ cation as an intermediate (Scheme 2.1).[112]



Where:

AgX = $AgBF_4$, $AgPF_6$.

R = Benzene, Hexamethylbenzene, Mesitylene.

R' = Benzene, Hexamethylbenzene, Mesitylene.

Acid = CF_3COOH, HBF_4, HPF_6.

Scheme 2.1: Synthesis of bis-arene complexes.

As mentioned in Chapter 1 the only significant coordination chemistry that has been reported for the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ dimer is the formation of simple bridge-cleaved adducts $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PR_3)]$[75] and $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NH_2C_6H_4Me)]$[75], and the preparation of *tris*-substituted species $[Ru(\eta^5\text{-}C_4Me_4S)L_3]^{2+}$ (L_3 = $(H_2O)_3$, $(NH_3)_3$, $(PH_3)_3$, arene, thiophene).[75,76] Given the well established synthetic utility of the $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ series of compounds, there is clearly considerable scope for the further development of the coordination chemistry of the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer. With this goal in mind this chapter presents a wide range of compounds which have been accessed using simple procedures from **44**.

2.2 RESULTS AND DISCUSSION

2.2.1 SYNTHESIS AND CHARACTERISATION OF $[Ru(\eta^5\text{-}C_4Me_4S)CL_2L]$ COMPLEXES

The compound $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** had previously been shown to be reactive towards bases forming complexes of the type $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2L]$.[75] The initial objective in this investigation was to expand the range of simple bridge cleaved compounds known. Thus this chemistry has been extended by forming complexes in which L = CO **60**, $PPhMe_2$ **61**, $P(OMe)_3$ **62**, NC_5H_5 **63**, and NC_5H_4CN **64**.

A saturated solution of carbon monoxide in dichloromethane reacts with $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** to give a yellow insoluble precipitate of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(CO)]$ **60**. The positive ion electrospray mass spectrum of this

compound exhibits a parent ion peak, at m/z 340, and shows fragmentation peaks due to the loss of chloride and CO (see Experimental). The infrared spectrum was recorded in the solid state as a KBr pellet and the spectrum contains a strong terminal ν(CO) stretching band at 1982 cm^{-1}. This is some 161 cm^{-1} lower than that of free carbon monoxide (ν(CO) = 2143 cm^{-1}). This denotes a significant amount of π back-bonding from the ruthenium metal centre to the π^* orbital of the carbon monoxide, consistent with a strong Ru-CO bond. Rauchfuss and co-workers had previously reported that the $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2]_n$ **49** polymer reacted with carbon monoxide to give the monocarbonyl adduct $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2(CO)]$ **65** (ν(CO) = 2043 cm^{-1}).[76] The comparison of the two stretching frequencies of these carbonyl compounds demonstrates that the '$Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2$' fragment is a weaker π-base than the '$Ru(\eta^5\text{-}C_4Me_4S)Cl_2$' fragment. The poor solubility of this material precluded the recording of any meaningful NMR data, although the microanalytical data is fully consistent with the proposed formulation.

Rauchfuss's group had previously reported the synthesis of a series of phosphine complexes of the type $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PR_3)]$ (R = Me, Bu, Ph, p-tolyl).[75] While the trialkylphosphine derivatives have unremarkable NMR spectra the variable temperature spectra of the triarylphosphine compounds are interesting. For example the room temperature ^{1}H-NMR spectrum of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PMe_3)]$ **66** displayed two sharp TMT methyl resonances as would be expected for a freely rotating TMT ligand.[75] However, the corresponding spectrum of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPh_3)]$ **67** showed two very broad resonances for the methyl groups of the TMT ligand.[75] These methyl

resonances sharpen when the temperature in the spectrometer was raised to +60 °C, but on cooling to -60 °C four methyl resonances were observed for the TMT ligand, accompanied by an increase in the complexity of the phenyl ring proton signals.[75] These studies indicated that there is a significant amount of steric interaction of the triarylphosphine ligand with the substituents on the thiophene ring giving rise to hindered rotation about both the Ru-P and Ru-TMT axes such that each methyl is chemically distinct at low temperature.[75]

A decision was taken to probe whether mixed alky/aryl phophine ligands also gave rise to significant interactions and to that end the compound [Ru(η^5-C_4Me_4S)Cl_2($PPhMe_2$)] **61** was prepared by the reaction of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] **44** with $PPhMe_2$ in dichloromethane. In the room temperature ^{1}H-NMR spectrum the methyl signals on the thiophene ligands appear as two widely spaced broad singlets, δ 1.30 and 1.88 ppm. On lowering the temperature of the NMR probe to -60 °C the signals sharpen, δ 1.28 and 1.87 ppm, but no splitting occurs. This leads to the deduction that even at this temperature the rotation of both the phosphine and thiophene ligands is still rapid. The remaining signals at this temperature are due to the complexed phosphine; the doublet at δ 1.85 ppm ($^2J_{PH}$ = 11.5 Hz) is due to the two equivalent methyl groups, and the broad multiplets at δ 7.45 and δ 7.68 ppm are due to the aromatic protons of the phenyl ring.

As no [Ru(η^5-C_4Me_4S)Cl_2(PR_3)] compound had been previously characterised by X-ray diffraction we decided to undertake such a study on **61**. Selected bond lengths and angles are reported in Table 2.1 and the structure is illustrated in Figure 2.1. If the assumption is made that the thiophene ligand

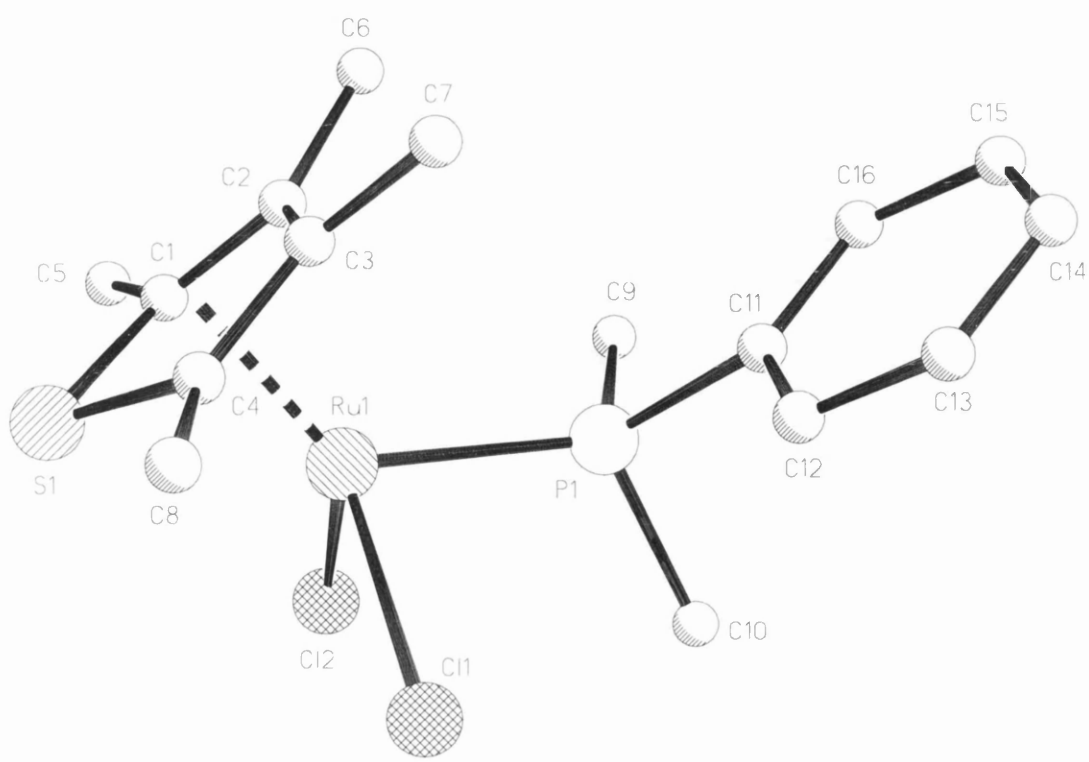
Table 2.1:

Selected Bond lengths (Å) and angles (°) for $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ 61.

Bond Lengths			
Ru(1)-C(1)	2.158(4)	Ru(1)-S(1)	2.4422(12)
Ru(1)-C(2)	2.221(4)	Ru(1)-P(1)	2.3303(10)
Ru(1)-C(3)	2.228(4)	Ru(1)-Cl(1)	2.4414(11)
Ru(1)-C(4)	2.169(4)	Ru(1)-Cl(2)	2.4419(11)
S(1)-C(1)	1.799(4)	C(1)-C(2)	1.427(7)
C(2)-C(3)	1.444(7)	C(3)-C(4)	1.425(7)
S(1)-C(4)	1.790(5)	P(1)-C(9)	1.835(4)
P(1)-C(10)	1.854(4)	P(1)-C(11)	1.842(4)
Bond Angles			
Cl(1)-Ru(1)-Cl(2)	90.82(4)	Cl(1)-Ru(1)-P(1)	86.84(4)
Cl(2)-Ru(1)-P(1)	83.17(4)	C(1)-S(1)-C(4)	90.3(2)
S(1)-C(1)-C(2)	110.9(3)	C(1)-C(2)-C(3)	112.9(4)
C(2)-C(3)-C(4)	112.5(4)	C(3)-C(4)-S(1)	111.5(4)

Figure 2.1:

The crystal structure of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ 61, showing the atom labelling scheme.



coordinates as a tridentate diolefin-thioether ligand, then it can be seen that this ligand occupies three facial sites on an octahedral ruthenium(II) ion. The only previously reported X-ray structure of a simple $[Ru(\eta^5\text{-}C_4Me_4S)L_3]$ compound was that of $[Ru(\eta^5\text{-}C_4Me_4S)(H_2O)_3][CF_3SO_3]_2$ **68**, which was severely disordered.[76] The thiophene ligand in **61** is approximately planar, but the sulfur atom is displaced 0.27 Å out of the plane formed by the atoms C(1), C(2), C(3), and C(4) on the side away from the metal. This slight folding of the ligand is also apparent in the angle of 12.5 ° formed between the planes [C(1)S(1)C(4)] and [C(1)C(2)C(3)C(4)]. Further distortions from planarity are observed for the methyl substituents on the thiophene, which are displaced somewhat from the metal, with deviations ranging from 6.1 to 7.5 °. Although inspection of the C-C bond lengths implies some localisation of the olefinic bonds the differences are not statistically significant in this structure. The Ru-C bond lengths form two pairs with those to the carbons adjacent to sulfur significantly shorter, av. 2.163(4) Å, than those to the other two carbon atoms, *av.* 2.224(4) Å. The Ru-S bond, 2.442(1) Å, is considerably longer than those observed in $[Ru(\eta^5\text{-}C_4Me_4S)(H_2O)_3][CF_3SO_3]_2$ **68** 2.307(6) Å,[76] or $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46** av. 2.355(2) Å,[75] but rather more comparable to those observed in the polynuclear compound $[\{Ru(\eta^5\text{-}C_4Me_4S)(\mu\text{-}Cl)\}_3(\mu^3\text{-}S)][PF_6]$ **45**, 2.414(4) - 2.432(4) Å.[75] The structure can be compared to that of the related isoelectronic Ru(arene) derivative $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PPhMe_2)]$ **69**,[93] and indeed with around 10 other crystal structures of $[Ru(\eta^6\text{-arene})Cl_2(PR_3)]$ compounds[113-119] documented on the Cambridge Crystallograpic Database. Interestingly, while the Ru-P bond length in this compound, 2.330(1) Å, does not differ greatly from

the average, 2.357 Å (range 2.291 - 2.379 Å), found for [Ru(η^6-arene)$Cl_2(PR_3)$] compounds the Ru-Cl bonds for **61**, 2.441(1) Å, are considerably longer than those observed in the Ru(arene) analogues, av. 2.406 Å (range 2.381 - 2.425 Å).

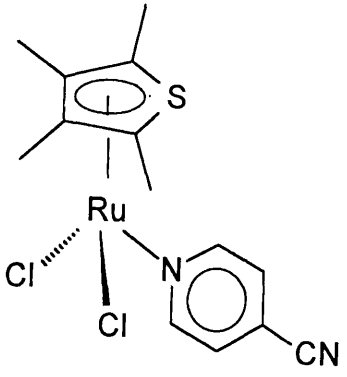
The reaction of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] **44** with $P(OCH_3)_3$ gives an analogous compound to **61**, namely [Ru(η^5-C_4Me_4S)$Cl_2(P(OCH_3)_3)$] **62**. Given the small cone angle (107 °) for this phosphite ligand one would anticipate that the ^{1}H-NMR spectrum would be essentially invariant with temperature. Indeed the spectrum remains unchanged in the range -60 to 0 °C, with only two tetramethylthiophene methyl resonances observed throughout, δ 1.98 and 2.00 ppm. At 20 °C the two singlets are unresolved, appearing as a symmetrical singlet at δ 1.99 ppm, but this is attributed to accidental coincidence of the chemical shifts, as a result of variation of temperature, rather than the result of some dynamic process. The FAB spectrum of this compound exhibited a parent molecular ion at m/z 438 due to the [Ru(η^5-C_4Me_4S)$Cl_2(P(OCH_3)_3)]^+$ ion, and the fragmentation pattern contained envelopes of peaks consistent with the loss of a chloride and $P(OCH_3)_3$ ligands from the compound.

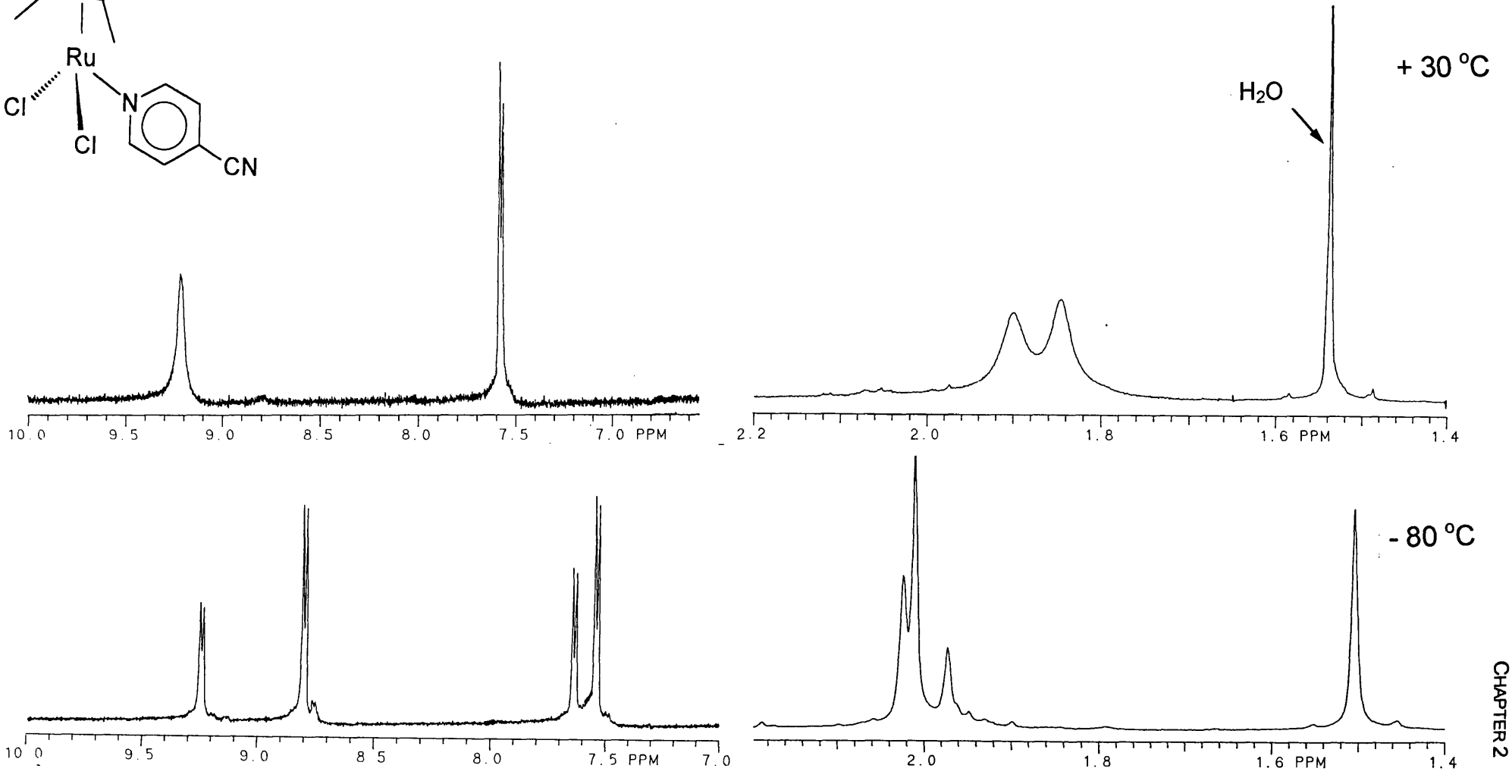
The reaction of [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] **44** with pyridine gives [Ru(η^5-C_4Me_4S)$Cl_2(NC_5H_5)$] **63** which has been routinely characterised (see Experimental). This compound was found to be insoluble in a number of solvents including chloroform, acetone and acetonitrile, although **63** was sufficiently soluble in CD_2Cl_2 solution to allow the recording of the ^{1}H-NMR spectrum. At 20 °C the spectrum exhibits two rather broad thiophene methyl

resonances, at δ 1.81 and 1.88 ppm, as well as three aromatic signals due to the protons of the pyridine ligand. These signals were observed as a doublet of doublets at δ 7.33 ppm due to the meta protons of the pyridine ring, a triplet at δ 7.76 ppm due to the *para* proton, and a broad resonance at δ 8.87 ppm integrating for 2 protons is assigned to the two ortho protons. On cooling to 0 °C the methyl signals become degenerate, and further cooling results in the precipitation of the compound from solution and no useful spectra could be obtained.

In contrast, if the 4-cyanopyridine analogue $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NC_5H_4CN)]$ **64** is prepared the NMR measurements can be made over a wide temperature range (Figure 2.2). At 30 °C in CD_2Cl_2 the ^{1}H-NMR spectrum consists of a pair of broad methyl resonaces, at δ 1.85 and 1.90 ppm, and two broad signals, at δ 7.57 and 9.21 ppm, due to the protons on the pyridyl ring. On cooling to -80 °C the spectrum changes dramatically, such that the pyridyl resonances are sharp and give rise to the eight-line pattern expected for an AA'BB' spin system, chemical shifts δ 7.54, 7.64, 8.80 and 9.24 ppm. At the same time the thiophene methyls appear as four singlets, δ 1.50, 1.97, 2.01 and 2.02 ppm. Clearly for **64** at low temperature in solution a structure has been frozen out in which each methyl is unique. Whether this arises due to restricted rotation about the Ru-N bond, or restricted rotation of the tetramethylthiophene ligand, or both, is unclear. However as Rauchfuss pointed out in his discussion of the NMR spectrum of $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPh_3)]$ **67** inhibiting the rotation about one Ru-ligand bond can be sufficient to render each methyl unique if the 'rotamer' stabilised at low temperature has the unique ligand, in this case 4-cyanopyridine, placed such that its projection bisects an S-C bond (Figure 2.3).

Figure 2.2: ***^{1}H-NMR spectra of [Ru(η^5-C_4Me_4S)Cl_2(NC_5H_4CN)] 64, recorded at +30 °C and -80 °C in a CD_2Cl_2 solution.***





The infrared spectrum of **64** exhibits a ν(CN) stretching band at 2235 cm^{-1} which is shifted to a lower wavenumber by 8 cm^{-1} from that of the free ligand (ν(CN) = 2243 cm^{-1}). This observation clearly demonstrates that the cyanopyridine ligand is bound via the pyridyl nitrogen and not *via* the cyano group, as one would expect a shift of at least 20 cm^{-1} if that were the case.

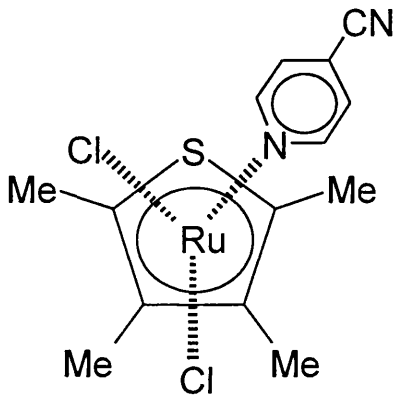


Figure 2.3: Low Temperature Structure of [Ru(η^5-C_4Me_4S)Cl_2(NC_5H_4CN)] 64.

Attempts were made to extend the range of these pyridine-based complexes, with a view to examining what effect placing bulky subsistents around the pyridyl nitrogen would have on the solution dynamics of these compounds. However both 2-methylpyridine and 2,6-lutidine may be refluxed with a dichloromethane solution of **44** for up to 72 hours without any apparent reaction, only starting materials being recovered on work-up. Clearly the steric repulsions associated with the methyl groups close to the nitrogen atom are too great to allow complexation to the 'Ru(η^5-C_4Me_4S)Cl_2' fragment.

2.2.2 SYNTHESIS AND CHARACTERISATION OF MONO AND DICATIONIC COMPLEXES OF RUTHENIUM TETRAMETHYLTHIOPHENE

In addition to simple bridge cleavage reactions it is possible to prepare compounds in which one or more of the chloride ligands have been displaced from the metal centre. Rauchfuss used silver reagents to remove the halides from $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44**, in the preparation of $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46**[75] and $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2]_n$ **49**[76] but for some ligands, at least, the use of the expensive silver reagent is unnecessary.

A) BIPYRIDYL COMPLEXES

Aqueous solutions of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** react rapidly with 2,2'-bipyridyl (bipy). When the reaction time is in excess of 30 minutes addition of $NH_4[PF_6]$ to the reaction mixture gives the well-known complex $[Ru(bipy)_3][PF_6]_2$ **70** as the only isolated product. However, if the reaction time is limited to a maximum of 15 minutes, and the work-up is performed rapidly, then the complex $[Ru(\eta^5\text{-}C_4Me_4S)Cl(bipy)][PF_6]$ **71** is obtained in good yield. Although the solid is stable solutions of **71** rapidly decompose. In the ^{1}H-NMR spectrum the proton resonances for the thiophene methyl groups are not resolved at ambient temperature and appear as a broad singlet at δ 2.10 ppm. However the four anticipated resonances for the aromatic protons of the 2,2'-bipyridyl ligand are clearly seen and integration of the spectrum confirms the ligand stoichiometry. The highest peak in the FAB mass spectrum corresponds to the $[Ru(\eta^5\text{-}C_4Me_4S)Cl(bipy)]^+$ ion and the sequential loss of chloride from this is observed (see Experimental). The analytical data are also consistent with the formulated compound.

Compound **71** will react further with $PPhMe_2/Ag[PF_6]$ to give $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)][PF_6]_2$ **72**, albeit in only a modest yield. The spectroscopic characterisation of **72** was routine, with intergration of the ^{1}H-NMR spectrum being consistent with a 1:1:1 ratio of the ligands C_4Me_4S, bipy, and $PPhMe_2$. Confirmation of the identity of **72** was obtained by an X-ray structure determination, Figure 2.4 and Table 2.2. The crystal used in the study was grown by the technique of vapour diffusion from a dichloromethane/hexane solvent system, thus explaining the presence of a molecule of solvent of crystallisation in the final structure. Unfortunately the crystal was of significantly poorer quality than that employed for the other three structural determinations reported in this chapter. Only *ca.* 60 % of the measured reflections were observed at the $2\sigma(I)$ level, hence the lower precision in the reported geometrical parameters. Nevertheless, the diffraction experiment clearly demonstrates the octahedral coordination at the metal. It is notable that the thiophene ring is closer to planarity than was observed to be the case for **61**. Interestingly, while the Ru-P distance, 2.364(4) Å, is somewhat longer than that observed for **61**, the Ru-S distance, 2.397(5) Å, is markedly shorter, by some 0.045 Å. It should be also noted that while 'Ru(arene)' analogues of **71** and **72** have been described previously[120], none of these have been characterised crystallographically.

B) POLY PYRAZOLYL COMPLEXES

The analogous compounds $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **73** and $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ **74** are synthesised from aqueous solutions of the

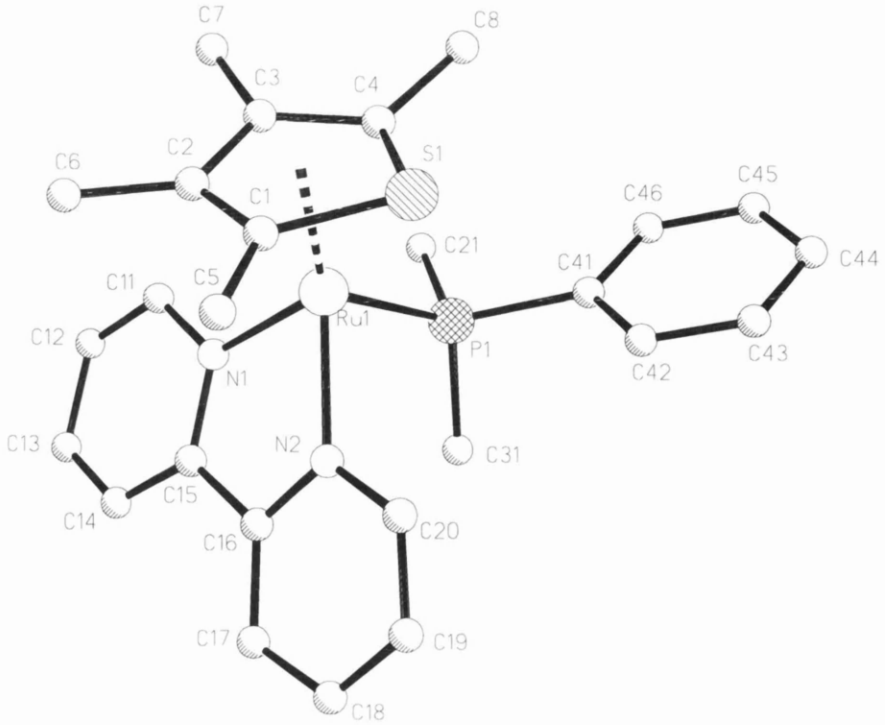
Table 2.2:

Selected Bond lengths (Å) and angles (°) for $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)[PF_6]_2.CH_2Cl_2$ 72.CH_2Cl_2.

Bond Lengths			
Ru(1)-C(1)	2.27(2)	Ru(1)-S(1)	2.397(5)
Ru(1)-C(2)	2.26(2)	Ru(1)-P(1)	2.364(4)
Ru(1)-C(3)	2.28(2)	Ru(1)-N(1)	2.089(14)
Ru(1)-C(4)	2.20(2)	Ru(1)-N(2)	2.091(14)
S(1)-C(1)	1.77(2)	C(1)-C(2)	1.40(2)
C(2)-C(3)	1.49(2)	C(3)-C(4)	1.44(3)
S(1)-C(4)	1.76(2)	P(1)-C(21)	1.82(2)
P(1)-C(31)	1.82(2)	P(1)-C(41)	1.83(2)
Bond Angles			
N(1)-Ru(1)-N(2)	77.4(5)	N(1)-Ru(1)-P(1)	87.4(4)
N(2)-Ru(1)-P(1)	89.7(4)	C(1)-S(1)-C(4)	91.8(8)
S(1)-C(1)-C(2)	112.3(13)	C(1)-C(2)-C(3)	113(2)
C(2)-C(3)-C(4)	110(2)	C(3)-C(4)-S(1)	112.6(10)
Ru(1)-N(1)-C(11)	125.7(14)	Ru(1)-N(1)-C(15)	115.5(12)
Ru(1)-N(2)-C(20)	124.5(12)	Ru(1)-N(2)-C(16)	117.7(11)

Figure 2.4:

The crystal structure of the cation in $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)[PF_6]_2.CH_2Cl_2$ 72.CH_2Cl_2, showing the atom labelling scheme.



$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer with the appropriate ligand or its salt. These reactions result in the displacement of all the chloride ligands from the metal and the introduction of the tridentate ligand on the metal, whilst still retaining the thiophene ligand, in a single synthetic step. These complexes are isolated from the aqueous reaction mixtures by anion metathesis using $NH_4[PF_6]$, and are obtained in analytically high purity, without the need for further purification. Interestingly $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ **74** is routinely isolated in yields in excess of 80 % while $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **73** is isolated in yields of less than 60 %. It is possible that this poorer yield is due to the degradation of the pyrazolylborate ligand, which is more susceptible to fragmentation than the chemical more robust pyrazolylmethane.

Surprisingly water proved to be the optimal solvent to conduct these, as well as many other reactions with the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer. Initially a number of reactions were attempted using polar organic solvents, although the reactivity of **44** and yields of the desired complexes were often poor. For example the synthesis of the $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}]^+$ cation was initially attempted in a range of "standard" solvents used in arene-ruthenium chemistry, namely acetonitrile, methanol and acetone. In the case of the acetonitrile and methanol reactions, no tractable materials were isolated from the reaction mixture. When the reaction was performed in acetone, the formation of the desired compound was observed, albeit in low yield (*ca.* 30 %) and purity (2-5 % contamination).

The characterisation of both these compounds was straightforward and the analysis of the spectroscopic data for $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **73**, discussed below, is typical. The infrared spectrum of **73** exhibits the characteristic "fingerprint" associated with the pyrazolyl groups as well as a ν(BH) band observed at 2502 cm^{-1}, consistent with the presence of the hydrido*tris*(pyrazolyl)borate ligand. The infrared spectrum also contains a strong band associated with the PF_6^- anion (835 cm^{-1}). The ^{1}H-NMR spectrum consists of the two methyl resonances of the thiophene ligand, singlets at δ 2.45 and 2.40 ppm, three pyrazolyl resonances at δ 8.14, 7.98, and 6.41 ppm, and a very broad signal at *ca.* 4.2 ppm, due to the proton on boron. The doublet of doublets resonance at δ 6.41 ppm can be unambiguously assigned to the protons at the '4' position of the pyrazolyl rings. The protons at the '3' and '5' position are assigned by analogy with NMR studies conducted by Claramunt and Cayon.[121] Thus the resonance at δ 8.14 ppm is due to the protons at the '3' position and that at δ 7.98 ppm is assigned to the protons of the '5' position.

Complete confirmation of the structure of $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **73** was obtained by a single crystal structure determination, Figure 2.5 (with selected bond distances and angles given in Table 2.3). The X-ray structure shows the ruthenium centre bound in a tridentate manner to the nitrogens of the hydrido*tris*(pyrazolyl)borate ligand and in an η^5-fashion to the thiophene ligand. The basic geometry is as described previously with psuedo-octahedral coordination around the ruthenium, though it should be noted that the angles subtended at ruthenium are somewhat smaller than in the two previous compounds, 83-85 °, as a consequence of the chelate bite of the

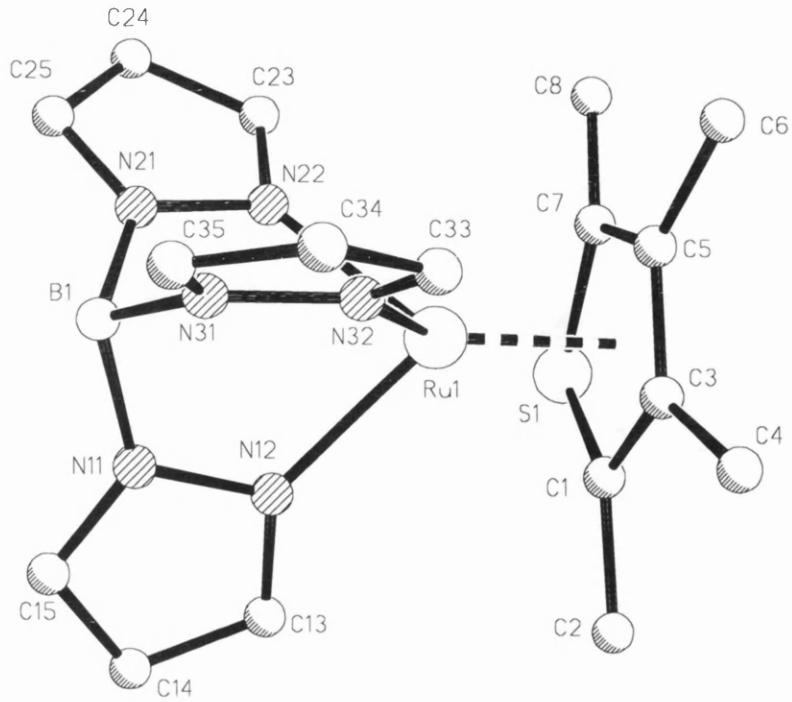
Table 2.3:

Selected Bond lengths (Å) and angles (°) for $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ 73.

Bond Lengths			
Ru(1)-C(1)	2.184(4)	Ru(1)-S(1)	2.4006(12)
Ru(1)-C(3)	2.240(4)	Ru(1)-N(12)	2.151(4)
Ru(1)-C(5)	2.245(4)	Ru(1)-N(22)	2.159(4)
Ru(1)-C(7)	2.204(4)	Ru(1)-N(32)	2.125(3)
S(1)-C(1)	1.795(5)	C(1)-C(3)	1.419(6)
C(3)-C(5)	1.464(7)	C(5)-C(7)	1.415(7)
S(1)-C(7)	1.800(5)		
Bond Angles			
N(12)-Ru(1)-N(22)	82.94(14)	N(12)-Ru(1)-N(32)	84.51(14)
N(22)-Ru(1)-N(32)	85.21(14)	C(1)-S(1)-C(7)	90.2(2)
S(1)-C(1)-C(3)	112.4(3)	C(1)-C(3)-C(5)	112.0(4)
C(3)-C(5)-C(7)	112.9(4)	C(5)-C(7)-S(1)	111.9(4)
Ru(1)-N(12)-N(11)	120.0(3)	Ru(1)-N(22)-N(21)	120.3(3)
Ru(1)-N(32)-N(31)	120.3(3)	N(11)-B(1)-N(21)	108.0(4)
N(11)-B(1)-N(31)	107.9(4)	N(21)-B(1)-N(31)	108.1(4)

Figure 2.5:

The crystal structure of the cation in $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ 73, showing the atom labelling scheme.



hydrido*tris*(pyrazolyl)borate ligand. While the thiophene ligand can be described as being approximately planar, there are small deviations from planarity similar to those described for [Ru(η^5-C_4Me_4S)Cl_2(PPhMe_2)] **61**. For example, the sulfur is displaced by 0.15 Å from the plane of the metallated carbons on the side away from the metal, and the folding of the thiophene ligand is 7.1 °, *cf.* 12.5 ° for **61**. The Ru-C bonds again form a long and a short pair, but the average Ru-C distance in **73**, 2.218(4) Å, is significantly longer than that for **61**, 2.194(4) Å, reflecting the superior sigma donor power of the N_3 ligand set in **73**, which is also reflected in the shorter Ru-S distance, 2.401(1) Å. The Ru-N distances can be usefully compared to those observed for the analogous ruthenium-arene compound, [Ru(η^6-*p*-cymene){κ^3-HB(Pz)$_3$}][PF_6] **75**[122]. As with **75** the Ru-N distances are unequal, with two longer, 2.151(4) and 2.159(4) Å, and one shorter, 2.125(3) Å, bond. Each of these bonds is approximately 0.03 Å longer in **73** reflecting the greater *trans* influence of the thiophene ligand, which is consistent with the fact that [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] **44** is prepared from [{Ru(η^6-*p*-cymene)Cl(μ-Cl)}$_2$] **40** *via* an arene displacement reaction.

The addition of *tris*(3,5-dimethylpyrazolyl)methane (a sterically more demanding ligand) to an aqueous solution of the [{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] results in the formation of the *bis*-chelated compound [Ru(η^5-C_4Me_4S){κ^2-HC(3,5-Me_2Pz)$_3$}Cl][PF_6] **76**. Even when this reaction is left for a protracted period of time before work-up with NH_4[PF_6], no conversion to the κ^3 compound is observed. Indeed attempts were made to obtain the tridentate complex by

abstraction of the chloride from **76** by treatment with stoichiometric amounts of $Ag[PF_6]$, but these proved fruitless. This clearly demonstrates that bidentate coordination of the pyrazolylmethane is preferred over tridentate coordination due to unfavourable steric interactions with the '$Ru(\eta^5\text{-}C_4Me_4S)$' fragment.

The FAB mass spectrum of **76** consists of a parent peak at m/z 575 due to the $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^2\text{-}HC(3,5\text{-}Me_2Pz)_3\}Cl]^+$ ion and shows fragmentation peaks due to the loss of chloride and tetramethylthiophene at m/z 539 and 435 respectively. The microanalytical data (including chloride analysis) are wholly consistent with the proposed formulation as is the infrared spectrum, which exhibits bands due to the PF_6^- anion and the Ru-Cl bond (see Experimental). The ^{1}H-NMR spectrum of **76** consists of nine sharp singlet resonances. The low field signal at δ 7.98 ppm originates from the proton of the bridgehead atom of the *tris*(3,5-dimethylpyrazolyl)methane ligand, the two aromatic resonances at δ 6.13 (1 proton) and δ 6.30 ppm (2 protons) are due to the protons at the '4' position of pyrazolyl rings, with the former being ascribed to the uncoordinated ring and the latter to the metallated rings of the pyrazolyl ligand. The remaining signals are due to disparate methyl groups of the various ligands, and are assigned by analogy with ^{1}H-NMR studies previously carried out in our group on polypyrazolyl complexes.[123] The resonances at δ 1.74 and δ 2.07 ppm correspond respectively to the methyls at the '5' and '3' positions of the uncoordinated pyrazolyl, and the signals at δ 2.42 and 2.61 ppm are due to the '5' and the '3' methyls of the metallated pyrazolyl rings. The presence of two sets of signals with a 2:1 integral ratio associated with the *tris*(3,5-dimethylpyrazolyl)methane ligand offers clear evidence for the formation of the *bis*-chelate compound. Moreover the signals of the unique pyrazolyl group

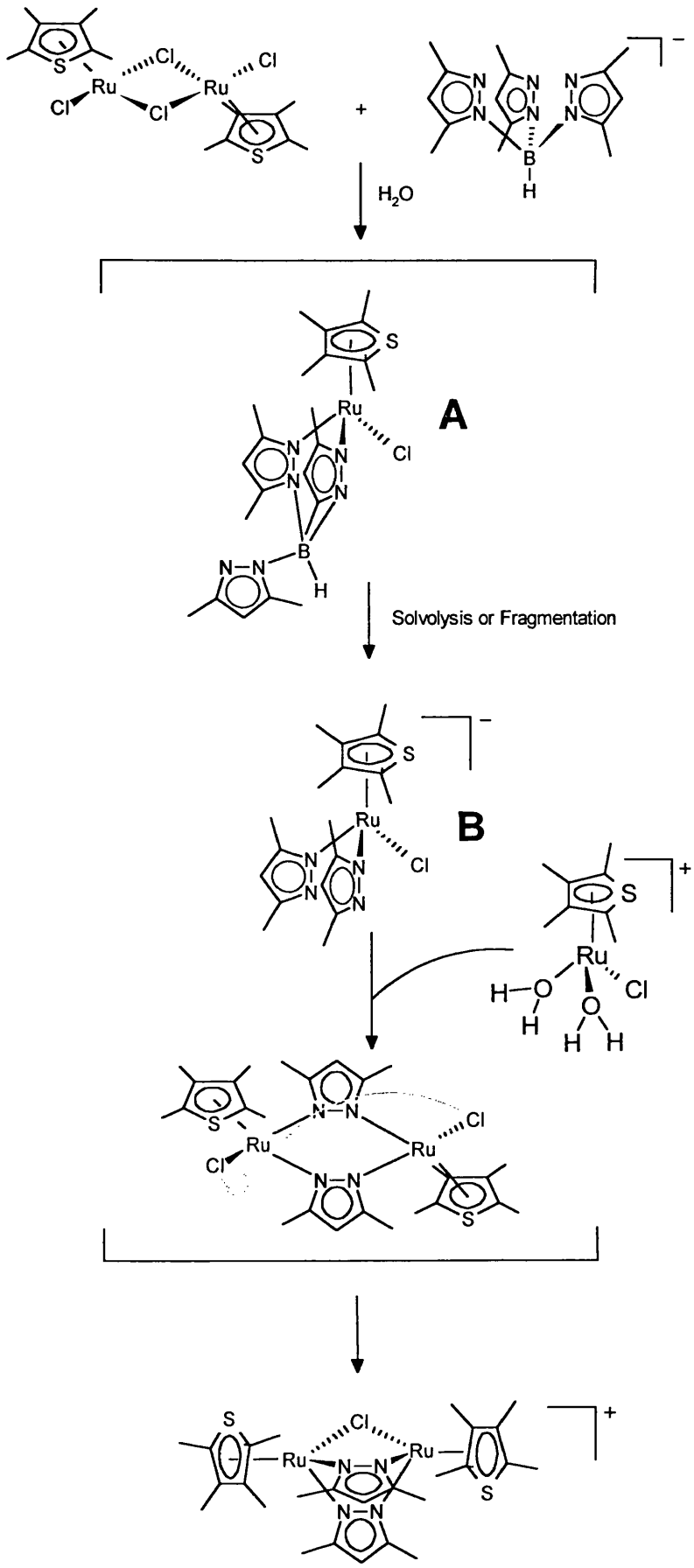
appear at higher field, consistent with fact that this non-metallated substituent would experience less deshielding. The remaining methyl signals at δ 2.17 and 1.80 ppm are assigned to the tetramethylthiophene ligand.

In an attempt to form an analogous compound to the type described above the reaction of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** with potassium hydrido*tris*(3,5-dimethylpyrazolyl)borate in aqueous solution was investigated, but this resulted in the isolation of an unexpected product. On examination of the spectroscopic data it quickly became apparent that the hydrido*tris*(3,5-dimethylpyrazolyl)borate ligand had fragmented. For example the ^{1}H-NMR spectrum of this product consisted of only four signals, which was far too simple to be consistent with the intact ligand still being present in the final product. Indeed conformation of this suspicion came from the infrared spectrum which shows no ν(BH) stretch. The fragmentation of poly(pyrazolyl)borate is by no means without precedent in the literature.[109, 124-126] These ligands are increasingly becoming infamous for their instability, with numerous reports of unexpected products being isolated as a result of the degradation of the ligands.[109, 123-126] Analysis of the spectroscopic data, discussed below, leads to the conclusion that the binuclear species $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)][PF_6]$ **77** has been formed in this reaction.

The ^{1}H-NMR spectrum exhibits resonances at δ 1.99 and 2.10 ppm due to the methyl groups of the thiophene ligand. The signal at δ 2.53 can be readily assigned to the equivalent methyl group2s of the bridging pyrazolate ligands, and the remaining singlet at δ 5.55 ppm is due to the proton at the '4' position on the pyrazolide. Oro and co-workers had previously reported the synthesis of

a series of binuclear ruthenium compounds containing bridging pyrazolate ligands.[127-128] The ^{1}H-NMR of one such compound $[Ru_2(\eta^6\text{-}p\text{-cymene})(\mu\text{-}3,5\text{-}Me_2Pz)(\mu\text{-}OH)_2][BF_4]$ **78** exhibits resonances for the pyrazolate at δ 2.55 (methyl resonance) and δ 6.00 (ring proton) ppm, which compare very favourably with the resonances observed in **77**.[128] The microanalysis of **77** is wholly consistent with the proposed formulation, but the molecular ion is not observed in the FAB mass spectrum. The spectrum does show a peak at m/z 674 which corresponds to the loss of a PF_6^- and a chloride from the proposed compound and a peak at m/z 579 consistent with the further loss of a Me_2Pz ligand. The envelope of peaks associated with these fragments fits the expected isotopic patterns. In particular the characteristic pattern for two rutheniums is present and this provides corroborative evidence for the formation of a binuclear ruthenium compound.

Pyrazolate bridging ligands are by no means unusual with many examples being described in the literature.[129] What makes the synthesis of $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)][PF_6]$ **77** somewhat unusual is the method of preparation. Attempts were made to rationalise the synthetic method by the reaction of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** with sodium 3,5-dimethylpyrazolate in a variety of solvents (H_2O, ethanol and dichloromethane); each attempt however resulted in the formation of intractable reaction mixtures. This might indicate that the hydrido*tris*(3,5-dimethylpyrazolyl)borate ligand is more intimately involved in the reaction mechanism and is more than just a source of pyrazolate.



Scheme 2.2: Proposed mechanism for the formation of the $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)]^+$ cation.

Scheme 2.2 shows a hypothetical mechanism that leads to the formation of $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)][PF_6]$ **77**. It seems reasonable to speculate that the formation of **77** proceeds *via* the *bis*-chelate intermediate $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^2\text{-}HB(3,5\text{-}Me_2Pz)_3\}Cl]$ **A**. This intermediate can then be envisaged to undergo B-N bond cleavage of the $[HB(3,5\text{-}Me_2Pz)_3]^-$ ligand. This could be as a consequence of steric strain in the coordination sphere of the intermediate resulting in the rupture of the B-N bonds. Alternatively the intermediate **A** may undergo solvolytic cleavage of the B-N bonds by the attack of the nucleophilic water at boron. Both these scenarios results in the formation of $[Ru(\eta^5\text{-}C_4Me_4S)(\sigma\text{-}3,5\text{-}Me_2Pz)_2Cl]^-$ **B**. This metallo-ligand is now perfectly poised to react with a '$Ru(\eta^5\text{-}C_4Me_4S)$' source. In Scheme 2.2 the *bis*-solvento species $[Ru(\eta^5\text{-}C_4Me_4S)(H_2O)_2Cl]^+$ provides this moiety, which reacts with **B** to yield the cation $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)]^+$.

There are several pieces of evidence that support the proposed mechanism; these are briefly discussed below:

1) The intermediate **A** is a direct analogue of the $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^2\text{-}HC(3,5\text{-}Me_2Pz)_3\}Cl]^+$ cation described above.
2) Steric forces play an important role in the polypyrazolylborate ligand class. Trofimenko and co-workers have shown that with selective substitution at the 3-position of the pyrazole ring with a bulky *iso*-propyl group it is possible to achieve a 1,2-boratropic shift involving B-N bond cleavage.[130] This, combined with the anecdotal evidence that the '$Ru(\eta^5\text{-}C_4Me_4S)$' fragment is sterically crowded, may provide an explanation for the fragmentation of the $[HB(3,5\text{-}Me_2Pz)_3]^-$ ligand; the anecdotal evidence comes from the reactions

with tridentate tertiary phosphine ligands which have been singularly unsuccessful.

3) Previous studies in our group have demonstrated the susceptibility of ruthenium complexes containing the $[HB(3,5\text{-}Me_2Pz)_3]^-$ ligand to nucleophilic attack at boron. For example, it was found that the $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^3\text{-}HB(3,5\text{-}Me_2Pz)_3\}]^+$ cation is attacked in ethanolic solutions. This attack results in the rupturing of one of the B-N bonds in the coordinated $[HB(3,5\text{-}Me_2Pz)_3]^-$ ligand, leading to the addition of an ethoxide functionality to the boron of the polypyrazolyl ligand, and the concomitant loss of one of the pyrazolyl groups, forming the novel compound $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^3\text{-}N,N,O\text{-}HB(3,5\text{-}Me_2Pz)_2(OCH_2CH_3)\}]^+$.[123]

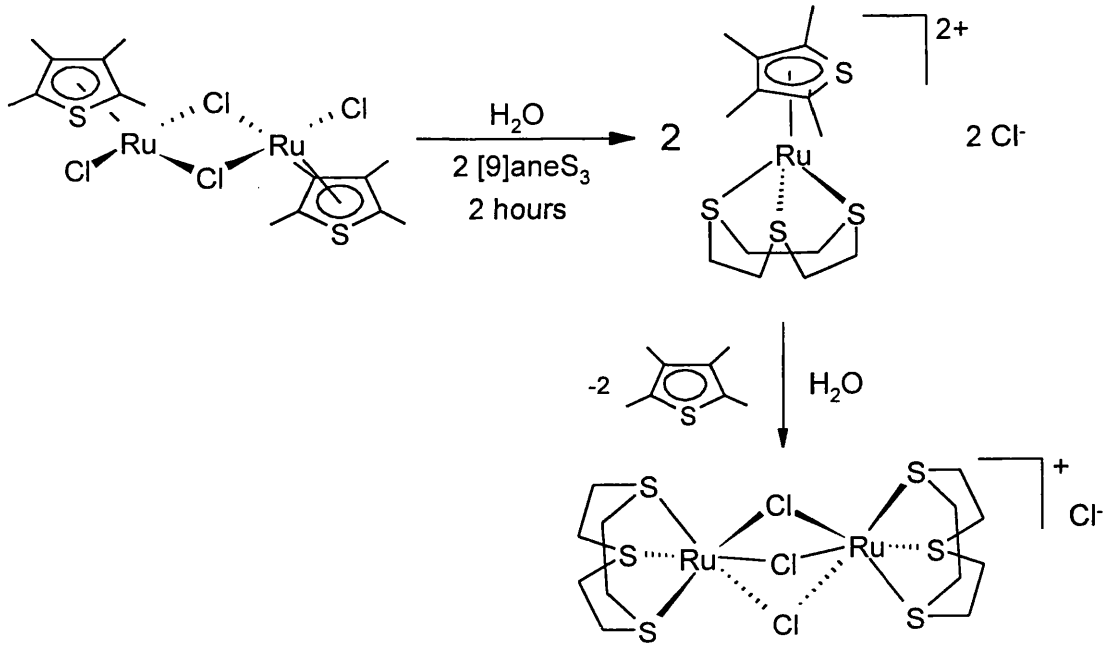
Although the proposed mechanism is intuitively reasonable it remains unproven; attempts to isolate intermediates by terminating the reaction after different time intervals did not yield any meaningful data. However, given the observations described above, and the fact that rational synthesis with sodium 3,5-dimethylpyrazolate did not give **77**, it is believed that there is considerable merit in proposing the intermediacy of **A** and **B** in the preparative method.

C) MACROCYCLIC COMPLEXES

The treatment of an aqueous suspension of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** with two molar equivalents of 1,4,7-trithiacyclononane ([9]aneS_3) results in the formation of a yellow solution over a period of 2 hours. The subsequent addition of an excess of aqueous $NH_4[PF_6]$ to the reaction mixture gives a yellow precipitate of $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$ **79** in good yield (72

%). The ^{1}H-NMR spectrum of this compound was recorded in a $(CD_3)_2CO$ solution. The spectrum displays two sharp resonances at δ 2.38 and 2.44 ppm, due to the methyl substituents of the thiophene ring and a third singlet at δ 3.24 ppm, due to the methylene protons of the [9]aneS_3 ligand. The observation of such a simple spectrum is consistent with rapid rotation of the π-bonded thiophene ring about the metal-ligand axis. The integration of the NMR spectrum, as well as the microanalytical and mass spectral data, were consistent with the proposed formulation of the compound. Post-work-up the filtrate was stored at ca. 0 °C for 48 hours; this resulted in the further precipitation of a yellow solid. This was initially assumed to be **79**, although it soon became apparent from its physical properties that this material was not the anticipated material **79**. The poor solubility of this solid precluded the recording of any meaningful NMR data. A rudimentary qualitative analysis of this material with $HNO_3/AgNO_3$ revealed that this compound contained chloride ions, and the infrared spectrum still contained the characteristically strong vibration, at 839 cm^{-1}, associated with PF_6^- counter-ion. The positive ion electrospray mass spectrum displayed the highest envelope of peaks at m/z 671; this envelope was successfully simulated to be $Ru_2Cl_3C_{12}H_{24}S_6$. Putting this information together suggested a binuclear compound formulated as $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$ **80**, which was subsequently confirmed by elemental analysis (C, H, Cl) (see Experimental).

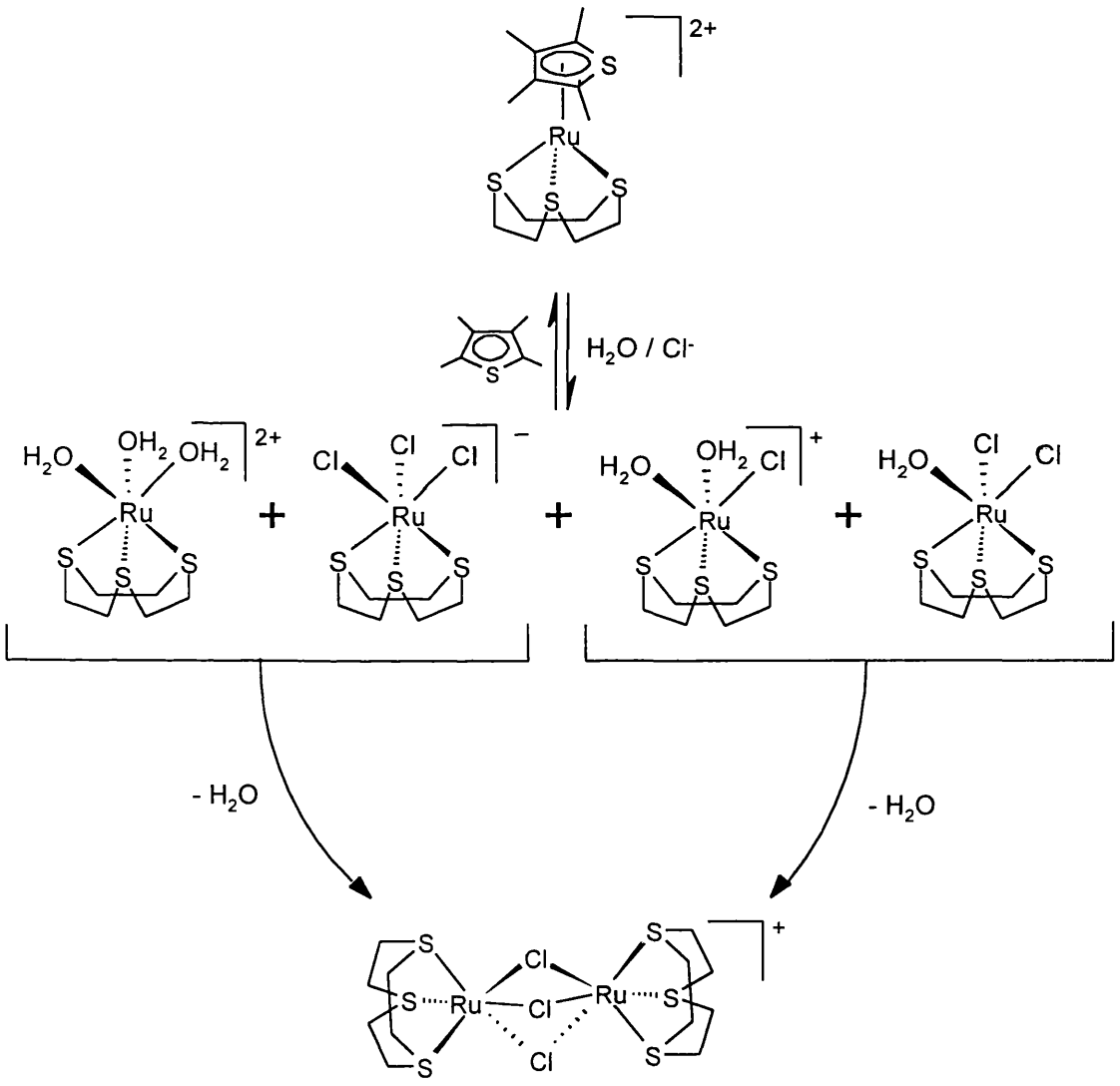
The formation of $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$ **80** was initially puzzling in that this compound was not detected in the original precipitate which contained exclusively $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$ **79**. The formation of the $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3]^+$ cation was only observed if the remaining reaction



Scheme 2.3: Preparation of [9]aneS$_3$ complexes.

mixture was allowed to stand for a considerable period of time. This would seem to indicate that **80** is formed from the $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)]^{2+}$ cation, Scheme 2.3. This hypothesis was tested by placing a sample of **79** in an aqueous solution containing an excess of both NaCl and NH_4PF_6. The mixture was then stirred for 4 days. Upon work-up of the sample it was observed that the bulk of **79** had been converted to the binuclear compound $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$ **80**. From this observation it is clear that in solution the tetramethylthiophene ligand in the $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)]^{2+}$ cation is lost with time. The ability of the macrocyclic ligand to labilise the thiophene ligand appears to be important, as attempts to adapt and extend this synthetic methodology to the other *tris*-chelate complexes reported in this chapter proved unsuccessful. Presumably the strong donor ability of the macrocyclic ligand is in part responsible for labilising the thiophene ligand and/or stabilising any intermediate that may be formed *en route* to the triply chloro-bridged complex. A possible mechanism for this reaction is illustrated in

Scheme 2.4. The loss of the thiophene ligand presumably results in the formation of a range of intermediates in which some combination of water and halide ligands are bound to the metal. These then combine in an appropriate fashion to give the $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3]^+$ the chloro-bridged binuclear complex. The poor solubility of **80** results in its immediate precipitation from solution, thus driving any equilibrium towards the formation of this compound.



Scheme 2.4: Possible mechanism for the formation of $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$ 80.

Attempts were made to replicate the chemistry of $[9]aneS_3$ with **44** using the related macrocyclic ligand 1-aza-4,7-dithiacyclononane ($[9]aneS_2N$). Using an analogous synthetic method in aqueous solution resulted in the formation of a

mixture of materials. The synthesis of the $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_2N)]^{2+}$ cation was therefore attempted utilising the more electrophilic reagent $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2]_n$ **49**.[76] This "polymer" was formed in a dichloromethane solution and reacted *in situ* with $[9]aneS_2N$. The reaction mixture was stirred for 12 hours at room temperature after which the solvent was removed. The residue was redissolved in ethanol and treated with $NH_4[PF_6]$ and an immediate yellow precipitate was formed. The mass spectrum of this material showed fragments consistent with the formation of $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_2N)][PF_6]_2$. The ^{1}H-NMR spectrum of this material was recorded in $(CD_3)_2CO$ and displays two sharp resonances, at δ 2.33 and 2.36 ppm, due to the methyl substituents of the thiophene ring. The methylene protons of the $[9]aneS_2N$ ligand appear as a series of ill-resolved multiplets in the range δ 2.7 – 3.5 ppm. Unfortunately further analysis of this material showed significant amounts of contaminants by an as yet unknown substance or substances. As a result no satisfactory microanalytical data were obtained. Attempts to recrystallise the mixture of products from a variety of solvents proved unsuccessful. However it is evident that the majority of the sample is the desired complex.

D) TRIPLY-CHLORO BRIDGED COMPLEX

It will have been noticed that many of the reactions described above have been performed in aqueous solution. Rauchfuss originally examined the behaviour of $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ in aqueous solution using ^{1}H-NMR spectroscopy,[75] and reported that in D_2O two species were present in an approximate ratio of 10:1. The minor species was identified as the ion $[Ru(\eta^5\text{-}$

$C_4Me_4S)(D_2O)_3]^{2+}$, which was synthesised independently, isolated as its triflate salt, and characterised by X-ray diffraction.[76] At the time of the original report the major component was not identified. Given the successful synthesis of a number of novel compounds in aqueous solutions, it was important to re-examine this reaction. When $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** is placed in an aqueous solution containing an excess of $NH_4[PF_6]$ a red solid deposits from solution over a period of 72 hours. The ^{1}H-NMR spectrum of this compound exhibits only one set of tetramethylthiophene signals, δ 2.15 and 2.10 ppm. The mass spectrum displays a peak at m/z 591, which displays the predicted isotope pattern for two ruthenium and three chlorine atoms. These data, together with the elemental analysis (see Experimental), suggest that the compound be formulated as $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ **81**, which was subsequently confirmed by X-ray diffraction. Figure 2.6 depicts the cation in this compound and selected geometrical parameters are reported in Table 2.4. The complex cation has a face-sharing bi-octahedral structure with the two ruthenium(II) ions bridged unsymmetrically by three chloride ions. There are four long Ru-Cl distances, 2.4600(7) - 2.4792(7) Å, and two short, 2.4168(7) and 2.4160(7) Å distances. The short bonds are approximately *trans* to the Ru-S bonds, S(1)-Ru(1)-Cl(3) 167.58(3) °, S(2)-Ru(2)-Cl(1) 167.24(3) °, and reflect the *trans* influence of the ligating sulfur atoms, which form shorter bonds to the metal, 2.3375(7) and 2.3353(7) Å, than seen in the other compounds reported in this thesis. Nevertheless the sulfur atoms are still displaced, 0.18 Å S(1) and 0.17 Å S(2), from the plane of the four metallated carbon atoms of the thiophene ligand, on the side away from the metal. Despite the wide range of

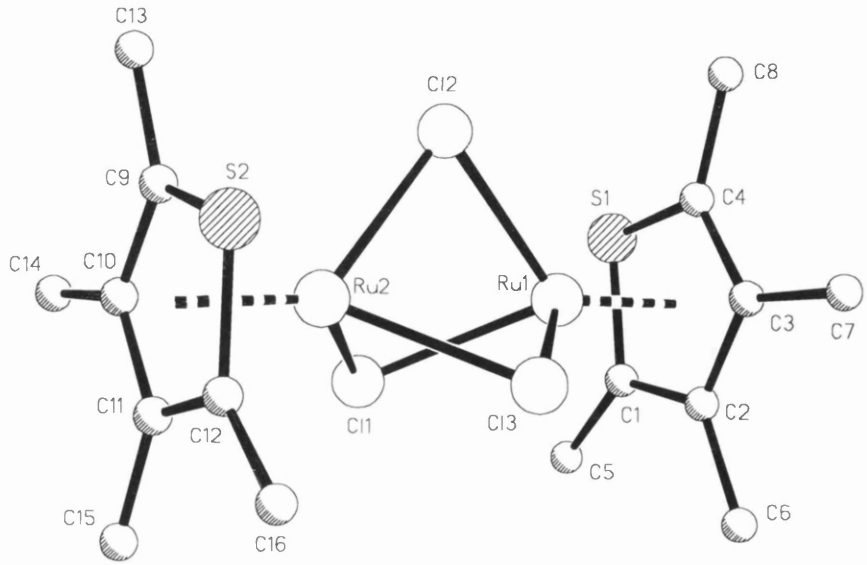
Table 2.4:

Selected Bond lengths (Å) and angles (°) for $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81.

Bond Lengths			
Ru(1)-Cl(1)	2.4792(7)	Ru(2)-Cl(1)	2.4160(7)
Ru(1)-Cl(2)	2.4615(7)	Ru(2)-Cl(2)	2.4600(7)
Ru(1)-Cl(3)	2.4167(7)	Ru(2)-Cl(3)	2.4752(7)
Ru(1)-S(1)	2.3375(7)	Ru(2)-S(2)	2.3353(7)
Ru(1)-C(1)	2.117(3)	Ru(2)-C(9)	2.114(3)
Ru(1)-C(2)	2.170(3)	Ru(2)-C(10)	2.153(3)
Ru(1)-C(3)	2.155(3)	Ru(2)-C(11)	2.172(3)
Ru(1)-C(4)	2.116(3)	Ru(2)-C(12)	2.133(3)
S(1)-C(1)	1.770(3)	S(2)-C(9)	1.773(3)
C(1)-C(2)	1.420(4)	C(9)-C(10)	1.414(4)
C(2)-C(3)	1.437(4)	C(10)-C(11)	1.441(4)
C(3)-C(4)	1.418(4)	C(11)-C(12)	1.420(4)
C(4)-S(1)	1.766(3)	C(12)-S(2)	1.764(3)
Bond Angles			
Cl(1)-Ru(1)-Cl(2)	80.73(2)	Cl(1)-Ru(2)-Cl(2)	82.03(2)
Cl(2)-Ru(1)-Cl(3)	80.93(2)	Cl(2)-Ru(2)-Cl(3)	79.81(2)
Cl(1)-Ru(1)-Cl(3)	80.29(2)	Cl(1)-Ru(2)-Cl(3)	80.39(2)
Ru(1)-Cl(1)-Ru(2)	83.39(2)	Ru(1)-Cl(2)-Ru(2)	82.86(2)
Ru(1)-Cl(3)-Ru(2)	83.46(2)	C(9)-S(2)-C(12)	91.30(14)
C(1)-S(1)-C(4)	90.96(14)	S(2)-C(9)-C(10)	111.0(2)
S(1)-C(1)-C(2)	111.6(2)	C(9)-C(10)-C(11)	113.3(3)
C(1)-C(2)-C(3)	112.2(2)	C(10)-C(11)-C(12)	111.9(3)
C(2)-C(3)-C(4)	112.7(2)	C(11)-C(12)-S(2)	111.8(2)
C(3)-C(4)-S(1)	111.6(2)		

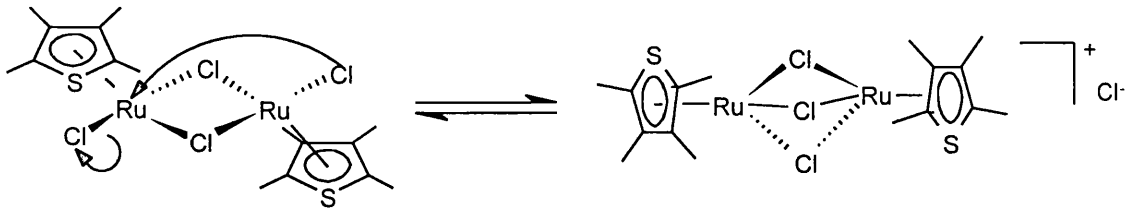
Figure 2.6:

The crystal structure of cation in $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81, showing the atom labelling scheme.



Ru-Cl distances the mean value, 2.4514(7) Å, is not very different from the mean value observed for the analogous $[Ru_2(\eta^6\text{-arene})_2(\mu\text{-Cl})_3]^+$ cations reported in the literature, 2.430 Å.[131-135] The angles Cl-Ru-Cl subtended at ruthenium are 80(±1) °, while the angles at the bridging chlorides are 83(±1) °. These values are unremarkable and fall within the normal range for compounds in which three halide ions bridge two metal centres in the absence of any metal-metal bond.

Although in the first instance it might seem unlikely that **81** can be formed in aqueous solution the rationale for its formation is, in fact, quite logical. In an aqueous solution an equilibrium must exist between the neutral doubly chloro-bridged dimer and the triply chloro-bridged ion, Equation 2.1. While the position of the equilibrium is not known it is nevertheless true that in the presence of an excess of hexafluorophosphate anion, the formation of the insoluble complex **81** occurs. Thus, even if the extent of the equilibrium is very small, over time, precipitation pulls the reaction to the right hand side and results in a formation of **81** in good yield.



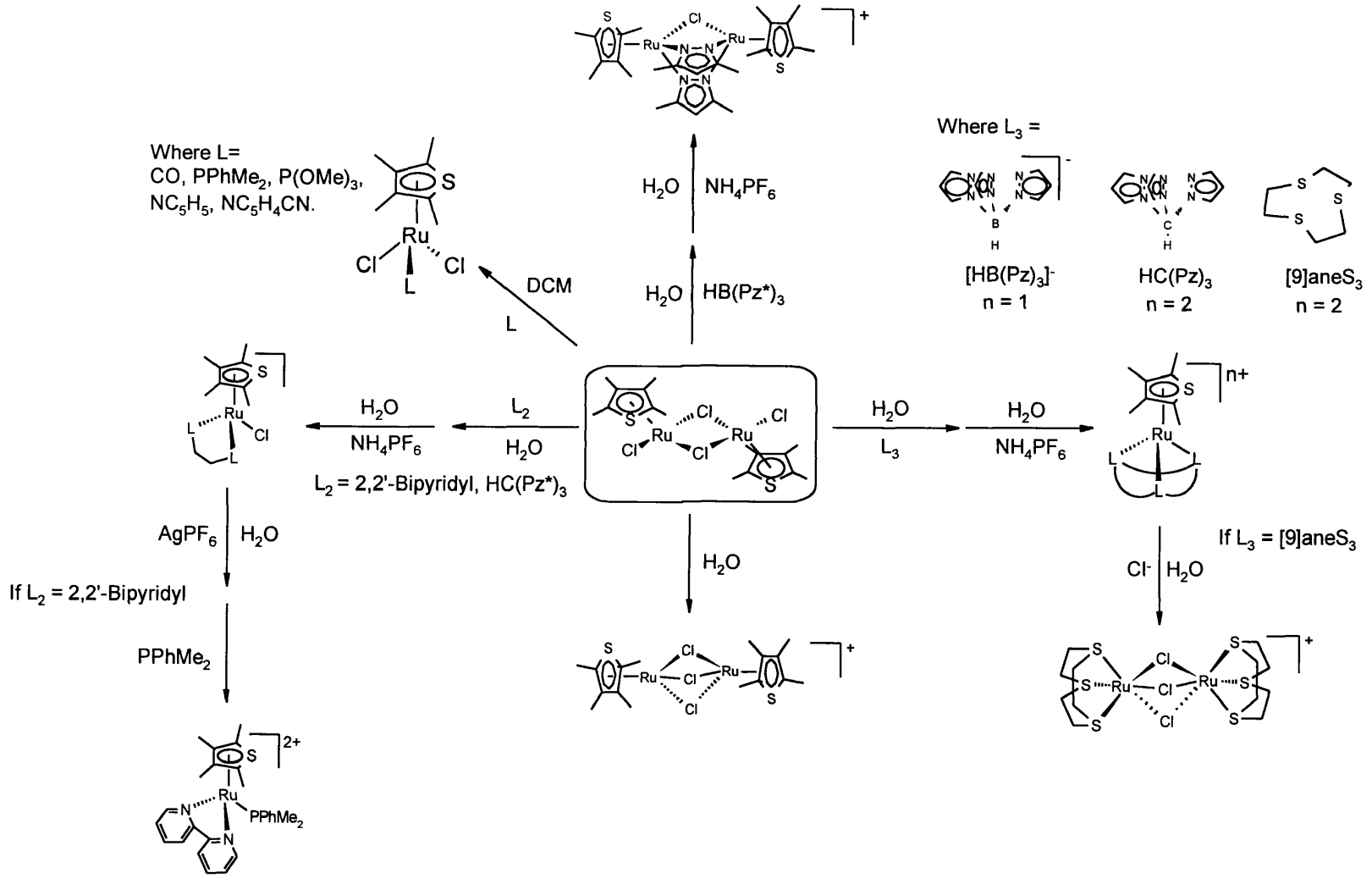
Equation 2.1

2.2.3 SUMMARY

While most reports in the literature of π-thiophene complexes of ruthenium(II) have focused on the reactivity of the metallated ligand, it was demonstrated

that there is considerable scope for developing the coordination chemistry of the '$Ru(\eta^5\text{-}C_4Me_4S)$' moiety. The $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer was shown to be a useful synthon for a range of derivatives. The range of simple bridge cleaved compounds has been extended by forming complexes of the type $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2L]$ (L = CO **60**, $PPhMe_2$ **61**, $P(OMe)_3$ **62**, NC_5H_5 **63** and NC_5H_4CN **64**). Complexes of the type $[Ru(\eta^5\text{-}C_4Me_4S)L_2Cl]^+$ (L_2 = 2,2-bipyridine **71** and $HC(3,5\text{-}Me_2Pz)_3$ **76**) containing bidenate ligands have also been formed. It was established that all the chloride ligands can be removed from the metal without having to resort to expensive silver reagents. This is a key feature of the chemistry leading to *tris*-substituted species of the type $[Ru(\eta^5\text{-}C_4Me_4S)L_3]^{n+}$ (n = 1, 2; L_3 = $HB(Pz)_3$ **73**, $HC(Pz)_3$, **74**, $[9]aneS_3$ **79**). The reactions described in this chapter are summarised in Scheme 2.5.

While the chemistry of the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer bears many similarities to that of the related arene systems it is not completely analogous. Reactions of $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ dimers are generally accomplished using polar organic solvents *via* the formation of solvento intermediates. However, using polar organic solvents in reactions involving **44** generally only results in the formation of complex ill-characterised mixtures. This may be due to the instability of intermediate solvento complexes that are formed and it may be speculated that these intermediates are prone to losing the thiophene ligand. Such labilisation was demonstrated with the $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)]^{2+}$ cation which, if left in a chloride rich solution, loses the thiophene to form the $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3]^+$ cation. In fact, if this reaction could be extended to a wider range of ligand systems it could prove a useful synthetic pathway to particular target compounds. Clearly there is still substantial scope for further



Scheme 2.5: A summary of the reactions presented in Chapter 2.

developments of both the aqueous and non-aqueous coordination chemistry of the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer and one might even speculate that given the lability of these systems these compounds or derivatives, might one day find a use as catalysts.

2.3 EXPERIMENTAL

2.3.1 INSTRUMENTAL

Infrared spectra were recorded on a Nicolet-205 spectrometer between 4000 and 400 cm^{-1}, as their KBr discs and between 400 and 250 cm^{-1} on a Perkin-Elmer 457 grating spectrometer, as Nujol mulls on CsI discs. The ^1H and ^{13}C-$\{^1H\}$-NMR spectra were recorded on either a Varian VXR-400 or Bruker-spectrospin AC-300 instruments, (referenced internally against the residual protons of the respective deuterated solvents, ^1H-NMR: $CDCl_3$, δ 7.27; $(CD_3)_2CO$, δ 2.04; CD_2Cl_2, δ 5.32 ppm; ^{13}C-$\{^1H\}$-NMR: $CDCl_3$, δ 77.0; $(CD_3)_2CO$, δ 29.9 ppm). Elemental analyses were carried out by the departmental service at University College London (UCL). Fast atom bombardment (FAB) mass spectra were recorded by the University of London Intercollegiate Research Service (ULIRS) at the London School of Pharmacy, while positive ion electrospray mass spectra were recorded at UCL on a Micromass Quattro L/C spectrometer (assignments based on the ^{102}Ru isotope). X-ray structural determinations were carried out at ambient temperature on a Nicolet R3mV diffractometer (UCL) or at low temperature (150 K) on a Nonius Kappa CCD equipped diffractometer (Kings College London). Data were processed routinely, crystal parameters, fractional

coordinates and bond lengths and angles are reported in tables at the end of the experimental section.

2.3.2 MATERIALS

All manipulations were carried out under anaerobic conditions in a nitrogen atmosphere using conventional Schlenk-line techniques. Diethylether was distilled from sodium benzophenone ketyl; dichloromethane was distilled from CaH_2; H_2O was distilled over KOH and redistilled under nitrogen. All reaction solvents were degassed prior to use, by three repetitions of freeze-pump-thaw cycles. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc. and purified before use by repeated dissolution in water and boiling to dryness. $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ was prepared according to literature methods.[75,76] Pyridine was distilled off KOH, and 4-cyano-pyridine was sublimed under vacuum prior to use. *Tris*(pyrazolyl)methane and *tris*(3,5-dimethylpyrazolyl)methane were synthesised by the reaction of the sodium pyrazolate (formed *insitu via* the treatment of the appropriate pyrazole with NaH) with $CHCl_3$ in refluxing THF, followed by the evaporation of the solvent and purification by vacuum sublimation.[136] Potassium hydrido*tris*(3,5-dimethylpyrazolyl)borate was synthesised from 3,5-dimethylpyrazole and KBH_4 by published methods.[137] 1,4.7-trithiacyclononane was synthesised by the template alkylation of bis(tetramethylammonium)3-thia-1,5-pentanedithiolate by published methods.[138] All other reagents were obtained from the usual commercial sources and were used as received.

2.3.3 SYNTHESIS

[Ru(η^5-C_4Me_4S)Cl_2(CO)] 60.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.078 g, 0.13 mmol) was added to a CO saturated solution of dichloromethane (30 cm^3), which was refluxed for 1 h under a gentle stream of CO. The flask was then sealed under a CO atmosphere and the solution stirred at room temperature for a further 2 h, after which time a yellow solid precipitated. The solid was filtered off and washed with dichloromethane (20 cm^3) and diethylether (20 cm^3) and then dried *in vacuo*. *Yield*: 0.051 g, 0.15 mmol, 59%. *Anal.*: Found: C, 31.16, H, 3.43 % (Calc. for $RuC_9H_{12}Cl_2OS$: C, 31.77, H, 3.56 %). *Infrared* (KBr): ν(CO) 1982(s) cm^{-1} *Mass spectrum* (positive ion electrospray): m/z 341, $[M+H]^+$; 305, $[M-Cl]^+$; 277, $[M-CO-Cl]^+$.

[Ru(η^5-C_4Me_4S)Cl_2($PPhMe_2$)] 61.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.144 g, 0.23 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of $PPhMe_2$ (0.05 cm^3) was added and the reaction mixture stirred for 2 h. The solution was concentrated to *ca.* 10 cm^3 and hexane was added giving an orange-red precipitate. The solid was isolated by filtration and washed with hexane (50 cm^3) and diethylether (30 cm^3) and then dried *in vacuo*. *Yield*: 0.183 g, 0.41 mmol, 88%. *Anal.*: Found: C, 42.38; H, 5.11 % (Calc. for $RuC_{16}H_{23}Cl_2PS$: C, 42.67; H, 5.10 %). *^{1}H-NMR* [$CDCl_3$, -60°C]: δ 1.29 (s, 6H, TMT); δ 1.85 (d, 6H, $^2J_{PH}$ = 11.5 Hz. P-Me); δ 1.88 (s, 6H, TMT); δ 7.45 (m, 3H, m/p-Ph); δ 7.68 (m, 2H, o-Ph) ppm. *Infrared* (Nujol, CsI): ν(Ru-Cl) 289(w) cm^{-1}. *Mass spectrum* (FAB): m/z 451, $[M+H]^+$; 415, $[M-Cl]^+$; 380, $[M-Cl-Cl]^+$, 277 $[M-PPhMe_2-Cl]$.

[Ru(η^5-C_4Me_4S)Cl_2($P(OCH_3)_3$)] 62.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.070 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of $P(OCH_3)_3$ (0.05 cm^3) was added and the reaction mixture stirred for 1 h. The solution was concentrated to *ca.* 10 cm^3 and hexane (40 cm^3) was added, giving an orange precipitate. The solid was isolated by filtration and washed with hexane (50 cm^3) and diethylether (30cm^3) and then dried *in vacuo*. *Yield*: 0.080 g, 0.18 mmol, 82%. *Anal.*: Found: C, 29.92, H, 4.77 % (Calc. for $RuC_{11}H_{21}O_3Cl_2PS$: C, 30.28, H, 4.86 %). ^{1}*H-NMR* [$CDCl_3$, -60 °C]: δ 1.99 (s, 6H, TMT), δ 2.00 (s, 6H, TMT); δ3.75 (d, 9H, $^3J_{PH}$ = 11.0 Hz., P-OCH_3) ppm. *Infrared* (KBr): ν(PO), 1029(s); δ(OPO), 536(w) cm^{-1}, (Nujol, CsI) ν(Ru-Cl) 288(w) cm^{-1}. *Mass spectrum* (FAB): m/z 436, $[M]^+$; 401, $[M-Cl]^+$; 277, $[M-P(OMe)_3-Cl]^+$.

[Ru(η^5-C_4Me_4S)Cl_2(NC_5H_5)] 63.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.070 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) to which an excess of pyridine (0.10 cm^3) was added. The reaction mixture was stirred for 20 h then the solution concentrated to *ca.* 10 cm^3. This resulted in the slow formation of a yellow solid. Hexane (10 cm^3) was added in order to complete the precipitation. The solid was filtered off and washed with hexane (20 cm^3) and diethylether (40 cm^3) and dried *in vacuo*. *Yield*: 0.065 g, 0.17 mmol, 75%. *Anal.*: Found: C, 39.61, H, 4.27, N, 3.34 % (Calc. for $RuC_{13}H_{17}Cl_2NS$: C, 39.90, H, 4.39, N, 3.58 %). ^{1}*H-NMR* [CD_2Cl_2]: δ 1.81 (br, 6H, TMT); δ 1.88 (br, 6H, TMT); (pyridine resonances) δ 7.33 (dd, 2H) δ 7.76(t, 1H), δ 8.87 (br, 2H) ppm. *Infrared* (Nujol, CsI) ν(Ru-Cl) 284(w) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 392, $[M+H]^+$; 356, $[M-Cl]^+$.

[Ru(η^5-C_4Me_4S)Cl_2(NC_5H_4CN)] 64.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.071 g, 0.11 mmol) was dissolved in dichloromethane (30 cm^3) and an excess of 4-cyanopyridine (0.103 g 0.36 mmol) added to the solution. The reaction mixture was stirred for 20 h, then filtered through celite to remove any undissolved material. The volume of solution was reduced *in vacuo* to *ca.* 10 cm^3, and a red solid precipitated. Addition of hexane (10 cm^3) to the concentrated solution ensured complete precipitation. The solid was filtered off and washed with hexane (20 cm^3) and diethylether (40 cm^3) and dried *in vacuo*. *Yield*: 0.074 g, 0.18 mmol, 78%. *Anal.*: Found: C, 40.27, H, 3.86, N, 6.48 %. (Calc. for $RuC_{14}H_{16}Cl_2N_2S$: C, 40.39, H, 3.88, N, 6.73 %). *^{1}H-NMR* [CD_2Cl_2, 30 °C]: δ 1.85 (br, 6H, TMT); δ 1.90 (br, 6H, TMT); (cyanopyridine resonances) δ 7.58 (m, 2H,), δ 9.20 (br, 2H,) ppm. *Infrared* (KBr): ν(CN), 2235(s) cm^{-1}, (Nujol, CsI) ν(Ru-Cl) 288(w) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 417, $[M+H]^+$; 381, $[M-Cl]^+$; 277 $[M-Cl-NC_5H_4CN]^+$.

[Ru(η^5-C_4Me_4S)(bipy)Cl][PF_6] 71.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.112 g, 0.18 mmol) was stirred in H_2O (20cm^3) for *ca.* 10 min. 2,2'-Bipyridyl (0.058 g, 0.37 mmol) was then added to the aqueous solution which became a dark orange/red colour. The mixture was stirred for 10 mins then filtered through celite. The celite was washed with H_2O (10cm^3) and the filtrate and washings combined. Addition of an excess of aqueous $NH_4[PF_6]$ resulted in the formation of a yellow precipitate on cooling in an ice bath. The solid was isolated by filtration, washed with hexane (30 cm^3) and then dried *in vacuo*. *Yield*: 0.149 g; 0.26 mmol; 72%. *Anal.*: Found: C, 37.62, H, 3.26, N, 4.78, Cl, 6.44 % (Calc. for $RuC_{18}H_{20}N_2SClPF_6$: C, 37.40, H, 3.50, N,

4.85, Cl, 6.13 %). *^{1}H-NMR* [$(CD_3)_2CO$]: δ 2.10 (br s, 12H, TMT); (2,2'-bipyridyl resonances) δ 7.81 (ddd, 2H) δ 8.28 (ddd, 2H) δ 8.63 (br dd, 2H), δ 9.25 (br, 2H) ppm. *Infrared* (KBr): ν(PF_6), 839(s) cm^{-1}, (Nujol, CsI): ν(Ru-Cl) 294(w) cm^{-1}. *Mass spectrum* (FAB): m/z 433, $[M-PF_6]^+$; 398, $[M-PF_6-Cl]^+$.

[Ru(η^5-C_4Me_4S)(bipy)($PPhMe_2$)][PF_6]$_2$ 72.

The compound [Ru(η^5-C_4Me_4S)(bipy)Cl][PF_6] (0.040 g, 0.07 mmol) was stirred in H_2O (20 cm^3) to which was added Ag[PF_6] (0.019 g, 0.07 mmol). The mixture was stirred for 30 min and then filtered through celite, to remove the AgCl precipate that had formed. The celite was washed with H_2O (10 cm^3) and the filtrate and the washings combined. An excess of $PPhMe_2$ (0.05 cm^3) was added to the clear yellow solution and resulted in the formation of an orange suspension. On cooling in an ice bath a yellow solid precipitated which was isolated by filtration, washed with hexane (50 cm^3), and dried *in vacuo*. *Yield*: 0.015 g; 0.02 mmol; 26%. *Anal.*: Found: C, 37.94, H, 3.61, N, 3.26 % (Calc. for $RuC_{26}H_{31}N_2SP_3F_{12}$: C, 37.82, H, 3.79, N, 3.39 %). *^{1}H-NMR* [CD_2Cl_2]: δ 1.85 (d, 6H, $^2J_{PH}$ = 9.9, P-Me); δ 2.04 (br s, 6H, TMT), δ 2.06 (br s, 6H, TMT); δ 6.58 (m, 2H), δ 7.05 (m, 2H), δ 7.29 (m, 1H) (phenyl resonances); δ 7.85 (dd, 2H), δ 7.93 (d, 2H), δ 8.11 (br dd, 2H), δ 8.93 (br d, 2H) ppm (2,2'-bypyridyl resonances). *Infrared* (KBr): ν(PF_6), 837 cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 681, $[M-PF_6]^+$; 649, $[M-PF_6-S]^+$; 541 $[M-PF_6-TMT]^+$.

[Ru(η^5-C_4Me_4S){κ^3-HB(Pz)$_3$}][PF_6] 73.

[{Ru(η^5-C_4Me_4S)Cl(μ-Cl)}$_2$] (0.055 g, 0.09 mmol) was stirred in H_2O (10 cm^3) to which Na[HB(Pz)$_3$] (0.046 g, 0.19 mmol) was added. The mixture was stirred

for 3 h at 20 °C, then filtered through celite. The celite was washed with water and the filtrate and washings combined. The volume of the solution was reduced to *ca.* 10 cm^3 and the solution was treated with an excess of aqueous $NH_4[PF_6]$. This resulted in the immediate formation of a yellow precipitate which was filtered off and washed with H_2O (20 cm^3), $CHCl_3$ (20 cm^3), diethylether (30 cm^3) and then dried *in vacuo*. *Yield*: 0.060 g, 0.10 mmol, 57%. *Anal.*: Found: C, 33.61, H, 3.51, N, 13.91 % (Calc. for $RuC_{17}H_{22}N_6F_6PBS$: C, 34.07, H, 3.70, N, 14.02 %). *^{1}H-NMR* [$(CD_3)_2CO$]: δ 2.40 (s, 6H, TMT), δ 2.45 (s, 6H, TMT); δ 6.41 (dd, 3H, 4Pz), δ 7.98 (d, 3H, $^2J_{4,5}$ = 2.5 Hz, 5Pz), δ 8.14 (d, 3H, $^2J_{3,4}$ = 2.2 Hz, 3Pz) (pyrazolyl resonances). *Infrared* (KBr): ν(BH), 2502(m); ν(PF_6), 835(s) cm^{-1}. *Mass spectrum* (FAB): m/z 455 $[M-PF_6]^+$.

$[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ 74.

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.201 g, 0.32 mmol) was stirred in H_2O (10 cm^3) for *ca.* 15 min then $HC(Pz)_3$ (0.140 g, 0.65 mmol) was added. The mixture was stirred for 3 h at 20 °C, then filtered through celite, which was washed with water. The filtrate and washings were combined and then treated with an excess of aqueous $NH_4[PF_6]$ resulting in the immediate formation of a yellow solid which was collected by filtration, washed with cold H_2O (10 cm^3), and diethylether (30 cm^3), and then dried *in vacuo*. *Yield*: 0.431 g, 0.58 mmol, 90%. *Anal.*: Found: C, 29.42, H, 2.54, N, 11.00 % (Calc. for $RuC_{18}H_{22}N_6F_{12}P_2S$: C, 29.00, H, 2.97, N, 11.27 %). *^{1}H-NMR* [$(CD_3)_2CO$]: δ 2.50 (s, 6H, TMT), δ 2.58 (s, 6H, TMT); δ 6.79 (dd, 3H, 4-Pz), δ 8.58 (d, 3H, $^2J_{4,5}$ = 2.5 Hz, 5-Pz), δ 8.62 (d, 3H, $^2J_{3,4}$ = 2.9 Hz, 3-Pz), δ 9.63 (s, 1H, $\underline{H}C(Pz)_3$). *^{13}C-{^{1}H}-NMR* [$(CD_3)_2CO$]: δ 11.3, 13.4 (TMT methyls), δ 98.8, 101.2 (TMT ring); δ 76.3

($H\underline{C}(Pz)_3$), δ 110.4 (4Pz), δ 136.8 (5Pz), δ 148.9 (3Pz). *Infrared* (KBr): ν(PF_6), 838(s) cm^{-1}. *Mass spectrum* (FAB): m/z 601 $[M-PF_6]^+$; 455 $[M-2PF_6-H]^+$.

$[Ru(\eta^5-C_4Me_4S)\{\kappa^2-HC(3,5-Me_2Pz)_3\}Cl][PF_6]$ 76.

$[\{Ru(\eta^5-C_4Me_4S)Cl(\mu-Cl)\}_2]$ (0.098 g, 0.16 mmol) was stirred in H_2O (10 cm^3) for *ca.* 15 min then $HC(3,5-Me_2Pz)_3$ (0.095 g, 0.32 mmol) was added. The mixture was stirred for 4 h at 20 °C, then filtered through celite. The celite was washed with water and the filtrate and the washings were combined. The orange solution was treated with an excess of aqueous $NH_4[PF_6]$ resulting in the immediate formation of a yellow/orange solid. This crude material was collected by filtration and then recrystallised from ethanol, collected by filtration and dried *in vacuo*. *Yield*: 0.116 g, 0.16 mmol, 51 %. *Anal.*: Found: C, 39.75, H, 4.40, N, 11.15, Cl, 5.33 % (Calc. for $RuC_{24}H_{34}N_6F_6PSCl$: C, 40.03, H, 4.76, N, 11.67, Cl, 4.92 %). *^{1}H-NMR* [$CDCl_3$]: δ 1.80 (s, 6H, TMT), δ 2.17 (s, 6H, TMT); δ 1.74 (s, 3H, non-metallated 5-Pz methyl), δ 2.07 (s, 3H, non-metallated 3-Pz methyl), δ 6.13 (s, 1H, non-metallated 4-Pz), δ 2.42 (s, 6H, metallated 5-Pz methyl), δ 2.61 (s, 6H, metallated 3-Pz methyl), δ 6.30 (s, 2H, metallated 4-Pz), δ 7.98 (s, 1H, HC-bridgehead). *Infrared* (KBr): ν(PF_6), 846(s) cm^{-1}; (Nujol, CsI): ν(Ru-Cl) 298(w) cm^{-1}. *Mass spectrum* (FAB): m/z 575 $[M-PF_6]^+$; 539 $[M-PF_6-Cl]^+$; 435 $[M-PF_6-TMT]^+$.

$[Ru_2(\eta^5-C_4Me_4S)_2(\mu-3,5-Me_2Pz)_2(\mu-Cl)][PF_6]$ 77.

$[\{Ru(\eta^5-C_4Me_4S)Cl(\mu-Cl)\}_2]$ (0.123 g, 0.19 mmol) was stirred in H_2O (10 cm^3) to which $K[HB(3,5-Me_2Pz)_3]$ (0.136 g, 0.41 mmol) was added. The mixture was stirred for 3 h at 20 °C, then filtered through celite. The celite was washed with

water and the filtrate and washings combined. The volume of the solution was reduced to *ca.* 10 cm^3 and this was treated with an excess of aqueous $NH_4[PF_6]$. This resulted in the immediate formation of a yellow/brown precipitate which was filtered off and washed with H_2O (20 cm^3) and diethylether (30 cm^3), then dried *in vacuo*. *Yield*: 0.048 g, 0.06 mmol, 29 %. *Anal.*: Found: C, 37.10, H, 4.56, N, 6.48, Cl, 3.82 % (Calc. for $Ru_2C_{26}H_{38}S_2N_4ClPF_6$: C, 36.60, H, 4.49, N, 6.57, Cl, 4.15 %). *^{1}H-NMR* [$(CD_3)_2CO$]: δ 1.99 (s, 12H, TMT), δ 2.10 (s, 12H, TMT); δ 2.53 (s, 12H, Pz methyls), δ 5.55 (s, 2H, 4-Pz) ppm. *Infrared* (KBr): ν(PF_6) 841(s) cm^{-1}; (Nujol, CsI): ν(Ru-Cl) 268(w) cm^{-1}. Mass spectrum (FAB): m/z 674 $[M-PF_6-Cl]^+$; 579 $[M-PF_6-Cl-Me_2Pz]^+$.

$[Ru(\eta^5-C_4Me_4S)(\kappa^3-[9]aneS_3)][PF_6]_2$ 79.

$[\{Ru(\eta^5-C_4Me_4S)Cl(\mu-Cl)\}_2]$ (0.250 g, 0.40 mmol) was stirred in H_2O (10 cm^3) for *ca.* 15 min then 1,4,7 trithiacyclononane (0.148 g, 0.82 mmol) was added. The mixture was stirred for 2 h at 20 °C and then filtered through celite. The celite was washed with water (10 cm^3) and the washing combined with the yellow filtrate. Addition of an excess of aqueous $NH_4[PF_6]$ resulted in the precipitation of a yellow solid. The solid was collected by filtration, washed with cold H_2O (25 cm^3), diethylether (50 cm^3) and then dried *in vacuo*. *Yield*: 0.412 g, 0.58 mmol, 72 %. *Anal.*: Found: C, 23.20, H, 2.97 % (Calc. for $RuC_{14}H_{24}F_{12}P_2S_4$: C, 23.63, H, 3.41 %). *^{1}H-NMR* [$(CD_3)_2CO$]: δ 2.38 (s, 6H, TMT), δ 2.44 (s, 6H, TMT); δ 3.24 (s, 12H, [9]$aneS_3$). *^{13}C-{^{1}H}-NMR* [$(CD_3)_2CO$]: δ 11.5, 12.8 (TMT methyls), δ 106.9, 108.6 (TMT ring); δ 36.2 ([9]$aneS_3$ methylenes). *Infrared* (KBr): ν(PF_6), 839(s) cm^{-1}. *Mass spectrum* (FAB): m/z 567 $[M-PF_6]^+$; 421 $[M-2PF_6-H]^+$.

$[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$ 80.

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.300 g, 0.48 mmol) was stirred in H_2O (20 cm^3) for *ca.* 15 min then 1,4,7 trithiacyclononane (0.176 g, 0.98 mmol) was added. After *ca.* 2 h an excess of NaCl (0.5 g) was added and the mixture allowed to stir for 48 h at 20 °C. The mixture was then filtered through celite, this was then washed with water (20 cm^3) and the washing combined with the yellow filtrate. Addition of an excess of aqueous $NH_4[PF_6]$ resulted in the precipitation of a yellow solid; this mixture was then stirred for a further 48 h. This mixture was then cooled to -20 °C for *ca.* 16 h and the yellow solid was collected by filtration. This solid was then washed with cold H_2O (25 cm^3) and acetone (30 cm^3) in order to remove any unreacted $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$ that had formed and then further washed with diethylether (50 cm^3) and then dried *in vacuo*. *Yield*: 0.203 g, 0.25 mmol, 52 %. *Anal.*: Found: C, 17.45, H, 2.68, Cl, 12.66 % (Calc. for $Ru_2C_{12}H_{24}S_6Cl_3PF_6$: C, 17.70, H, 2.97, Cl, 13.06 %). *Infrared* (KBr): $\nu(PF_6)$, 839(s) cm^{-1}; (Nujol, CsI): ν(Ru-Cl) 264(w) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 671 $[M\text{-}PF_6]$.

$[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81.

$[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ (0.051g, 0.08 mmol) was dissolved in H_2O (20 cm^3) containing an excess of $NH_4[PF_6]$. The solution was stirred for 72 hours at room temperature during which time a red solid was deposited. This was isolated by filtration, washed with cold water (10 cm^3) and diethylether (50 cm^3), and then dried *in vacuo*. *Yield*: 0.043 g, 0.06 mmol, 71%. *Anal.*: (Found: C, 26.25, H, 3.00, Cl, 14.65 %. Calc. for $Ru_2C_{16}H_{24}Cl_3S_2PF_6$: C, 26.18, H, 3.30, Cl, 14.49 %). *^{1}H-NMR* $[(CD_3)_2CO]$: δ 2.10 (s, 12H, TMT), δ 2.15 (s, 12H, TMT)

ppm. *Infrared* (KBr): $\nu(PF_6)$ 841(s) cm^{-1}; (Nujol, CsI): ν(Ru-Cl) 259(w) cm^{-1}.

Mass spectrum (FAB): m/z 591 $[M-PF_6]^+$.

2.3.4 X-RAY CRYSTALLOGRAPHIC DATA

Table 2.5:
Crystal data and structure refinement for [Ru(η^5-C_4Me_4S)Cl_2(PPhMe_2)] 61.

Empirical formula	$C_{16}H_{23}Cl_2PRuS$
Formula weight	450.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	Cc
Unit cell dimensions	a = 9.380(2) Å
	b = 15.614(3) Å
	c = 13.107(3) Å
	α = 90 °
	β = 100.06(3) °
	γ = 90 °
Volume	1890.1(7) $Å^3$
Z	4
Density (calculated)	1.583 g cm^{-3}
Absorption coefficient	1.299 mm^{-1}
F(000)	912
Crystal size	0.58 x 0.54 x 0.48 mm^3
Theta range for data collection	2.56 to 27.58 °
hkl index ranges	0 → 12, 0 → 20, -17 → 16
Reflections collected	2298
Independent reflections	2298 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2295 / 0 / 189
Goodness of fit on F^2	1.051
Final R indices [$I>2\sigma(I)$]	R1 = 0.0220, wR2 = 0.0555
R indices (all data)	R1 = 0.0235, wR2 = 0.0607
Absolute structure parameter	-0.04(3)
Extinction coefficient	0.0095(4)
Largest diff. peak and hole	0.652 and -0.477 e $Å^{-3}$

Table 2.6:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x 10^3$) for [Ru(η^5-C_4Me_4S)Cl_2($PPhMe_2$)] 61.

	x	y	z	U(eq)
Ru(1)	10000	8097(1)	10000	21(1)
Cl(1)	8919(1)	8386(1)	11530(1)	35(1)
Cl(2)	12196(1)	8865(1)	10764(1)	35(1)
S(1)	10816(1)	6611(1)	10183(1)	37(1)
P(1)	9216(1)	9458(1)	9424(1)	24(1)
C(1)	11187(5)	7267(3)	9131(3)	35(1)
C(2)	9880(5)	7492(3)	8453(3)	36(1)
C(3)	8598(5)	7264(3)	8862(3)	38(1)
C(4)	8930(6)	6860(3)	9850(4)	33(1)
C(5)	12722(6)	7349(4)	8941(5)	51(1)
C(6)	9846(9)	7850(4)	7374(4)	60(2)
C(7)	7066(6)	7374(4)	8277(5)	55(1)
C(8)	7897(7)	6480(4)	10486(5)	54(1)
C(9)	10308(5)	9930(3)	8535(3)	36(1)
C(10)	9374(5)	10277(3)	10462(3)	35(1)
C(11)	7314(4)	9602(3)	8801(3)	28(1)
C(12)	6224(5)	9340(3)	9342(3)	35(1)
C(13)	4760(5)	9502(3)	8937(4)	43(1)
C(14)	4383(5)	9915(4)	7989(4)	48(1)
C(15)	5446(6)	10168(4)	7439(4)	47(1)
C(16)	6926(5)	10009(3)	7837(3)	36(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2.7:
Bond lengths Å and angles ° for [Ru(η^5-C_4Me_4S)Cl_2($PPhMe_2$)] 61.

Ru(1)-C(1)	2.158(4)	C(1)-C(2)	1.427(7)
Ru(1)-C(4)	2.169(4)	C(1)-C(5)	1.509(7)
Ru(1)-C(2)	2.221(4)	C(2)-C(3)	1.444(7)
Ru(1)-C(3)	2.228(4)	C(2)-C(6)	1.516(7)
Ru(1)-P(1)	2.3303(10)	C(3)-C(4)	1.425(7)
Ru(1)-Cl(2)	2.4419(11)	C(3)-C(7)	1.516(7)
Ru(1)-Cl(1)	2.4414(11)	C(4)-C(8)	1.507(7)
Ru(1)-S(1)	2.4422(12)	C(11)-C(16)	1.404(5)
S(1)-C(4)	1.790(5)	C(11)-C(12)	1.404(6)
S(1)-C(1)	1.799(4)	C(12)-C(13)	1.406(6)
P(1)-C(9)	1.835(4)	C(13)-C(14)	1.389(8)
P(1)-C(11)	1.842(4)	C(14)-C(15)	1.387(8)
P(1)-C(10)	1.854(4)	C(15)-C(16)	1.417(7)
C(1)-Ru(1)-C(4)	72.0(2)	C(11)-P(1)-Ru(1)	118.79(13)
C(1)-Ru(1)-C(2)	38.0(2)	C(10)-P(1)-Ru(1)	114.26(14)
C(4)-Ru(1)-C(2)	65.8(2)	C(2)-C(1)-C(5)	128.1(4)
C(1)-Ru(1)-C(3)	66.1(2)	C(2)-C(1)-S(1)	110.9(3)
C(4)-Ru(1)-C(3)	37.8(2)	C(5)-C(1)-S(1)	119.5(4)
C(2)-Ru(1)-C(3)	37.9(2)	C(2)-C(1)-Ru(1)	73.4(2)
C(1)-Ru(1)-P(1)	122.62(12)	C(5)-C(1)-Ru(1)	129.1(3)
C(4)-Ru(1)-P(1)	131.88(14)	S(1)-C(1)-Ru(1)	75.6(2)
C(2)-Ru(1)-P(1)	97.43(12)	C(1)-C(2)-C(3)	112.9(4)
C(3)-Ru(1)-P(1)	101.52(13)	C(1)-C(2)-C(6)	123.2(5)
C(1)-Ru(1)-Cl(2)	91.99(13)	C(3)-C(2)-C(6)	123.6(5)
C(4)-Ru(1)-Cl(2)	144.88(14)	C(1)-C(2)-Ru(1)	68.6(2)
C(2)-Ru(1)-Cl(2)	119.17(13)	C(3)-C(2)-Ru(1)	71.3(2)
C(3)-Ru(1)-Cl(2)	156.67(13)	C(6)-C(2)-Ru(1)	133.2(3)
P(1)-Ru(1)-Cl(2)	83.17(4)	C(4)-C(3)-C(2)	112.5(4)
C(1)-Ru(1)-Cl(1)	150.53(12)	C(4)-C(3)-C(7)	123.1(5)
C(4)-Ru(1)-Cl(1)	89.25(14)	C(2)-C(3)-C(7)	124.2(4)
C(2)-Ru(1)-Cl(1)	149.98(13)	C(4)-C(3)-Ru(1)	68.9(2)
C(3)-Ru(1)-Cl(1)	112.13(13)	C(2)-C(3)-Ru(1)	70.8(2)
P(1)-Ru(1)-Cl(1)	86.84(4)	C(7)-C(3)-Ru(1)	132.0(3)
Cl(2)-Ru(1)-Cl(1)	90.82(4)	C(3)-C(4)-C(8)	128.1(5)
C(1)-Ru(1)-S(1)	45.53(12)	C(3)-C(4)-S(1)	111.5(4)
C(4)-Ru(1)-S(1)	45.19(14)	C(8)-C(4)-S(1)	118.9(4)
C(2)-Ru(1)-S(1)	69.54(12)	C(3)-C(4)-Ru(1)	73.3(2)
C(3)-Ru(1)-S(1)	69.45(13)	C(8)-C(4)-Ru(1)	129.2(4)
P(1)-Ru(1)-S(1)	166.86(4)	S(1)-C(4)-Ru(1)	75.5(2)
Cl(2)-Ru(1)-S(1)	101.45(4)	C(16)-C(11)-C(12)	119.3(4)
Cl(1)-Ru(1)-S(1)	105.25(4)	C(16)-C(11)-P(1)	122.3(3)
C(4)-S(1)-C(1)	90.3(2)	C(12)-C(11)-P(1)	118.4(3)
C(4)-S(1)-Ru(1)	59.30(14)	C(11)-C(12)-C(13)	120.4(4)
C(1)-S(1)-Ru(1)	58.87(13)	C(14)-C(13)-C(12)	120.0(4)
C(9)-P(1)-C(11)	105.9(2)	C(13)-C(14)-C(15)	120.2(4)
C(9)-P(1)-C(10)	101.9(2)	C(14)-C(15)-C(16)	120.4(4)
C(11)-P(1)-C(10	100.9(2)	C(11)-C(16)-C(15)	119.6(4)
C(9)-P(1)-Ru(1)	113.1(2)		

Table 2.8:
Crystal data and structure refinement for
$[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)][PF_6]_2.CH_2Cl_2$ 72.CH_2Cl_2.

Empirical formula	$C_{27}H_{33}Cl_2F_{12}N_2P_3RuS$
Formula weight	910.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 12.843(3) Å
	b = 12.873(3) Å
	c = 22.869(5) Å
	α = 90 °
	β = 90 °
	γ = 90 °
Volume	3781(2) $Å^3$
Z	4
Density (calculated)	1.600 g cm^{-3}
Absorption coefficient	0.820 mm^{-1}
F(000)	1824
Crystal size	0.74 x 0.42 x 0.38 mm^3
Theta range for data collection	2.86 to 25.06 °
hkl index ranges	0 → 15, 0 → 15, 0 → 27
Reflections collected	3707
Independent reflections	3707 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3697 / 0 / 434
Goodness-of-fit on F^2	1.065
Final R indices [$I>2\sigma(I)$]	R1 = 0.0665, wR2 = 0.1449
R indices (all data)	R1 = 0.1332, wR2 = 0.2137
Absolute structure parameter	0.01(13)
Extinction coefficient	0.0022(4)
Largest diff. peak and hole	1.023 and -0.754 e $Å^{-3}$

Table 2.9:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)][PF_6]_2.CH_2Cl_2$ 72.CH_2Cl_2.

	x	y	z	U(eq)
Ru(1)	9700(1)	638(1)	9097(1)	53(1)
S(1)	11128(4)	1798(4)	9268(2)	67(1)
P(1)	8451(4)	821(4)	9850(2)	62(1)
N(1)	8776(11)	-559(11)	8763(5)	60(3)
N(2)	8705(10)	1425(11)	8524(5)	54(3)
C(1)	11176(12)	1074(14)	8612(7)	55(4)
C(2)	11187(16)	-2(15)	8713(8)	69(5)
C(3)	11155(15)	-270(13)	9346(8)	63(5)
C(4)	11042(13)	663(17)	9691(6)	63(4)
C(5)	11250(15)	1621(18)	8031(6)	74(6)
C(6)	11287(17)	-807(19)	8240(9)	94(7)
C(7)	11284(18)	-1347(17)	9590(10)	103(8)
C(8)	11181(15)	690(22)	10356(7)	98(7)
C(11)	8863(17)	-1606(15)	8906(10)	90(7)
C(12)	8253(23)	-2357(17)	8630(13)	114(9)
C(13)	7560(20)	-2064(21)	8167(13)	108(9)
C(14)	7510(18)	-1040(20)	8045(10)	101(8)
C(15)	8088(15)	-275(16)	8327(8)	73(5)
C(16)	8022(13)	854(14)	8212(7)	59(4)
C(17)	7303(15)	1322(21)	7815(8)	88(7)
C(18)	7282(19)	2401(18)	7779(9)	88(7)
C(19)	7992(16)	2984(19)	8098(8)	81(6)
C(20)	8681(14)	2467(14)	8455(7)	63(5)
C(21)	8365(17)	-344(14)	10299(8)	85(6)
C(31)	7119(14)	1045(16)	9605(9)	83(6)
C(41)	8691(14)	1916(14)	10342(7)	63(4)
C(42)	8818(16)	2913(15)	10116(9)	82(6)
C(43)	9002(19)	3786(17)	10468(10)	96(7)
C(44)	9048(20)	3665(21)	11073(11)	104(8)
C(45)	8908(20)	2672(21)	11310(9)	102(8)
C(46)	8731(16)	1814(15)	10954(8)	78(5)
P(2)	10575(4)	-246(4)	12095(2)	76(2)
F(1)	10788(12)	850(11)	11797(6)	129(5)
F(2)	10423(14)	-1388(10)	12354(5)	130(5)
F(3)	9499(12)	-351(15)	11780(8)	165(8)
F(4)	11117(20)	-737(17)	11550(7)	211(10)
F(5)	9989(18)	191(17)	12643(8)	205(9)
F(6)	11613(13)	-143(17)	12435(10)	216(11)
P(3)	10559(5)	5199(4)	8559(3)	86(2)
F(7)	10748(15)	4219(14)	8953(8)	181(7)
F(8)	10703(20)	5902(16)	9099(8)	223(10)
F(9)	9349(12)	5128(15)	8652(11)	191(9)
F(10)	11753(11)	5252(17)	8431(8)	166(8)
F(11)	10379(18)	6178(14)	8163(9)	200(9)
F(12)	10389(17)	4469(18)	8007(8)	202(9)
C(50)	10106(20)	1878(24)	13786(11)	133(10)
Cl(1)	9480(10)	1468(6)	14435(4)	183(4)
Cl(2)	11362(7)	2159(10)	13863(5)	188(5)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2.10:
Bond lengths Å and angles ° for
[Ru(η^5-C_4Me_4S)(bipy)(PPhMe$_2$)][PF$_6$]$_2$.CH$_2$Cl$_2$ 72.CH$_2$Cl$_2$.

Ru(1)-N(1)	2.089(14)	C(14)-C(15)	1.39(3)
Ru(1)-N(2)	2.091(14)	C(15)-C(16)	1.48(3)
Ru(1)-C(4)	2.20(2)	C(16)-C(17)	1.43(2)
Ru(1)-C(2)	2.26(2)	C(17)-C(18)	1.39(3)
Ru(1)-C(1)	2.27(2)	C(18)-C(19)	1.39(3)
Ru(1)-C(3)	2.28(2)	C(19)-C(20)	1.38(2)
Ru(1)-P(1)	2.364(4)	C(41)-C(42)	1.39(2)
Ru(1)-S(1)	2.397(5)	C(41)-C(46)	1.41(2)
S(1)-C(4)	1.76(2)	C(42)-C(43)	1.40(2)
S(1)-C(1)	1.77(2)	C(43)-C(44)	1.39(3)
P(1)-C(41)	1.83(2)	C(44)-C(45)	1.40(3)
P(1)-C(31)	1.82(2)	C(45)-C(46)	1.39(3)
P(1)-C(21)	1.82(2)	P(2)-F(6)	1.55(2)
N(1)-C(15)	1.38(2)	P(2)-F(4)	1.56(2)
N(1)-C(11)	1.39(2)	P(2)-F(3)	1.56(2)
N(2)-C(20)	1.35(2)	P(2)-F(1)	1.590(14)
N(2)-C(16)	1.35(2)	P(2)-F(5)	1.57(2)
C(1)-C(2)	1.40(2)	P(2)-F(2)	1.597(13)
C(1)-C(5)	1.50(2)	P(3)-F(8)	1.54(2)
C(2)-C(3)	1.49(2)	P(3)-F(10)	1.56(2)
C(2)-C(6)	1.50(2)	P(3)-F(11)	1.57(2)
C(3)-C(7)	1.50(2)	P(3)-F(9)	1.57(2)
C(3)-C(4)	1.44(3)	P(3)-F(7)	1.57(2)
C(4)-C(8)	1.53(2)	P(3)-F(12)	1.59(2)
C(11)-C(12)	1.39(3)	C(50)-Cl(2)	1.66(3)
C(12)-C(13)	1.43(3)	C(50)-Cl(1)	1.77(3)
C(13)-C(14)	1.35(3)		
N(1)-Ru(1)-N(2)	77.4(5)	C(3)-Ru(1)-P(1)	115.2(5)
N(1)-Ru(1)-C(4)	133.0(7)	N(1)-Ru(1)-S(1)	162.4(4)
N(2)-Ru(1)-C(4)	149.4(6)	N(2)-Ru(1)-S(1)	105.5(4)
N(1)-Ru(1)-C(2)	93.9(6)	C(4)-Ru(1)-S(1)	44.7(5)
N(2)-Ru(1)-C(2)	116.7(6)	C(2)-Ru(1)-S(1)	69.1(5)
C(4)-Ru(1)-C(2)	65.3(6)	C(1)-Ru(1)-S(1)	44.4(5)
N(1)-Ru(1)-C(1)	118.6(6)	C(3)-Ru(1)-S(1)	69.6(5)
N(2)-Ru(1)-C(1)	94.8(5)	P(1)-Ru(1)-S(1)	109.8(2)
C(4)-Ru(1)-C(1)	69.1(6)	C(4)-S(1)-C(1)	91.8(8)
C(2)-Ru(1)-C(1)	36.2(6)	C(4)-S(1)-Ru(1)	61.5(6)
N(1)-Ru(1)-C(3)	100.3(6)	C(1)-S(1)-Ru(1)	63.9(5)
N(2)-Ru(1)-C(3)	155.1(6)	C(41)-P(1)-C(31)	103.0(9)
C(4)-Ru(1)-C(3)	37.6(7)	C(41)-P(1)-C(21)	107.3(8)
C(2)-Ru(1)-C(3)	38.3(6)	C(31)-P(1)-C(21)	104.3(10)
C(1)-Ru(1)-C(3)	64.1(6)	C(41)-P(1)-Ru(1)	114.2(6)
N(1)-Ru(1)-P(1)	87.4(4)	C(31)-P(1)-Ru(1)	115.4(7)
N(2)-Ru(1)-P(1)	89.7(4)	C(21)-P(1)-Ru(1)	111.7(6)
C(4)-Ru(1)-P(1)	94.6(4)	C(15)-N(1)-C(11)	119(2)
C(2)-Ru(1)-P(1)	153.2(5)	C(15)-N(1)-Ru(1)	115.5(12)
C(1)-Ru(1)-P(1)	154.0(5)	C(11)-N(1)-Ru(1)	125.7(14)

C(20)-N(2)-C(16)	118(2)	N(2)-C(20)-C(19)	124(2)
C(20)-N(2)-Ru(1)	124.5(12)	C(42)-C(41)-C(46)	117(2)
C(16)-N(2)-Ru(1)	117.7(11)	C(42)-C(41)-P(1)	120.1(13)
C(2)-C(1)-C(5)	127(2)	C(46)-C(41)-P(1)	123(2)
C(2)-C(1)-S(1)	112.3(13)	C(41)-C(42)-C(43)	123(2)
C(5)-C(1)-S(1)	120.3(14)	C(44)-C(43)-C(42)	119(2)
C(2)-C(1)-Ru(1)	71.6(12)	C(43)-C(44)-C(45)	119(2)
C(5)-C(1)-Ru(1)	126.9(12)	C(44)-C(45)-C(46)	121(2)
S(1)-C(1)-Ru(1)	71.7(5)	C(41)-C(46)-C(45)	121(2)
C(1)-C(2)-C(3)	113(2)	F(6)-P(2)-F(4)	92.9(14)
C(1)-C(2)-C(6)	124(2)	F(6)-P(2)-F(3)	177.3(13)
C(3)-C(2)-C(6)	123(2)	F(4)-P(2)-F(3)	89.5(13)
C(1)-C(2)-Ru(1)	72.3(12)	F(6)-P(2)-F(1)	89.5(9)
C(3)-C(2)-Ru(1)	71.5(11)	F(4)-P(2)-F(1)	86.6(10)
C(6)-C(2)-Ru(1)	127.1(14)	F(3)-P(2)-F(1)	91.8(9)
C(7)-C(3)-C(4)	125(2)	F(6)-P(2)-F(5)	88.9(13)
C(7)-C(3)-C(2)	125(2)	F(4)-P(2)-F(5)	176.7(13)
C(4)-C(3)-C(2)	110(2)	F(3)-P(2)-F(5)	88.5(12)
C(7)-C(3)-Ru(1)	131(2)	F(1)-P(2)-F(5)	96.1(11)
C(4)-C(3)-Ru(1)	68.1(10)	F(6)-P(2)-F(2)	89.9(10)
C(2)-C(3)-Ru(1)	70.1(11)	F(4)-P(2)-F(2)	88.8(9)
C(3)-C(4)-C(8)	123(2)	F(3)-P(2)-F(2)	89.0(10)
C(3)-C(4)-S(1)	112.6(10)	F(1)-P(2)-F(2)	175.3(9)
C(8)-C(4)-S(1)	121(2)	F(5)-P(2)-F(2)	88.5(11)
C(3)-C(4)-Ru(1)	74.3(10)	F(8)-P(3)-F(10)	90.4(12)
C(8)-C(4)-Ru(1)	135.0(12)	F(8)-P(3)-F(11)	90.5(12)
S(1)-C(4)-Ru(1)	73.7(6)	F(10)-P(3)-F(11)	90.1(12)
C(12)-C(11)-N(1)	121(2)	F(8)-P(3)-F(9)	92.5(13)
C(11)-C(12)-C(13)	120(2)	F(10)-P(3)-F(9)	176.9(12)
C(14)-C(13)-C(12)	116(2)	F(11)-P(3)-F(9)	88.8(12)
C(13)-C(14)-C(15)	125(3)	F(8)-P(3)-F(7)	89.7(11)
N(1)-C(15)-C(14)	119(2)	F(10)-P(3)-F(7)	89.5(10)
N(1)-C(15)-C(16)	115(2)	F(11)-P(3)-F(7)	179.5(13)
C(14)-C(15)-C(16)	126(2)	F(9)-P(3)-F(7)	91.6(12)
N(2)-C(16)-C(17)	122(2)	F(8)-P(3)-F(12)	178.9(13)
N(2)-C(16)-C(15)	114(2)	F(10)-P(3)-F(12)	90.7(12)
C(17)-C(16)-C(15)	124(2)	F(11)-P(3)-F(12)	89.7(12)
C(18)-C(17)-C(16)	118(2)	F(9)-P(3)-F(12)	86.4(12)
C(17)-C(18)-C(19)	120(2)	F(7)-P(3)-F(12)	90.1(12)
C(20)-C(19)-C(18)	118(2)	Cl(2)-C(50)-Cl(1)	115(2)

Table 2.11:
Crystal data and structure refinement for
[Ru(η^5-C_4Me_4S){κ^3-HB(Pz)$_3$}][PF_6] 73.

Empirical formula	C_{17} H_{22} B F_6 N_6 P Ru S
Formula weight	599.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.483(2) Å
	b = 15.130(3) Å
	c = 13.442(3) Å
	α = 90 °
	β = 92.83(3) °
	γ = 90 °
Volume	2332.5(8) $Å^3$
Z	4
Density (calculated)	1.707 g cm^{-3}
Absorption coefficient	0.896 mm^{-1}
F(000)	1200
Crystal size	0.38 x 0.36 x 0.28 mm^3
Theta range for data collection	2.65 to 25.05 °
hkl Index ranges	0 → 13, 0 → 18, -16 → 15
Reflections collected	4287
Independent reflections	4075 [R(int) = 0.0312]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4074 / 0 / 298
Goodness-of-fit on F^2	1.043
Final R indices [I>2σ(I)]	R1 = 0.0391, wR2 = 0.1000
R indices (all data)	R1 = 0.0530, wR2 = 0.1204
Largest diff. peak and hole	0.745 and -0.471 e $Å^{-3}$

Table 2.12:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ 73.

	x	y	z	U(eq)
Ru(1)	7346(1)	612(1)	1115(1)	30(1)
S(1)	6332(1)	-762(1)	1300(1)	44(1)
C(1)	6833(4)	-163(3)	2392(3)	39(1)
C(2)	6018(4)	29(4)	3224(4)	49(1)
C(3)	8066(4)	-93(3)	2476(3)	38(1)
C(4)	8698(4)	233(4)	3404(4)	52(1)
C(5)	8613(4)	-452(3)	1601(4)	40(1)
C(6)	9924(4)	-542(4)	1489(5)	56(1)
C(7)	7794(4)	-787(3)	875(4)	44(1)
C(8)	8064(5)	-1305(3)	-44(4)	58(1)
B(1)	7198(5)	2561(4)	65(4)	47(1)
N(11)	6148(3)	2412(2)	723(3)	43(1)
N(12)	6057(3)	1631(2)	1248(3)	39(1)
C(13)	5023(4)	1669(4)	1701(4)	50(1)
C(14)	4451(5)	2459(4)	1465(4)	58(1)
C(15)	5183(5)	2904(4)	839(4)	55(1)
N(21)	7179(4)	1831(3)	-732(3)	45(1)
N(22)	7177(3)	959(2)	-444(3)	38(1)
C(23)	7042(4)	482(3)	-1291(3)	45(1)
C(24)	6981(5)	1041(4)	-2126(4)	54(1)
C(25)	7064(5)	1887(4)	-1741(4)	53(1)
N(31)	8333(3)	2453(2)	737(3)	41(1)
N(32)	8560(3)	1671(2)	1233(3)	36(1)
C(33)	9599(4)	1776(3)	1737(4)	43(1)
C(34)	10046(5)	2617(4)	1560(4)	53(1)
C(35)	9229(5)	3026(3)	929(4)	54(1)
P(1)	7600(1)	6209(1)	1105(1)	49(1)
F(1)	7544(3)	6393(2)	-69(2)	72(1)
F(2)	7666(5)	6033(3)	2281(3)	118(2)
F(3)	8297(5)	5316(3)	962(4)	112(2)
F(4)	8816(4)	6723(4)	1185(4)	126(2)
F(5)	6423(4)	5688(4)	1009(5)	129(2)
F(6)	6938(6)	7111(3)	1248(4)	139(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2.13:
Bond lengths Å and angles ° for [Ru(η^5-C_4Me_4S){κ^3-HB(Pz)$_3$}][PF$_6$] 73.

Ru(1)-N(32)	2.125(3)	N(11)-N(12)	1.384(5)
Ru(1)-N(12)	2.151(4)	N(12)-C(13)	1.362(6)
Ru(1)-N(22)	2.159(4)	C(13)-C(14)	1.393(7)
Ru(1)-C(1)	2.184(4)	C(14)-C(15)	1.393(8)
Ru(1)-C(7)	2.204(4)	N(21)-C(25)	1.359(6)
Ru(1)-C(3)	2.240(4)	N(21)-N(22)	1.375(5)
Ru(1)-C(5)	2.245(4)	N(22)-C(23)	1.350(6)
Ru(1)-S(1)	2.4006(12)	C(23)-C(24)	1.405(7)
S(1)-C(1)	1.795(5)	C(24)-C(25)	1.382(8)
S(1)-C(7)	1.800(5)	N(31)-C(35)	1.361(6)
C(1)-C(3)	1.419(6)	N(31)-N(32)	1.377(5)
C(1)-C(2)	1.521(6)	N(32)-C(33)	1.352(6)
C(3)-C(5)	1.464(7)	C(33)-C(34)	1.397(7)
C(3)-C(4)	1.496(7)	C(34)-C(35)	1.380(8)
C(5)-C(7)	1.415(7)	P(1)-F(5)	1.564(5)
C(5)-C(6)	1.526(6)	P(1)-F(6)	1.579(5)
C(7)-C(8)	1.509(7)	P(1)-F(3)	1.587(4)
B(1)-N(21)	1.539(7)	P(1)-F(4)	1.597(4)
B(1)-N(11)	1.546(7)	P(1)-F(1)	1.600(3)
B(1)-N(31)	1.557(7)	P(1)-F(2)	1.603(4)
N(11)-C(15)	1.350(6)		
N(32)-Ru(1)-N(12)	84.51(14)	C(5)-Ru(1)-S(1)	70.13(12)
N(32)-Ru(1)-N(22)	85.21(14)	C(1)-S(1)-C(7)	90.2(2)
N(12)-Ru(1)-N(22)	82.94(14)	C(1)-S(1)-Ru(1)	60.72(14)
N(32)-Ru(1)-C(1)	123.2(2)	C(7)-S(1)-Ru(1)	61.35(14)
N(12)-Ru(1)-C(1)	96.1(2)	C(3)-C(1)-C(2)	125.2(4)
N(22)-Ru(1)-C(1)	151.5(2)	C(3)-C(1)-S(1)	112.4(3)
N(32)-Ru(1)-C(7)	125.3(2)	C(2)-C(1)-S(1)	120.9(3)
N(12)-Ru(1)-C(7)	150.1(2)	C(3)-C(1)-Ru(1)	73.4(2)
N(22)-Ru(1)-C(7)	95.9(2)	C(2)-C(1)-Ru(1)	132.4(3)
C(1)-Ru(1)-C(7)	70.9(2)	S(1)-C(1)-Ru(1)	73.5(2)
N(32)-Ru(1)-C(3)	94.8(2)	C(1)-C(3)-C(5)	112.0(4)
N(12)-Ru(1)-C(3)	120.0(2)	C(1)-C(3)-C(4)	122.1(4)
N(22)-Ru(1)-C(3)	157.0(2)	C(5)-C(3)-C(4)	125.6(4)
C(1)-Ru(1)-C(3)	37.4(2)	C(1)-C(3)-Ru(1)	69.2(2)
C(7)-Ru(1)-C(3)	65.4(2)	C(5)-C(3)-Ru(1)	71.2(2)
N(32)-Ru(1)-C(5)	96.1(2)	C(4)-C(3)-Ru(1)	132.0(3)
N(12)-Ru(1)-C(5)	158.2(2)	C(7)-C(5)-C(3)	112.9(4)
N(22)-Ru(1)-C(5)	118.9(2)	C(7)-C(5)-C(6)	121.7(5)
C(1)-Ru(1)-C(5)	65.3(2)	C(3)-C(5)-C(6)	125.2(5)
C(7)-Ru(1)-C(5)	37.1(2)	C(7)-C(5)-Ru(1)	69.9(2)
C(3)-Ru(1)-C(5)	38.1(2)	C(3)-C(5)-Ru(1)	70.7(2)
N(32)-Ru(1)-S(1)	164.75(10)	C(6)-C(5)-Ru(1)	131.5(3)
N(12)-Ru(1)-S(1)	105.82(11)	C(5)-C(7)-C(8)	126.4(5)
N(22)-Ru(1)-S(1)	106.88(11)	C(5)-C(7)-S(1)	111.9(4)
C(1)-Ru(1)-S(1)	45.81(13)	C(8)-C(7)-S(1)	120.2(4)
C(7)-Ru(1)-S(1)	45.76(13)	C(5)-C(7)-Ru(1)	73.0(3)
C(3)-Ru(1)-S(1)	70.43(12)	C(8)-C(7)-Ru(1)	132.6(4)

S(1)-C(7)-Ru(1)	72.9(2)	C(35)-N(31)-B(1)	130.3(4)
N(21)-B(1)-N(11)	108.0(4)	N(32)-N(31)-B(1)	120.3(4)
N(21)-B(1)-N(31)	108.1(4)	C(33)-N(32)-N(31)	106.5(4)
N(11)-B(1)-N(31)	107.9(4)	C(33)-N(32)-Ru(1)	133.2(3)
C(15)-N(11)-N(12)	109.2(4)	N(31)-N(32)-Ru(1)	120.3(3)
C(15)-N(11)-B(1)	130.8(4)	N(32)-C(33)-C(34)	110.1(4)
N(12)-N(11)-B(1)	119.8(4)	C(35)-C(34)-C(33)	105.6(4)
C(13)-N(12)-N(11)	106.3(4)	N(31)-C(35)-C(34)	108.4(4)
C(13)-N(12)-Ru(1)	133.3(3)	F(5)-P(1)-F(6)	91.5(3)
N(11)-N(12)-Ru(1)	120.0(3)	F(5)-P(1)-F(3)	90.0(3)
N(12)-C(13)-C(14)	110.3(5)	F(6)-P(1)-F(3)	178.5(4)
C(13)-C(14)-C(15)	105.1(5)	F(5)-P(1)-F(4)	178.5(4)
N(11)-C(15)-C(14)	109.1(5)	F(6)-P(1)-F(4)	89.7(3)
C(25)-N(21)-N(22)	109.8(4)	F(3)-P(1)-F(4)	88.7(3)
C(25)-N(21)-B(1)	130.3(4)	F(5)-P(1)-F(1)	90.8(3)
N(22)-N(21)-B(1)	119.6(4)	F(6)-P(1)-F(1)	88.5(2)
C(23)-N(22)-N(21)	106.1(4)	F(3)-P(1)-F(1)	91.5(2)
C(23)-N(22)-Ru(1)	133.5(3)	F(4)-P(1)-F(1)	88.5(2)
N(21)-N(22)-Ru(1)	120.3(3)	F(5)-P(1)-F(2)	89.8(3)
N(22)-C(23)-C(24)	110.6(5)	F(6)-P(1)-F(2)	91.3(3)
C(25)-C(24)-C(23)	104.9(4)	F(3)-P(1)-F(2)	88.7(3)
N(21)-C(25)-C(24)	108.6(5)	F(4)-P(1)-F(2)	90.9(3)
C(35)-N(31)-N(32)	109.4(4)	F(1)-P(1)-F(2)	179.4(3)

Table 2.14:
Crystal data and structure refinement for $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81.

Empirical formula	$C_{16}H_{24}Cl_3F_6PRu_2S_2$
Formula weight	733.93
Temperature	173(2) K
Wavelength	0.71070 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.1369(4) Å
	b = 11.4708(3) Å
	c = 12.7140(5) Å
	α = 114.6810(10) °
	β = 110.5470(10) °
	γ = 95.4330(10) °
Volume	1206.24(7) $Å^3$
Z	2
Density (calculated)	2.021 g cm^{-3}
Absorption coefficient	1.873 mm^{-1}
F(000)	720
Crystal size	0.20 x 0.10 x 0.10 mm^3
Theta range for data collection	3.43 to 26.00 °
hkl index ranges	0 → 12, -13 → 13, -16 → 15
Reflections collected	4426
Independent reflections	4426 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4414 / 0 / 272
Goodness-of-fit on F^2	1.095
Final R indices [$I>2\sigma(I)$]	R1 = 0.0254, wR2 = 0.0620
R indices (all data)	R1 = 0.0290, wR2 = 0.0869
Extinction coefficient	0.0065(5)
Largest diff. peak and hole	0.476 and -0.808 e $Å^{-3}$

Table 2.15:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81.

	x	y	z	U(eq)
Ru(1)	7143(1)	5232(1)	7098(1)	16(1)
Ru(2)	9513(1)	7355(1)	7096(1)	16(1)
Cl(1)	7273(1)	7509(1)	7351(1)	20(1)
Cl(2)	8004(1)	5052(1)	5466(1)	20(1)
Cl(3)	9733(1)	6308(1)	8480(1)	23(1)
S(1)	4699(1)	3918(1)	5993(1)	21(1)
S(2)	11675(1)	7659(1)	6849(1)	22(1)
P(1)	3992(1)	1349(1)	7740(1)	24(1)
F(1)	5531(2)	2348(2)	8888(2)	39(1)
F(2)	4662(2)	1146(2)	6731(2)	45(1)
F(3)	2453(2)	343(2)	6587(2)	44(1)
F(4)	3309(2)	1557(2)	8744(2)	43(1)
F(5)	3511(2)	2582(2)	7597(2)	45(1)
F(6)	4469(2)	115(2)	7880(2)	44(1)
C(1)	5427(3)	5056(3)	7655(3)	21(1)
C(2)	6591(3)	4720(3)	8383(3)	20(1)
C(3)	7001(3)	3650(3)	7584(3)	20(1)
C(4)	6135(3)	3163(3)	6257(3)	20(1)
C(5)	4661(4)	6070(3)	8126(3)	31(1)
C(6)	7306(4)	5418(3)	9822(3)	28(1)
C(7)	8204(3)	3088(3)	8080(3)	28(1)
C(8)	6164(4)	2015(3)	5138(3)	29(1)
C(9)	10073(3)	7846(3)	5850(3)	21(1)
C(10)	9636(3)	8913(3)	6580(3)	20(1)
C(11)	10492(3)	9488(3)	7944(3)	21(1)
C(12)	11587(3)	8843(3)	8241(3)	21(1)
C(13)	9494(4)	7067(3)	4423(3)	28(1)
C(14)	8401(4)	9397(3)	5991(3)	28(1)
C(15)	10271(4)	10649(3)	8919(3)	28(1)
C(16)	12726(3)	9178(3)	9527(3)	30(1)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 2.16:
Bond lengths Å and angles ° for $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$ 81.

Ru(1)-C(4)	2.116(3)	P(1)-F(1)	1.595(2)
Ru(1)-C(1)	2.117(3)	P(1)-F(6)	1.596(2)
Ru(1)-C(3)	2.155(3)	P(1)-F(2)	1.597(2)
Ru(1)-C(2)	2.170(3)	P(1)-F(5)	1.598(2)
Ru(1)-S(1)	2.3375(7)	P(1)-F(3)	1.599(2)
Ru(1)-Cl(3)	2.4167(7)	P(1)-F(4)	1.602(2)
Ru(1)-Cl(2)	2.4615(7)	C(1)-C(2)	1.420(4)
Ru(1)-Cl(1)	2.4792(7)	C(1)-C(5)	1.493(4)
Ru(2)-C(9)	2.114(3)	C(2)-C(3)	1.437(4)
Ru(2)-C(12)	2.133(3)	C(2)-C(6)	1.500(4)
Ru(2)-C(10)	2.153(3)	C(3)-C(4)	1.418(4)
Ru(2)-C(11)	2.172(3)	C(3)-C(7)	1.500(4)
Ru(2)-S(2)	2.3353(7)	C(4)-C(8)	1.493(4)
Ru(2)-Cl(1)	2.4160(7)	C(9)-C(10)	1.414(4)
Ru(2)-Cl(2)	2.4600(7)	C(9)-C(13)	1.494(4)
Ru(2)-Cl(3)	2.4752(7)	C(10)-C(11)	1.441(4)
S(1)-C(4)	1.766(3)	C(10)-C(14)	1.503(4)
S(1)-C(1)	1.770(3)	C(11)-C(12)	1.420(4)
S(2)-C(12)	1.764(3)	C(11)-C(15)	1.494(4)
S(2)-C(9)	1.773(3)	C(12)-C(16)	1.490(4)
C(4)-Ru(1)-C(1)	73.12(11)	C(9)-Ru(2)-C(12)	73.10(11)
C(4)-Ru(1)-C(3)	38.77(11)	C(9)-Ru(2)-C(10)	38.68(11)
C(1)-Ru(1)-C(3)	67.42(11)	C(12)-Ru(2)-C(10)	67.15(11)
C(4)-Ru(1)-C(2)	67.33(11)	C(9)-Ru(2)-C(11)	67.57(11)
C(1)-Ru(1)-C(2)	38.66(11)	C(12)-Ru(2)-C(11)	38.50(11)
C(3)-Ru(1)-C(2)	38.79(11)	C(10)-Ru(2)-C(11)	38.91(11)
C(4)-Ru(1)-S(1)	46.39(8)	C(9)-Ru(2)-S(2)	46.64(8)
C(1)-Ru(1)-S(1)	46.51(8)	C(12)-Ru(2)-S(2)	46.23(8)
C(3)-Ru(1)-S(1)	71.88(8)	C(10)-Ru(2)-S(2)	71.73(8)
C(2)-Ru(1)-S(1)	71.78(8)	C(11)-Ru(2)-S(2)	71.69(8)
C(4)-Ru(1)-Cl(3)	124.22(8)	C(9)-Ru(2)-Cl(1)	124.33(8)
C(1)-Ru(1)-Cl(3)	127.52(8)	C(12)-Ru(2)-Cl(1)	126.81(8)
C(3)-Ru(1)-Cl(3)	95.87(8)	C(10)-Ru(2)-Cl(1)	95.86(8)
C(2)-Ru(1)-Cl(3)	97.52(8)	C(11)-Ru(2)-Cl(1)	96.89(8)
S(1)-Ru(1)-Cl(3)	167.58(3)	S(2)-Ru(2)-Cl(1)	167.24(3)
C(4)-Ru(1)-Cl(2)	96.30(8)	C(9)-Ru(2)-Cl(2)	96.04(8)
C(1)-Ru(1)-Cl(2)	151.03(8)	C(12)-Ru(2)-Cl(2)	150.66(8)
C(3)-Ru(1)-Cl(2)	120.58(8)	C(10)-Ru(2)-Cl(2)	120.68(8)
C(2)-Ru(1)-Cl(2)	159.30(8)	C(11)-Ru(2)-Cl(2)	159.53(8)
S(1)-Ru(1)-Cl(2)	106.75(2)	S(2)-Ru(2)-Cl(2)	106.60(3)
Cl(3)-Ru(1)-Cl(2)	80.93(2)	Cl(1)-Ru(2)-Cl(2)	82.03(2)
C(4)-Ru(1)-Cl(1)	154.79(8)	C(9)-Ru(2)-Cl(3)	154.42(8)
C(1)-Ru(1)-Cl(1)	97.39(8)	C(12)-Ru(2)-Cl(3)	98.18(8)
C(3)-Ru(1)-Cl(1)	157.73(8)	C(10)-Ru(2)-Cl(3)	158.69(8)
C(2)-Ru(1)-Cl(1)	119.54(8)	C(11)-Ru(2)-Cl(3)	120.31(8)
S(1)-Ru(1)-Cl(1)	110.23(3)	S(2)-Ru(2)-Cl(3)	110.03(3)
Cl(3)-Ru(1)-Cl(1)	80.29(2)	Cl(1)-Ru(2)-Cl(3)	80.39(2)
Cl(2)-Ru(1)-Cl(1)	80.73(2)	Cl(2)-Ru(2)-Cl(3)	79.81(2)

Ru(2)-Cl(1)-Ru(1)	83.39(2)	C(4)-C(3)-C(2)	112.7(2)
Ru(2)-Cl(2)-Ru(1)	82.86(2)	C(4)-C(3)-C(7)	122.9(3)
Ru(1)-Cl(3)-Ru(2)	83.46(2)	C(2)-C(3)-C(7)	124.4(3)
C(4)-S(1)-C(1)	90.96(14)	C(4)-C(3)-Ru(1)	69.1(2)
C(4)-S(1)-Ru(1)	60.17(9)	C(2)-C(3)-Ru(1)	71.2(2)
C(1)-S(1)-Ru(1)	60.19(9)	C(7)-C(3)-Ru(1)	128.1(2)
C(12)-S(2)-C(9)	91.30(14)	C(3)-C(4)-C(8)	128.6(3)
C(12)-S(2)-Ru(2)	60.84(9)	C(3)-C(4)-S(1)	111.6(2)
C(9)-S(2)-Ru(2)	60.09(9)	C(8)-C(4)-S(1)	119.1(2)
F(1)-P(1)-F(6)	90.46(12)	C(3)-C(4)-Ru(1)	72.1(2)
F(1)-P(1)-F(2)	90.23(12)	C(8)-C(4)-Ru(1)	129.2(2)
F(6)-P(1)-F(2)	90.79(12)	S(1)-C(4)-Ru(1)	73.44(11)
F(1)-P(1)-F(5)	89.70(12)	C(10)-C(9)-C(13)	128.1(3)
F(6)-P(1)-F(5)	179.83(12)	C(10)-C(9)-S(2)	111.0(2)
F(2)-P(1)-F(5)	89.28(12)	C(13)-C(9)-S(2)	120.2(2)
F(1)-P(1)-F(3)	179.78(13)	C(10)-C(9)-Ru(2)	72.2(2)
F(6)-P(1)-F(3)	89.35(12)	C(13)-C(9)-Ru(2)	129.0(2)
F(2)-P(1)-F(3)	89.67(12)	S(2)-C(9)-Ru(2)	73.27(10)
F(5)-P(1)-F(3)	90.49(13)	C(9)-C(10)-C(11)	113.3(3)
F(1)-P(1)-F(4)	90.06(11)	C(9)-C(10)-C(14)	123.3(3)
F(6)-P(1)-F(4)	89.64(12)	C(11)-C(10)-C(14)	123.4(3)
F(2)-P(1)-F(4)	179.49(14)	C(9)-C(10)-Ru(2)	69.2(2)
F(5)-P(1)-F(4)	90.29(12)	C(11)-C(10)-Ru(2)	71.3(2)
F(3)-P(1)-F(4)	90.04(12)	C(14)-C(10)-Ru(2)	127.9(2)
C(2)-C(1)-C(5)	128.4(3)	C(12)-C(11)-C(10)	111.9(3)
C(2)-C(1)-S(1)	111.6(2)	C(12)-C(11)-C(15)	124.5(3)
C(5)-C(1)-S(1)	119.3(2)	C(10)-C(11)-C(15)	123.6(3)
C(2)-C(1)-Ru(1)	72.7(2)	C(12)-C(11)-Ru(2)	69.3(2)
C(5)-C(1)-Ru(1)	128.8(2)	C(10)-C(11)-Ru(2)	69.8(2)
S(1)-C(1)-Ru(1)	73.30(10)	C(15)-C(11)-Ru(2)	130.0(2)
C(1)-C(2)-C(3)	112.2(2)	C(11)-C(12)-C(16)	128.2(3)
C(1)-C(2)-C(6)	123.3(3)	C(11)-C(12)-S(2)	111.8(2)
C(3)-C(2)-C(6)	124.4(3)	C(16)-C(12)-S(2)	119.4(2)
C(1)-C(2)-Ru(1)	68.7(2)	C(11)-C(12)-Ru(2)	72.2(2)
C(3)-C(2)-Ru(1)	70.0(2)	C(16)-C(12)-Ru(2)	129.1(2)
C(6)-C(2)-Ru(1)	128.8(2)	S(2)-C(12)-Ru(2)	72.94(10)

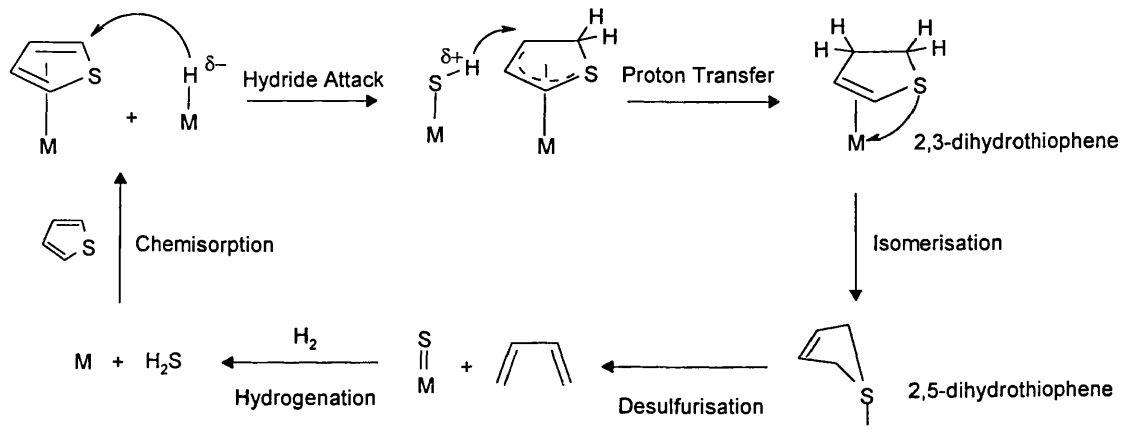
CHAPTER 3

ATTACK OF NUCLEOPHILES ON RUTHENIUM ACTIVATED TETRAMETHLYLTHIOPHENE.

3.1 INTRODUCTION

As described in Chapter 1 reactions of thiophenes and related molecules have been widely studied with the aim of understanding the mechanistic aspects of the HDS process. Numerous models and mechanisms have been presented over the years for the HDS reaction and significantly several papers have implicated nucleophiles as being important reagents in this process.[7,8,45,65,68,69,70] As part of a noteworthy review by Angelici a plausible mechanism for the HDS process was presented (reproduced here as Scheme 3.1).[7] This mechanism is based around the initial η^5-absorption of a thiophene molecule to the metal site which activates the thiophene towards nucleophilic attack by a surface metal-hydride. This attack results in the formation of 2-hydrothiophene which then undergoes a proton transfer reaction to form 2,3-dihydrothiophene (the second proton being furnished by a nearby acidic SH group). The results of these first two steps are equivalent to the addition of a molecule of dihydrogen. Indirect evidence for this process is provided by the observation that HDS catalysts are also known to catalyse olefin hydrogenation reactions.[7,139] The 2,3-dihydrothiophene species undergoes an isomerisation to give the thermodynamically more stable 2,5-dihydrothiophene isomer. Angelici argued that this isomerisation process could take place by one of the "traditional" mechanisms for olefin isomerisation on heterogeneous or homogeneous catalysts.[7] The desulfurisation step involves the elimination of a butadiene molecule promoted by the abstraction of sulfur from the S-bound 2,5-dihydrothiophene. It is further argued that the observed C4 products (butenes and butane) formed from thiophene by HDS are generated by hydrogenation of butadiene, a reaction known to occur over HDS catalysts.[7] The final step in the

process converts the surface sulfide to H_2S by the reaction with dihydrogen. It is notable that Angelici placed a caveat on his mechanism, as "although the thiophene HDS mechanism is the first to be based on reactions that are known to occur on metal centres and the overall mechanism is intuitively reasonable, it has not been proven (or disproven) to occur on any HDS catalyst." [7]



Scheme 3.1: Proposed mechanism for thiophene hydrodesulfurisation.

Nucleophilic addition reactions to coordinated unsaturated hydrocarbon ligands like arenes, butadienes and ethylenes, as well as allyl and enyl ligands, have for many years been recognised as an important area for study.[140] When these polyene species are coordinated to cationic transition metal centres their reactivity is enhanced as a result of electron density transfer from the hydrocarbon to the positively charged metal centre such that nucleophiles like H^-, CN^- or MeO^- readily attack the activated ligand.[141] In general these nucleophiles add to these cationic complexes in highly controllable ways, such that they can provide viable routes towards the regio- and stereo-specific functionalisation of these polyene ligands.[142,143] The analysis of many of the products of these reactions, together with theoretical considerations led Davies, Green and Mingos to propose a series of rules which predict the direction of

kinetically controlled nucleophilic attack in 18 electron complexes containing unsaturated hydrocarbon ligands.[141]

In an extension to previous studies on the reactions of nucleophiles with thiophenes (see Chapter 1) the work presented in this chapter investigates whether there is any variation in the chemistry of the complexed thiophene ligand upon changing the nature of the auxiliary ligands on the same metal centre. To that end, and as a part of the study reported in this thesis into the coordination chemistry of the $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$ **44** dimer, (see Chapter 2) a range of complexes which contained the same basic structural motif, an η^5-bound tetramethylthiophene ligand with the remaining three facial sites of the ruthenium metal centre being occupied by the tridentate ancillary ligand, were prepared. A range of co-ligands were chosen to impart different steric and electronic effects on the '$Ru(\eta^5\text{-}C_4Me_4S)$' fragments. Thus a series of model compounds which might mimic a wide variety of active sites of an HDS catalyst, were investigated.

3.2 RESULTS AND DISCUSSION

3.2.1 POLY-PYRAZOLYL COMPLEXES.

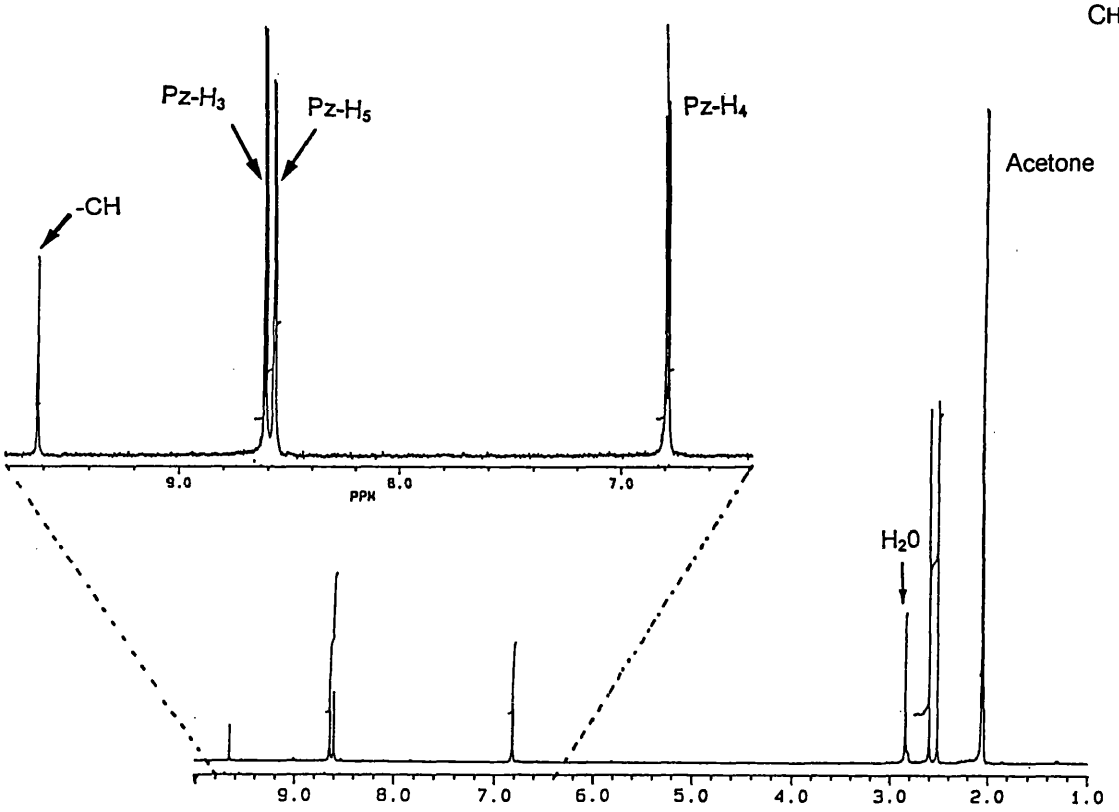
The initial investigation looked at the reactions of $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$ **73** with a range of nucleophiles (H^-, OMe^-, CN^-, OH^-). Surprisingly, even under the most forcing of conditions this cation showed no reactivity, and in most cases only the starting materials were recovered after work-up. The absence of any reactivity was ascribed to the uni-positive charge on this complex being insufficient to promote nucleophilic attack. Upon

investigating the isostructural, but dicationic complex $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ **74** reactions with nucleophiles were observed. The treatment of a suspension of **74** in methanol with either $Na[BH_4]$ or Na[OMe] results in the formation of a yellow solution. Water was added to this solution and the products extracted with dichloromethane. The dichloromethane solution was dried over potassium carbonate, and then the solvent was removed by evaporation. The crude product was recrystallised from chloroform/hexane. Both $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$ **82** and $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$ **83** were obtained by this method, but both complexes were unstable and rapidly decomposed both in the solution and solid states. As a result, when repeating the reactions the preparation and subsequent work-up of these materials were performed as rapidly as possible. Interestingly, analogous reactions of $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ **74** with KOH or KCN, did not give rise to any well-defined products.

The data obtained from both $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$ **82** and $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$ **83** are consistent with nucleophilic attack occurring at the 2-position of the thiophene ring. The addition of a nucleophile to the ring at this position results in a complete loss of symmetry in these complexes, and as a consequence the ^{1}H-NMR spectra of these materials are considerably more complex than the spectrum obtained for the starting material. As an illustration of this, Figure 3.1 shows the ^{1}H-NMR spectra of the starting complex **74** and the product of OMe^- attack **82**. The spectrum of **82** will now be discussed in detail. The addition of the methoxy functionality to the thiophene renders each of the methyl groups of the

thiopheneyl moiety unique, such that the spectrum now exhibits four methyl resonances for the new ligand (δ 1.29, 1.91, 2.24 and 2.31 ppm). There is an additional singlet at δ 3.21 ppm for the methoxy substituent on the ring. The spectrum of this compound exhibits nine distinct pyrazolyl resonances, one for each of the pyrazolyl protons of the *tris*(pyrazolyl)methane ligand, and a low field resonance at δ 9.63 ppm due to the acidic proton of the bridgehead carbon atom. The series of doublet of doublets resonances at δ 6.27, 6.42 and 6.55 ppm can all be unequivocally assigned to the protons at the '4' position on the pyrazolyl rings. The remaining sets of doublets are due to the protons at the '3' and '5' positions. The resonances at δ 7.51, 7.59 and 8.51 ppm are tentatively assigned to the protons at the '3' position, while the resonances at δ 8.23, 8.34 and 8.41 ppm are assigned to those protons at the '5' position of the pyrazolyl rings. The assignment of these signals to either the '3' or '5' positions is based on the fact that the resonances associated with the '3' position have the widest chemical shift range due to their proximity to the ruthenium-thiopheneyl fragment. In contrast the signals associated with the '5' position show less variation in chemical shifts as would be expected for the pyrazolyl protons farthest from the metal centre and its thiopheneyl ligand.

Rapid isolation and recording of the spectra of these compounds is essential in obtaining good data. Both compounds decomposed within a period of minutes in solution, giving a dark green colour. Following the decomposition process by NMR did not lead to any identifiable organometallic products. Post-decomposition the ^{1}H-NMR spectra showed only the presence of free $HC(Pz)_3$ and C_4Me_4S, although not in a 1:1 ratio (there is less C_4Me_4S). It is possible that the decomposition of these complexes is via a "chemical event" occurring



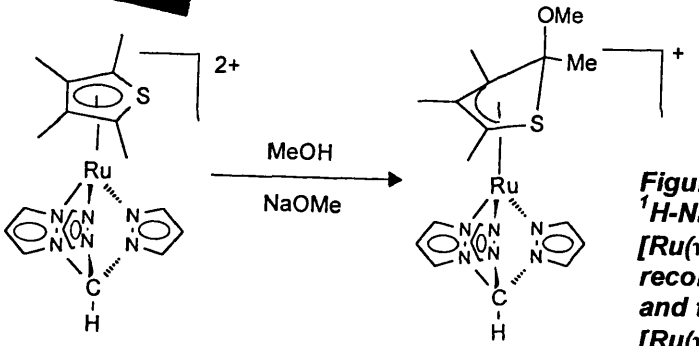
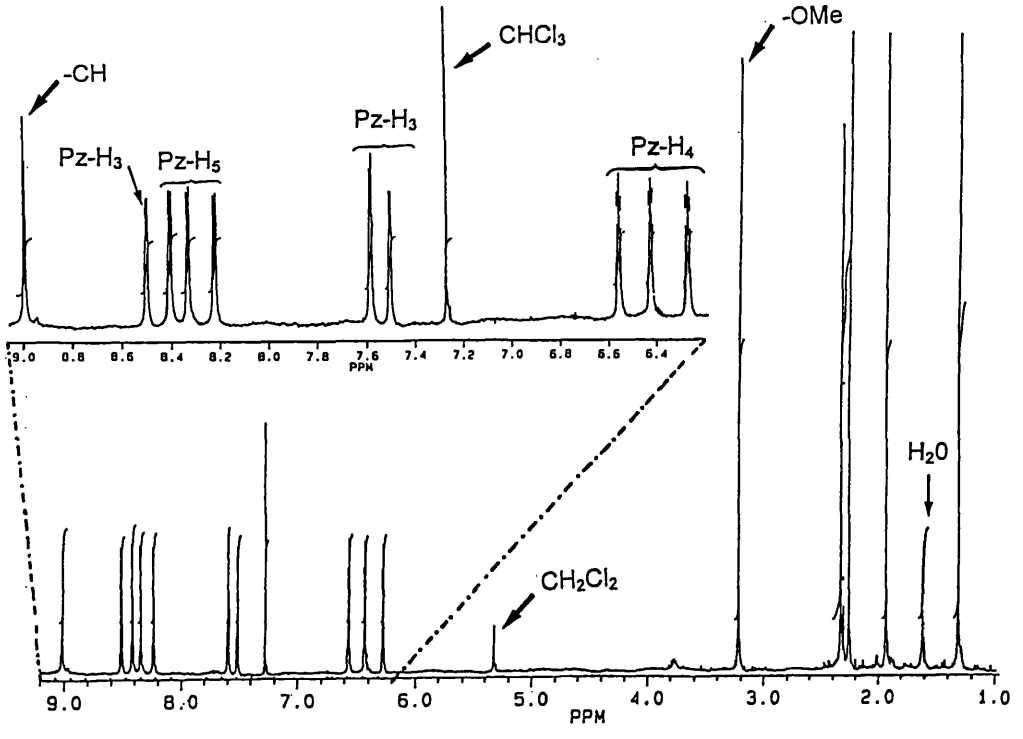


Figure 3.1:
^{1}H-NMR spectrum of $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$ 74, recorded in an $(CD_3)_2CO$ solution; and the ^{1}H-NMR spectrum of $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$ 82, recorded in a $CDCl_3$ solution.



at the thiopheneyl ligand (for example C-S bond cleavage) resulting in the formation of a new highly unstable complex which is quickly lost.

3.2.2 [9]aneS$_3$ COMPLEXES.

$[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$ **79** reacts in alcohols with a number of nucleophiles (Nuc^-) including hydride, alkoxides and cyanide salts, to give the corresponding complexes, $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}Nuc)(\kappa^3\text{-}[9]aneS_3)][PF_6]$, (Nuc = OMe **84**, OEt **85**, H **86**, CN **87**). The synthesis and characterisation of these complexes are presented in the experimental section, with a representative compound being described below.

The reaction between $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$ **79** and a freshly prepared solution of sodium ethoxide in ethanol proceeds smoothly to give an orange-yellow suspension. Addition of water, followed by extraction with dichloromethane, and subsequent recrystallisation from chloroform/hexane gives the product $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\kappa^3\text{-}[9]aneS_3)][PF_6]$ **85**, in moderate yield (26 %). The ^{1}H-NMR spectrum of this material exhibits four singlets at δ 1.33, 1.86, 2.06 and 2.28 ppm, due to the methyl groups on the thiophene derived ligands together with the triplet and quartet, δ 1.18 and 3.28 ppm, of the ethoxy functionality. The methylene protons of the [9]aneS$_3$ ligand give rise to a series of ill-resolved overlapping multiplet signals in the range δ 2.0-3.1 ppm. As with the tris(pyrazolyl)methane complexes studied previously any attack on the tetramethylthiophene ligand results in the formation of a complex with low symmetry. As a consequence each of the methylene protons on the [9]aneS$_3$ ligand are rendered unique, thus each proton is coupling to its nearest neighbours leading to the observation of an extremely complex region in the

proton NMR spectrum. The coupling is well illustrated by the ^{1}H-^{1}H-COSY-NMR spectrum (Figure 3.2), which shows a number of cross-peaks in this region. Although these signals are not well resolved in the proton NMR spectrum, examination of the ^{13}C-{^{1}H}-NMR spectrum clearly reveals that there six signals, δ 31.7, 32.7, 33.8, 33.9, 34.4, 36.6 ppm, associated with the methylene carbon atoms of the [9]aneS_3 ligand.

Unlike their *tris*(pyrazolyl)methane analogues these [Ru(η^4-C_4Me_4S-2-Nuc)(κ^3-[9]aneS_3)][PF_6] complexes are all stable, both in solution and the solid state. The stability of these materials allowed the structural determination of [Ru(η^4-C_4Me_4S-2-OEt)(κ^3-[9]aneS_3)][PF_6] **85** (Figure 3.3 and Table 3.1) and [Ru(η^4-C_4Me_4S-2-H)(κ^3-[9]aneS_3)][PF_6] **86** (Figure 3.4 and Table 3.2). Unsurprisingly the metal to ligand bond distances in these complexes are substantially identical. Both structures contain a κ^3-coordinated [9]aneS_3 ligand occupying three facial sites on an octahedral ruthenium(II) ion, with the remaining sites on the metal occupied by a thiopheneyl ligand. These tetramethylthiophene derived ligands are bound in a planar η^4-fashion to the metal through S(1), C(2), C(3), and C(4), with a maximum deviation from the plane of 0.04 Å in **85** and 0.05 Å in **86**. The sp^3 hybridised carbon C(1), is 0.63 Å in **85** and 0.65 Å in **86**, out of the ring plane, with a non-bonded Ru(1)-C(1) of 2.86 Å in **85** and 2.88 Å in H **86**, with dihedral angles between the planes [S(1)C(4)C(3)C(2)] and [S(1)C(1)C(2)] of 35.7 ° and 37.3 ° for **85** and **86** respectively. It is interesting to note in **85** that the ethoxy substituent on the ligand adopts a conformation that places the methylene carbon C(9), over the centroid of the π-

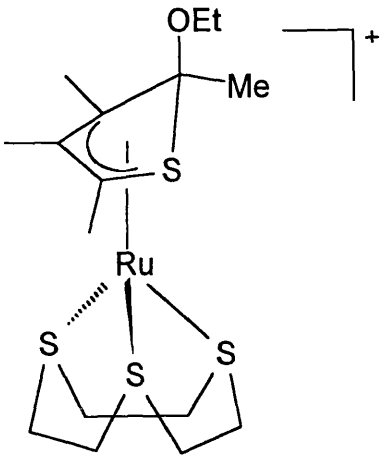


Figure 3.2:
^{1}H and 2D ^{1}H-^{1}H-COSY NMR spectra of $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\kappa^3\text{-}[9]aneS_3)][PF_6]$ 85, recorded in a $CDCl_3$ solution.

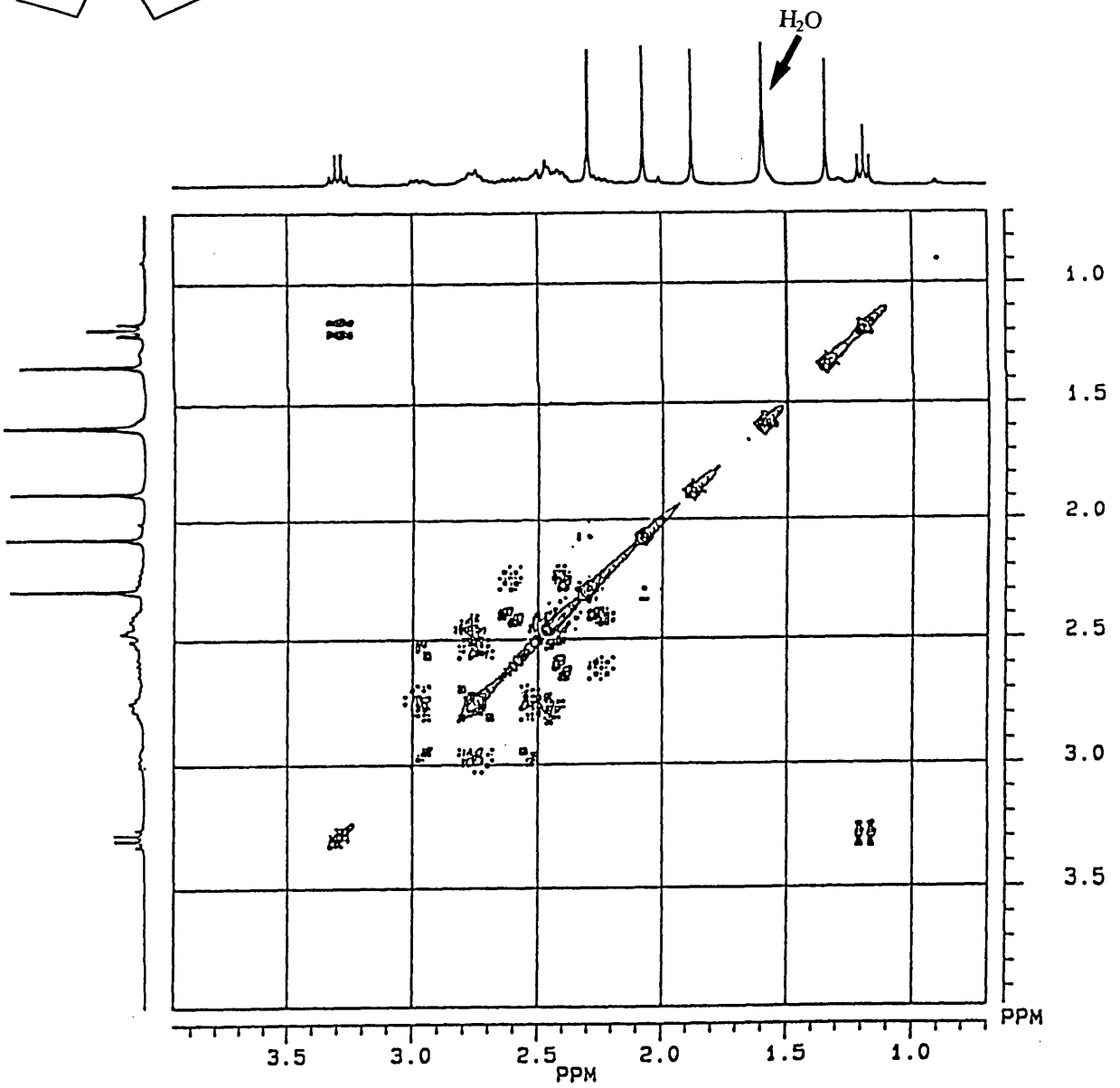


Table 3.1:

Selected Bond lengths (Å) and angles (°) for [Ru(η^4-C_4Me_4S-OEt)(κ^3-[9]aneS_3)][PF_6] 85.

Bond Lengths			
Ru(1)-S(1)	2.4046(18)	Ru(1)-S(2)	2.2737(19)
Ru(1)-C(2)	2.212(8)	Ru(1)-S(3)	2.3456(19)
Ru(1)-C(3)	2.167(7)	Ru(1)-S(4)	2.326(2)
Ru(1)-C(4)	2.117(7)	S(1)-C(1)	1.869(8)
S(1)-C(4)	1.792(8)	C(1)-C(2)	1.513(11)
C(2)-C(3)	1.448(11)	C(3)-C(4)	1.406(11)
C(1)-O(1)	1.429(9)	O(1)-C(9)	1.437(9)
C(9)-C(10)	1.504(10)		
Bond Angles			
S(2)-Ru(1)-S(3)	86.82(7)	S(2)-Ru(1)-S(4)	87.83(7)
C(4)-S(1)-C(1)	92.7(3)	S(1)-C(1)-C(5)	109.0(6)
S(1)-C(1)-O(1)	114.1(5)	C(5)-C(1)-O(1)	104.5(6)
C(16)-S(2)-C(11)	100.3(4)	C(12)-S(3)-C(13)	101.2(4)
C(15)-S(4)-C(14)	101.6(4)	S(1)-Ru(1)-S(2)	160.94(7)

Figure 3.3:

The crystal structure of cation in [Ru(η^4-C_4Me_4S-OEt)(κ^3-[9]aneS_3)][PF_6] 85, showing the atom labelling scheme.

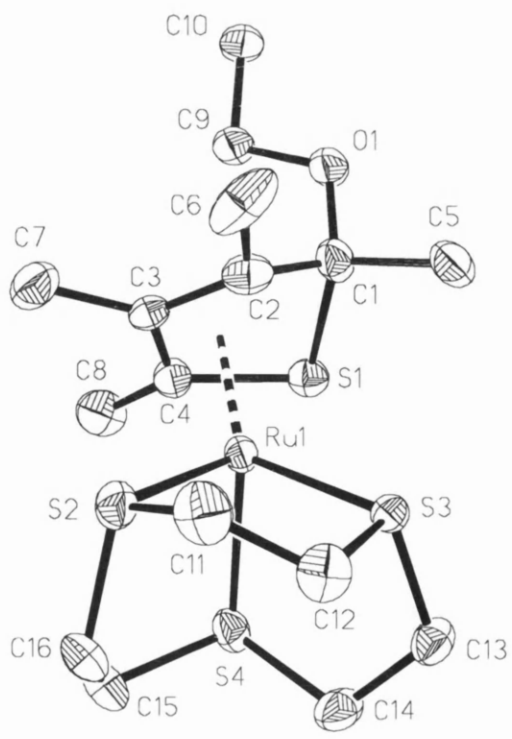


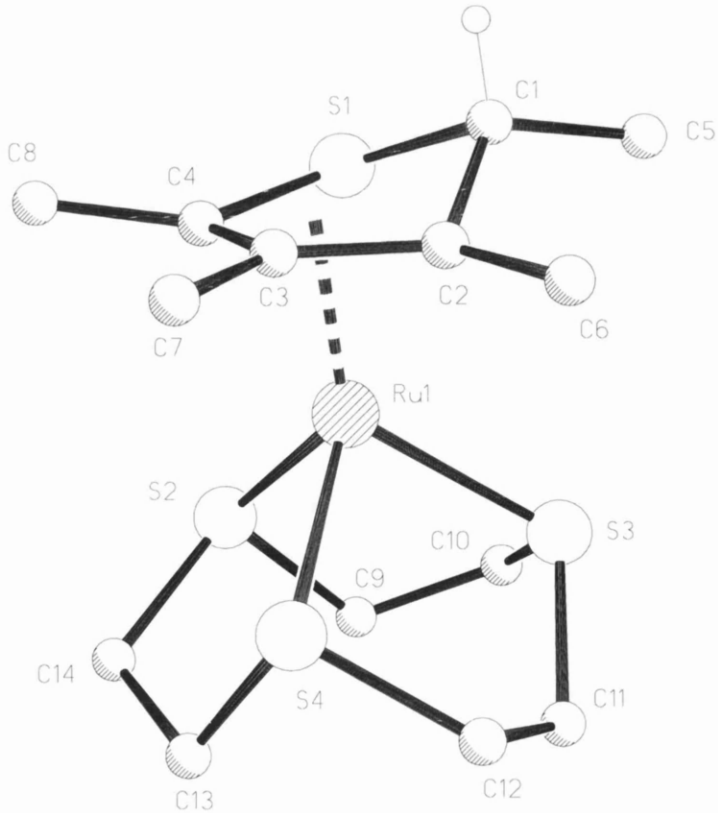
Table 3.2:

Selected Bond lengths (Å) and angles (°) for [Ru(η^4-C_4Me_4S-H)(κ^3-[9]aneS_3)][PF_6] 86.

Bond Lengths			
Ru(1)-S(1)	2.3914(9)	Ru(1)-S(2)	2.3428(9)
Ru(1)-C(2)	2.209(3)	Ru(1)-S(3)	2.3544(9)
Ru(1)-C(3)	2.173(3)	Ru(1)-S(4)	2.2846(9)
Ru(1)-C(4)	2.119(3)	S(1)-C(1)	1.848(4)
S(1)-C(4)	1.793(4)	C(1)-C(2)	1.528(5)
C(2)-C(3)	1.432(5)	C(3)-C(4)	1.509(5)
Bond Angles			
S(2)-Ru(1)-S(3)	87.78(3)	S(2)-Ru(1)-S(4)	87.74(3)
S(4)-Ru(1)-S(3)	87.39(3)	S(4)-Ru(1)-S(1)	160.97(3)
C(4)-S(1)-C(1)	93.99(17)	S(1)-C(1)-C(5)	110.6(3)
S(1)-C(1)-C(2)	97.9(2)	C(9)-S(2)-C(14)	100.85(17)
C(10)-S(3)-C(11)	101.00(17)	C(13)-S(4)-C(11)	99.79(16)

Figure 3.4:

The crystal structure of cation in [Ru(η^4-C_4Me_4S-H)(κ^3-[9]aneS_3)][PF_6] 86, showing the atom labelling scheme.



bonded thiopheneyl ring. The metal to ligand bond distances in **85** and **86** are somewhat longer than those reported previously in the η^4-thiopheneyl complex, $[Mn(\eta^4\text{-}C_4H_5S\text{-}2\text{-}CN)(CO)_3]$ **19**,[45] which is only to be expected for a second row metal. However these distances are similar to those reported for the *endo* complex $[Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)(\eta^6\text{-}C_6Me_6)][PF_6]$ **88**[79] and the only other crystallographically characterised η^4-thiopheneyl, $[Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OH)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]$ **23**[48]. Analysis of the bond lengths from the metal to the sulfurs of the [9]aneS_3 ligands were found to be dissimilar, with two long bonds, (2.3456(17) and 2.326(2) Å for **85** and 2.3544(9) and 2.3428(9) Å for **86**), and one short bond (2.2737(19) Å for **85** and 2.2846(9) Å for **86**) in each case. It is notable that the short bond in both examples are formed approximately *trans* to the thiopheneyl sulfur and thus it is tempting to ascribe this observation to a *trans* influence of that ligand. However it should be noted that this pattern has also been found in other [9]aneS_3 complexes.[144-145] For example, even in $[Ru(CH_3CN)_3(\kappa^3\text{-}[9]aneS_3)][CF_3SO_3]_2$ **89**, where all the sulfurs are *trans* to the same ligand, the ruthenium-sulfur bond distances show a similar pattern of two long (2.298(2) and 2.296(2) Å) and one short (2.281(2) Å) bond.[144] Both of the structures reported here demonstrate definitively that the tetramethylthiophene ligand is attacked at the carbon in the "2" position, with the nucleophile adding to the ring in an exo fashion.

It was interesting to note that the reaction of KOH with the $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)]^{2+}$ cation failed to yield any tractable material. It is likely that the thiophene ligand will undergo base hydrolysis leading to the formation of sulfoxide and/or acyl-thiolate complexes rather than yielding an analogous

compound to those described above. Moreover it is possible that in this reaction the [9]aneS$_3$ ligand is not acting as an inert spectator ligand. Bennett and co-workers have shown that [Ru(η^6-C$_6$Me$_6$)([9]aneS$_3$)][PF$_6$]$_2$ **90** undergoes base-induced fragmentation of the [9]aneS$_3$ ligand resulting in the formation of complexes containing vinyl thioethers, [Ru(η^6-C$_6$Me$_6$)(κ^2-S(CHCH$_2$)CH$_2$CH$_2$S)(σ-SCHCH$_2$)] **91** and [Ru(η^6-C$_6$Me$_6$)(κ^3-S(CHCH$_2$)CH$_2$CH$_2$SCH$_2$CH$_2$S)][PF$_6$] **92**.[146-147] If any of these processes were to occur with the [Ru(η^5-C$_4$Me$_4$S)(κ^3-[9]aneS$_3$)]$^{2+}$ cation, the resulting vinyl thioether, sulfoxide, or acyl thiolate complexes may not have been sufficiently stable to allow isolation.

In an attempt to assess whether the thiopheneyl complexes were intermediates in the HDS reaction a sealed NMR tube containing a solution of [Ru(η^4-C$_4$Me$_4$S-2-H)(κ^3-[9]aneS$_3$)][PF$_6$] **86** in CDCl$_3$ was heated for two weeks at 60 °C. The solution was monitored periodically by ^{1}H-NMR spectroscopy, but no change in the spectrum occurred over this period. This is in direct contrast to studies on related systems carried out previously. Nucleophilic attack on [Ru(η^5-C$_5$H$_5$)(η^5-Th)]$^+$ complexes (Th = C$_4$H$_4$S, 2-MeC$_4$H$_3$S, 2,5-Me$_2$C$_4$H$_2$S) results in the isolation of products in which C-S bond cleavage had occurred,[65,68,70] and it is particularly notable that the [Ru(η^4-C$_4$H$_4$S-2-H)(η^6-C$_6$Me$_6$)]$^+$ cation underwent C-S bond cleavage spontaneously (55 °C, $t_{1/2}$ = 2.58 h).[80] The new result described here seem to indicate that the [9]aneS$_3$ ligand is stabilising the η^4-thiopheneyl moiety in a way that other ancillary ligands apparently do not.

3.2.3 [2.2]-PARACYCLOPHANE COMPLEXES.

Generally *bis*-arene complexes of ruthenium(II) of the type $[Ru(\eta^6\text{-}C_6R_6)(\eta^6\text{-}C_6R'_6)]^{2+}$ have been shown to undergo both single and double nucleophilic addition reactions, the latter yielding neutral *bis*(cyclohexadienyl) derivatives.[142,148] However upon incorporating the [2.2]-*para*cyclophane arene ligand into mixed sandwich complexes of this general type a different mode of reactivity is observed.[148-149] The [2.2]-*para*cyclophane ligand can be described as being a comparatively inert spectator ligand, the uncoordinated deck shielding the coordinated deck from nucleophilic attack. This deactivated ligand thus directs the site of nucleophilic attack onto the other less hindered arene, resulting in the isolation of diene complexes.[148-149] These diene compounds can then be protonated to give agostic complexes that can then be subsequently deprotonated to yield new dienes.[148]

With this background in mind it is interesting to investigate whether analogous behaviour could be observed with thiophene complexes. To this end $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}para\text{cyclophane})][CF_3SO_3]_2$ **93** was prepared by the straightforward reaction of $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2]_n$ **49** with [2.2]-*para*cyclophane in a dichloromethane solution from which the desired complex can be isolated on work-up. The ^{1}H-NMR spectrum of this complex is straightfoward to assign, showing two sets of ligand resonances that integrate in a 1:1 ratio. The tetramethylthiophene ligand appears as two singlet resonances at δ 2.43 and 2.44 ppm, with the remaining resonances in the ^{1}H-NMR spectrum being due to the cyclophane ligand. The AA'XX' pattern, at δ 3.29 and 3.38 ppm, is assigned to the protons of the methylene bridges; the signal due to the coordinated arene protons is at δ 6.35 ppm, whereas the

uncoordinated arene protons appear at δ 7.02 ppm (*cf.* δ 6.49 ppm for the free ligand). The positive ion electrospray mass spectrum shows fragmentation envelopes consistent with the loss of triflate counterions, and the infrared spectrum containing a strong ν(SO) band at 1266 cm^{-1}, which provides strong evidence of the presence of the triflate counterions. However since the triflate salt is somewhat hydroscopic, no consistent microanalytical data were obtained for this material. Nevertheless this material was used to generate new compounds, by reactions with nucleophiles which have been fully characterised both spectroscopically and by elemental analysis.

In modelling the reaction of η^5-absorbed thiophenes with hydride bound to the surface of HDS catalyst, it is clearly important to examine the reactions of the $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]^{2+}$ cation with a number of hydride sources. Although a number of reactions were attempted using tetrahydrofuran as a solvent, no tractable materials were ever isolated. Similarly, attempts were made to synthesise products which had undergone double nucleophilic addition, but these products were never observed even under the most forcing of conditions.

In contrast to the above the addition of an excess of KCN to a methanolic suspension of $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]_2$ **93** instantly results in the formation of a pale yellow solution, which after work-up and recrystallisation from chloroform/hexane gives a pale lemon yellow solid. The infrared spectrum of this material did not exhibit any ν(CN) bands but did show that a triflate counterion was still present. The key characterisation of this complex comes from the ^{1}H-NMR spectrum (Figure 3.5), which clearly

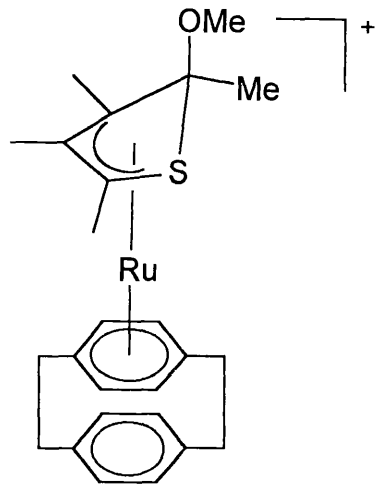
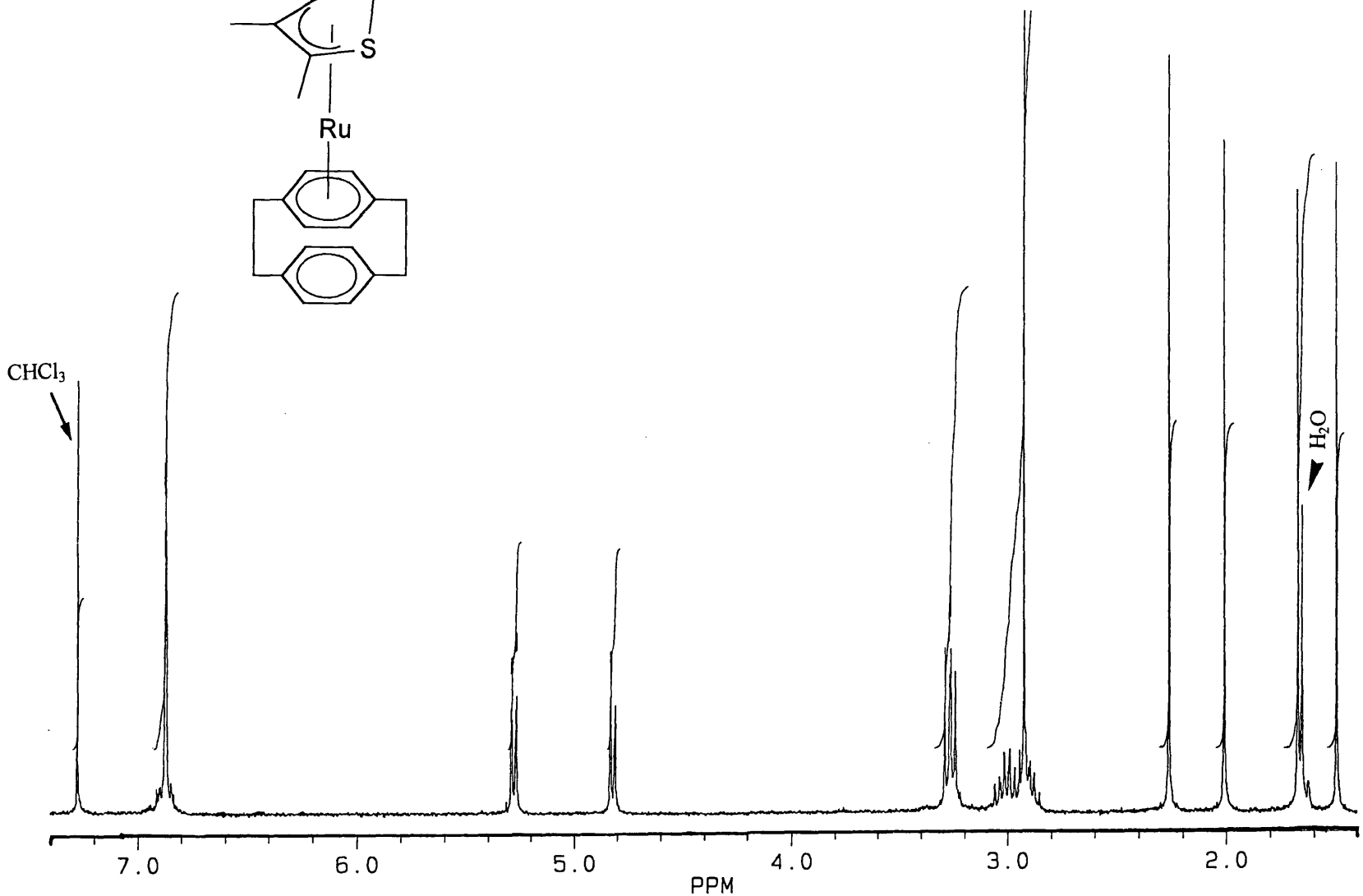


Figure 3.5:
^{1}H-NMR spectrum of [Ru(η^4-C_4Me_4S-OMe)(η^6-[2.2]-paracyclophane)][CF_3SO_3] 94, recorded in a $CDCl_3$ solution.



demonstrates that the product obtained is that of OMe^- attack and not that of CN^- attack! The addition of a methoxy functionality is clearly indicated by the singlet in the ^{1}H-NMR spectrum at δ 2.92 ppm, with the remaining signals for the tetramethylthiophene derivative appearing as four singlet resonances at δ 1.49, 1.67, 2.00 and 2.25 ppm. Once again the consequences of having formed a chiral ligand are particularly felt by the ancillary ligand. The arene rings of the [2.2]-*para*cyclophane now appear consistent with an AA'BB' spin system. The AA'BB' signals centred at δ 6.87 and 6.86 ppm are associated with the uncoordinated arene, whereas the proton resonances of the coordinated arene are more widely spaced and found at δ 4.70 and 5.13 ppm. The protons of the methylene bridges of the cyclophane ligand now form an AA'XX' spin system, resulting in the observation of two multiplet resonances centred at δ 2.93 and 3.25 ppm. These data provide strong evidence pointing to the fact that the compound formed is [Ru(η^4-C_4Me_4S-2-OMe)(η^6-[2.2]-*para*cyclophane)] [CF_3SO_3] **94**. Despite problems with the characterisation of **93** the microanalytical and mass spectral data for **94** are entirely consistent with the proposed formulation (see Experimental).

Interestingly, when the reactions of **93** with the nucleophilic reagents KOH and $NaBH_4$ were studied in methanol an identical compound to that described above, namely [Ru(η^4-C_4Me_4S-2-OMe)(η^6-[2.2]-*para*cyclophane)] [CF_3SO_3] **94**, was formed. Several control reactions were carried out in an attempt to clarify the route by which this compound was formed:

1) A methanolic suspension of [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)] [CF_3SO_3]$_2$ **93** was stirred for 16 h in the absence of any additional nucleophilic reagents. No reaction was observed and only the starting

material was recovered. The inference of this observation is that the methanol (or any contaminant in the methanol) is not reacting directly with the $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]^+$ cation.

2) When the reaction of KCN and $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]_2$ **93** is executed in an aqueous medium then the desired complex $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}CN)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$ **95** is isolated after work-up.

3) The reaction of KCN and $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]_2$ **93** in ethanol results in the isolation of a mixture of two products, $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}CN)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$ **95** and $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$ **96** in an approximate 1:4 ratio (determined by ^{1}H-NMR spectroscopy).

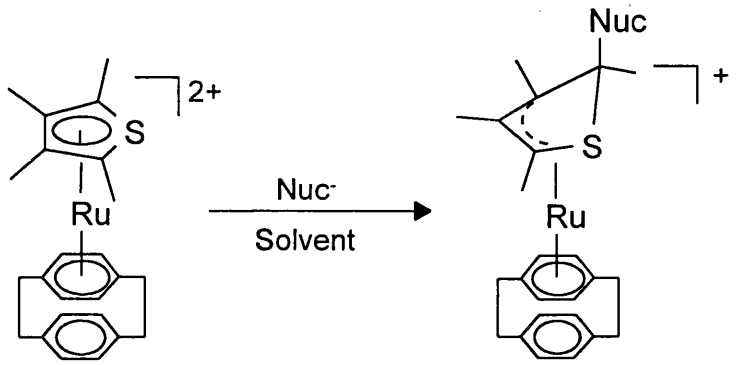
4) When compound **95** was stirred in either pure methanol or in a methanolic solution containing Na[OMe], only the starting materials were recovered. This demonstrates that $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}CN)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]^+$ cation is not an intermediate in the formation of the methoxy product.

5) The hexafluorophosphate salt of the $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]^{2+}$ cation was prepared and reacted with KCN in methanol. Only the methoxy-containing product was isolated on work-up. This observation seems to indicate that the mechanism for this reaction does not involve the counteranion.

The only explanation that can be offered for the above observations is that when a nucleophile such as CN^-, OH^-, H^- is introduced into a methanolic solution, an equilibrium is set up leading to the formation of a small quantity of OMe^- ion. The kinetics which control nucleophilic attack on the $[Ru(\eta^5\text{-}$

$C_4Me_4S)(\eta^6$-[2.2]-*para*cyclophane)]$^{2+}$ cation then come into play. The methoxide ion present in solution must react far more rapidly than the nucleophile initially intended for reaction with the [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)]$^{2+}$ cation, such that the methoxide anion scavenges all the available ruthenium complex, thereby resulting in the isolation of [Ru(η^4-C_4Me_4S-2-OMe)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3] **94** only. What remains unclear is why the kinetics of this reaction favour the formation of **94**. It is clear that the [2.2]-paracyclophane ligand must play a fundamental role in this, since a number of analogous compounds (*i.e.* the [9]aneS_3 and HC(Pz)$_3$ complexes) were successfully reacted in methanolic solutions without any obvious complications (*vida supra*).

The rational syntheses of [Ru(η^4-C_4Me_4S-2-Nuc)(η^6-[2.2]-*para*cyclophane)] [CF_3SO_3], (Nuc = OMe **94**, OEt **96**, CN **95**, SEt **97**) complexes were successfully accomplished by using the appropriate alcohol or an aqueous medium (see Figure 3.6 and experimental). The NMR data for all these



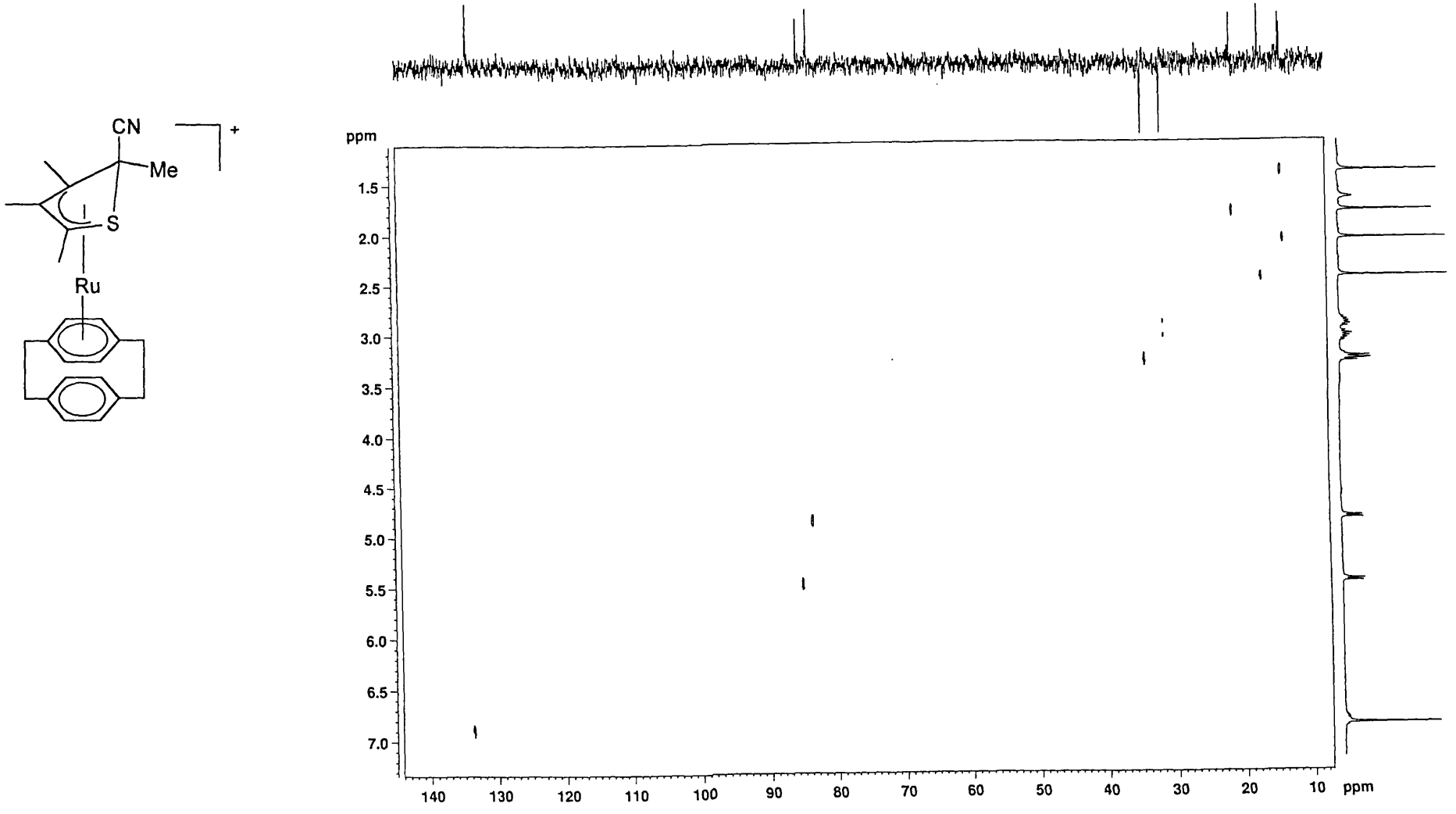
For Nuc⁻ = CN⁻, SEt⁻ ; Solvent = water.
For Nuc⁻= OMe⁻ ; Solvent = methanol.
For Nuc⁻ = OEt⁻ ; Solvent = ethanol.

Figure 3.6: Nucleophilic reactivity of [Ru(η^5-C_4Me_4S)(η^6-[2.2]-paracyclophane)][CF_3SO_3]$_2$ 93.

materials were closely similar; Figure 3.7 illustrates typical NMR data (^{1}H-NMR, DEPT-135, 2D C-H HETCOR spectra) for the [Ru(η^4-C_4Me_4S-2-CN)(η^6-[2.2]-*para*cyclophane)]$^+$ cation.

While the reaction described above are straightforward the situation with regard to attack by hydroxide is more complex. When the compound [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ **93** was placed into an aqueous solution containing an excess of potassium hydroxide. A nucleophilic addition reaction of the type discussed above was not observed; instead base hydrolysis was found to take place. The initial attack of the hydroxide was found to occur at the thiophene sulfur resulting in the formation of [Ru(η^4-C_4Me_4S-1-O)(η^6-[2.2]-*para*cyclophane)] **98**. The infrared spectrum of this material was recorded on a polyethylene film and was found to contain a band at 1024 cm^{-1}, due to the ν(SO) stretch of the newly formed ligand. The symmetric nature of this product was clearly apparent in the ^{1}H-NMR spectrum, with two singlet resonances at δ 1.67 and 1.84 ppm, due to the methyl groups of the new heterocyclic ligand. The signals for the arene protons of the [2.2]-*para*cyclophane are observed as two singlet resonances, at δ 4.44 ppm for the metalled ring and at δ 6.69 ppm for the non-metalled ring, with the protons of the methylene bridges appearing as an AA'XX' pattern at δ 2.76 and 3.15 ppm. The compound [Ru(η^4-C_4Me_4S-1-O)(η^6-[2.2]-*para*cyclophane)] **98** could never be isolated in a pure form, as the sulfoxide complex undergoes isomerisation, *via* C-S bond cleavage, into the acyl-thiolate complex [Ru(σ,η^3-$SC_3Me_3C(O)Me$)(η^6-[2.2]-*para*cyclophane)] **99**. Despite rapid work-up only a

Figure 3.7:
^{1}H, DEPT-135 and 2D C-H correlated NMR spectra for [Ru(η^4-C_4Me_4S-2-CN)(η^6-[2.2]-paracyclophane)][CF_3SO_3] 95, recorded in a $CDCl_3$ solution.



mixture of these two compounds could be isolated. If the base hydrolysis reaction was allowed to continue for 16 hours prior to work-up, then only the acyl-thiolate compound is isolated from the reaction mixture. The ^{1}H-NMR spectrum of this material exhibits four signals at δ 1.44, 1.81, 1.99, 2.33 ppm for the methyl groups of the acyl-thiolate ligand. The resonances of the cyclophane ligand now appear with increased complexity, consistent with the loss of symmetry in the complex as a result of the chemical transformation. In addition the ^{13}C-{^{1}H}-NMR spectrum contains a signal at δ 207.0 ppm associated with the carbonyl functionality, with the ν(CO) stretch being detected in the infrared spectrum at 1652 cm^{-1}.

Rauchfuss and co-workers had previously described base hydrolysis processes on a series of thiophene complexes of the type $[Ru(\eta^5\text{-}C_4R_4S)(\eta^6\text{-}C_6R_6)]^{2+}$.[82] In general these studies showed that sulfoxide complexes rearrange to give an initial kinetic acyl-thiolate product, which then itself isomerised to give the thermodynamic product (the details of this process are summarised in Chapter 1, Section 1.4).[82] The results obtained here with the *para*cyclophane derivative are not directly analogous to those previously observed by Rauchfuss's group, as only one acyl-thiolate product is observed in this study.

3.2.4 SUMMARY

A series of structurally-related compounds of the general formulation $[Ru(\eta^5\text{-}C_4Me_4S)(L_3)]^{2+}$ (L_3 = $HC(Pz)_3$, [9]aneS_3, [2.2]-*para*cyclophane) were reacted with a number of nucleophilic reagents. In general, the nucleophilic addition reactions were found to have the same mode of attack, in that the incoming nucleophile attacks at the carbon of the '2' position of the thiophene ligand,

resulting in the formation of η^4-thiopheneyl complexes. The X-ray crystal structures of $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\kappa^3\text{-}[9]aneS_3)][PF_6]$ **85** and $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)(\kappa^3\text{-}[9]aneS_3)][PF_6]$ **86** definitively established this to be the case, and also clearly demonstrate that the incoming nucleophile has added in an *exo* fashion to the thiophene ligand. Previous studies by Angelici and co-workers on the reaction of thiophene complexes with nucleophiles, showed that only products in which C-S bond cleavage had occurred could be isolated.[68,69,70] Interestingly Angelici postulated that an η^4-thiopheneyl moiety (of the type reported here) was an intermediate in this process but his study never observed such a species.[68]

The reaction of $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]_2$ with hydroxide ion results in the attack occurring at the sulfur, rather than at a carbon atom of the tetramethylthiophene ligand. The complex formed initially subsequently rearranges to an acyl-thiolate derivative. This chemistry closely parallels that observed previously by Rauchfuss for $[Ru(\eta^5\text{-}C_4R_4S)(\eta^6\text{-}C_6R_6)]^{2+}$ complexes[82], however there are some subtle differences in the details of the new results.

3.3 EXPERIMENTAL

3.3.1 INSTRUMENTAL AND MATERIALS

All instrumental methods and starting materials are as described in Chapter 2 (Section 2.3). In addition to this, methanol was dried and distilled from CaH_2,

and Na[SEt] was synthesised by the direct reaction of metallic sodium and ethanethiol.

3.3.2 SYNTHESIS

[Ru(η^4-C_4Me_4S-2-OMe){κ^3-HC(Pz)$_3$}][PF_6] 82.

A fresh solution of Na[OMe] was prepared (0.1 g Na, 25 cm^3 methanol) and was degassed by three repetitions of freeze-pump-thaw cycles. [Ru(η^5-C_4Me_4S){κ^3-HC(Pz)$_3$}][PF_6]$_2$ (0.051 g, 0.07 mmol) was added to the solution and the mixture was stirred for *ca.* 15 min. Water (15 cm^3) was added and the product was isolated by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to 30 cm^3 and dried over potassium carbonate. The clear yellow solution was then filtered through celite and the solvent removed by evaporation. This crude material was recrystallised from chloroform/hexane to produce an air sensitive and unstable pale yellow solid, which was collected by filtration, washed with hexane (25 cm^3) and then dried *in vacuo*. *Yield:* 0.021 g, 0.03 mmol, 49 %. *Anal.*: Found: C, 37.71, H, 4.25, N, 12.95 % (Calc. for $RuC_{19}H_{25}N_6SOPF_6$: C, 36.13, H, 3.99, N, 13.31 %). *^{1}H-NMR* [$CDCl_3$]: 2-methoxy-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.29 (s, 3H, Me), δ 1.91 (s, 3H, Me), δ 2.24 (s, 3H, Me), δ 2.31 (s, 3H, Me), δ 3.21 (s, 3H, OMe) ppm; *tris*(pyrazolyl)methane resonances δ 6.27 (dd, 1H, 4Pz), δ 6.42 (dd, 1H, 4Pz), δ 6.55 (dd, 1H, 4Pz), δ 7.51 (d, 1H, $^3J_{3,4}$ = 2.1 Hz, 3Pz), δ 7.59 (d, 1H, $^3J_{3,4}$ = 2.1 Hz, 3Pz), δ 8.23 (d, 1H, $^3J_{4,5}$ = 2.8, 5Pz), δ 8.34 (d, 1H, $^3J_{4,5}$ = 2.8, 5Pz), δ 8.41 (d, 1H, $^3J_{4,5}$ = 2.8, 5Pz), δ 8.51 (d, 1H, $^3J_{3,4}$ = 2.1 Hz, 3Pz), δ 9.01 (s, 1H, CH) ppm. *Infrared* (KBr): $\nu(PF_6)$, 843(s) cm^{-1}. *Mass spectrum* (FAB): m/z 487 $[M-PF_6]^+$; 453 $[M-PF_6-S]^+$.

[Ru(η^4-C_4Me_4S-2-H){κ^3-HC(Pz)$_3$}][PF_6] 83.

A suspension of [Ru(η^5-C_4Me_4S){κ^3-HC(Pz)$_3$}][PF_6]$_2$ (0.054 g, 0.07 mmol) in methanol (20 cm^3) was treated with an excess of Na[BH_4] (0.1 g). The mixture was stirred for *ca.* 15 min at 25 °C then cooled to *ca.* 0 °C and water (15 cm^3) was added cautiously to quench any of the unreacted borohydride. The product was extracted with CH_2Cl_2 (3 x 30 cm^3); these extracts were combined and the volume reduced to *ca.* 30 cm^3. The solution was dried over potassium carbonate and the clear yellow solution was filtered through celite and the solvent removed by evaporation. The crude material was recrystallised from chloroform/hexane to produce an air sensitive and unstable pale yellow solid. This solid was collected by filtration, washed with hexane (25 cm^3) and dried *in vacuo*. *Yield*: 0.019 g, 0.03 mmol, 44 %. *Anal.*: Found: C, 35.68, H, 3.85, N, 13.36 % (Calc. for $RuC_{18}H_{23}N_6SPF_6$: C, 35.94, H, 3.85, N, 13.97 %). *^{1}H-NMR* [$CDCl_3$]: 2-hydro-2,3,4,5-tetramethylthiopheneyl resonances, δ 0.99 (d, 3H, $^3J_{HH}$ = 6.4 Hz, 2-Me), δ 1.29 (s, 3H, Me), δ 2.36 (s, 3H, Me), δ 2.44 (s, 3H, Me), δ 3.58 (q, 1H, $^3J_{HH}$ = 6 3 Hz, 2-H) ppm; *tris*(pyrazolyl)methane resonances δ 6.23 (dd, 1H, 4Pz), δ 6.37 (dd, 1H, 4Pz), δ 6.59 (dd, 1H, 4Pz), δ 7.44 (d, 1H, $^3J_{3,4}$ = 1.9 Hz, 3Pz), δ 7.46 (d, 1H, $^3J_{3,4}$ = 1.9 Hz, 3Pz), δ 8.22 (d, 1H, $^3J_{4,5}$ = 2.8, 5Pz), δ 8.30 (d, 1H, $^3J_{4,5}$ = 3.0, 5Pz), δ 8.30 (d, 1H, $^3J_{3,4}$ = 1.4 Hz, 3Pz), δ 8.45 (d, 1H, $^3J_{4,5}$ = 2.6, 5Pz), δ 9.03 (s, 1H, CH) ppm. *Infrared* (KBr): ν(PF_6), 842(s) cm^{-1}. *Mass spectrum* (FAB): m/z 457 [M-PF_6]$^+$.

[Ru(η^4-C_4Me_4S-2-OMe)(κ^3-[9]aneS_3)][PF_6] 84.

A fresh solution of Na[OMe] was prepared (0.1 g Na, 25 cm^3 methanol), and was degassed by three repetitions of freeze-pump-thaw cycles. [Ru(η^5-

$C_4Me_4S)(\kappa^3$-[9]ane$S_3)][PF_6]_2$ (0.051 g, 0.07 mmol) was added and the mixture was stirred for 1 h to give an orange-yellow suspension. Water (20 cm^3) was added and the product extracted with CH_2Cl_2 (3 x 20 cm^3). The volume of the combined extracts was reduced to *ca.* 30 cm^3 and washed with 10 cm^3 of H_2O. The CH_2Cl_2 layer was isolated and dried over potassium carbonate. After the drying agent was removed the solution was filtered through celite and the solvent removed by evaporation. The crude material was recrystallised from chloroform/hexane to give a dark yellow solid that was filtered off and dried *in vacuo*. *Yield*: 0.011 g, 0.02 mmol, 26 %. *Anal.*: Found: C, 30.11, H, 4.48 %. (Calc. for $RuC_{15}H_{27}S_4OPF_6$: C, 30.14, H, 4.55 %). *^{1}H-NMR* [$CDCl_3$]: 2-methoxy-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.33 (s, 3H, Me), δ 1.85 (s, 3H, Me), δ 2.08 (s, 3H, Me), δ 2.29 (s, 3H, Me), δ 3.14 (s, 3H, OCH_3) ppm; δ 2.0 - 3.1 ppm a series of broad overlapping multiplets, total intergral 12H, corresponding to the methylene protons of the [9]aneS_3 ligand. *Infrared* (KBr): $\nu(PF_6)$, 839(s) cm^{-1}. *Mass spectrum* (FAB): m/z 567 $[M\text{-}OMe]^+$; 453 $[M\text{-}PF_6]^+$.

[Ru(η^4-C_4Me_4S-2-OEt)(κ^3-[9]aneS_3)][PF_6] 85.

A fresh solution of Na[OEt] was prepared (0.1 g Na, 25 cm^3 absolute ethanol) and this solution was then degassed by three repetitions of freeze-pump-thaw cycles. [Ru(η^5-C_4Me_4S)(κ^3-[9]aneS_3)][PF_6]$_2$ (0.048 g, 0.07 mmol) was added and the mixture was stirred for 1 h to give an orange-yellow suspension. Water (15 cm^3) was added and the product extracted with CH_2Cl_2 (3 x 30 cm^3). The volume of the combined extracts was reduced to *ca.* 30 cm^3 and then dried over potassium carbonate. After removing the drying agent the solution was filtered through celite and the solvent removed by evaporation. This crude material was recrystallised from chloroform/hexane to give a dark orange solid

that was filtered off and dried *in vacuo*. *Yield*: 0.011 g, 0.02 mmol, 27 %. *Anal.*: Found: C, 30.09, H, 4.58 % (Calc. for $RuC_{16}H_{29}S_4OPF_6.H_2O$: C, 30.52, H, 4.96 %). *^{1}H-NMR* [$CDCl_3$]: 2-ethoxy-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.18 (t, 3H, $^3J_{HH}$ = 7.0 Hz, $OCH_2C\underline{H_3}$), δ 1.33 (s, 3H, Me), δ 1.86 (s, 3H, Me), δ 2.06 (s, 3H, Me), δ 2.28 (s, 3H, Me), δ 3.28 (q, 2H, $^3J_{HH}$ = 7.0 Hz, $OC\underline{H_2}CH_3$) ppm; δ 2.0 - 3.1 ppm a series of broad overlapping multiplets, total intergral 12H, corresponding to the methylene protons of the [9]aneS_3 ligand. *^{13}C-{^{1}H}-NMR* [$CDCl_3$]: δ 12.5, 13.7, 15.4, 16.1 (thiopheneyl methyls), δ 23.3 ($OCH_2\underline{C}H_3$), δ 60.8 ($O\underline{C}H_2CH_3$), δ 63.3, 80.4, 98.0, 115.9 (thiopheneyl ring); δ 31.7, 32.7, 33.8, 33.9, 34.4, 36.6 ([9]aneS_3 methylenes). *Infrared* (KBr): ν(PF_6), 841(s) cm^{-1}. *Mass spectrum* (FAB): m/z 467 $[M-PF_6]^+$.

[Ru(η^4-C_4Me_4S-2-H)(κ^3-[9]aneS_3)][PF_6] 86.

A suspension of [Ru(η^5-C_4Me_4S)(κ^3-[9]aneS_3)][PF_6]$_2$ (0.049 g, 0.06 mmol) in methanol (20 cm^3) was treated with an excess of Na[BH_4] (0.1 g). The mixture was stirred for *ca.* 30 min and then cooled to *ca.* 0 °C and water (20 cm^3) was added cautiously to quench any of the unreacted borohydride. The product was extracted with CH_2Cl_2 (3 x 20 cm^3), and the volume of the combined extracts reduced to *ca.* 30 cm^3 before being washed again with 10 cm^3 of H_2O. The CH_2Cl_2 layer was isolated and dried over potassium carbonate. After the drying agent was removed, the solution was filtered through celite and the solvent removed by evaporation. This crude material was recrystallised from chloroform/hexane to give a light orange solid which was isolated by filtration and dried *in vacuo*. *Yield*: 0.022 g, 0.04 mmol, 56 %. *Anal.*: Found: C, 27.50, H, 4.04 % (Calc. for $RuC_{14}H_{23}S_4OPF_6.CH_2Cl_2$: C, 27.61, H, 4.17 %). *^{1}H-NMR* [$CDCl_3$]: 2-hydro-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.15 (s, 3H,

Me), δ 1.63 (d, 3H, $^3J_{HH}$ = 6.6 Hz, 2-Me), δ 2.09 (s, 3H, Me), δ 2.06 (s, 3H, Me), δ 2.44 (s, 3H, Me), δ 4.60 (q, 1H, $^3J_{HH}$ = 6.5 Hz, 2-H) ppm; δ 2.0 - 3.1 ppm a series of broad overlapping multiplets, total intergral 12H, corresponding to the methylene protons of the [9]aneS$_3$ ligand. *^{13}C-{^{1}H}-NMR* [CDCl$_3$]: δ 12.7, 15.3, 15.7, 16.7 (thiopheneyl methyls); δ 55.4, 74.0, 81.8, 97.5, (thiopheneyl ring); δ 31.2, 32.4, 33.1, 33.6, 33.7, 34.4, ([9]aneS$_3$ methylenes) ppm. *Infrared* (KBr): ν(PF$_6$), 838(s) cm^{-1}. *Mass spectrum* (FAB): m/z 423 [M-PF$_6$]$^+$; 395 [M-PF$_6$-CH$_3$CH]$^+$.

[Ru(η^4-C$_4$Me$_4$S-2-CN)(κ^3-[9]aneS$_3$)][PF$_6$] 87.

A suspension of [Ru(η^5-C$_4$Me$_4$S)(κ^3-[9]aneS$_3$)][PF$_6$]$_2$ (0.051 g, 0.07 mmol) in methanol (30 cm^3) was stirred with an excess of KCN (0.1 g) for 2 h. A yellow precipitate formed and was isolated by filtration. The solid was washed with H$_2$O (2 x 30 cm^3), methanol (30 cm^3) and chloroform (30 cm^3) in order to remove any traces of unreacted KCN and organic material. The highly insoluble golden yellow solid was then dried *in vacuo*. *Yield*: 0.016 g, 0.03 mmol, 38 %. *Anal.*: Found: C, 26.28, H, 3.58, N, 1.99 % (Calc. for RuC$_{16}$H$_{25}$S$_4$NPF$_6$.CHCl$_3$: C, 26.99, H, 3.54, N, 1.97 %). *Infrared* (KBr): ν(CN), 2219(w) cm^{-1}, ν(PF$_6$), 838(s) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 448 [M-PF$_6$]$^+$; 416 [M-PF$_6$-S]$^+$; 395 [M-PF$_6$-C(CH$_3$)CN]$^+$.

[Ru(η^5-C$_4$Me$_4$S)(η^6-[2.2]-*para*cyclophane)][CF$_3$SO$_3$]$_2$ 93.

A dichloromethane (20 cm^3) solution of [{Ru(η^5-C$_4$Me$_4$S)Cl(μ-Cl)}$_2$] (0.233 g; 0.37 mmol) was reacted with 4 equivalents of silver trifluoromethanesulfonate (0.388 g; 1.51 mmol) in the dark for 2 h. The resulting suspension was filtered

to remove the precipitated silver chloride and the red filtrate was treated with a slight excess of [2.2]-*para*cyclophane (0.157 g, 0.75 mmol). After stirring for 16 h the solution was concentrated to *ca.* 10 cm^3 and cooled to 0 °C. This resulted in the formation of a yellow precipitate, which was isolated by filtration, washed with cold dichloromethane (10 cm^3) and hexane (10 cm^3), and subsequently dried *in vacuo*. *Yield* 0.363 g, 0.49 mmol, 65 %. *Anal.:* Found C, 40.36, H, 3.63 % (Calc. for $RuC_{26}H_{28}F_6O_6S_3$: C, 41.76, H, 3.78 %). *^{1}H-NMR* [$(CD_3)_2CO$]: tetramethylthiophene resonances, δ 2.43 (s, 6H, CH_3), δ 2.44 (s, 6H, CH_3) ppm; *para*-cyclophane resonance, δ 3.29 and 3.38 (AA'BB', 8H, methylene bridges), δ 6.35 (s, 4H, coordinated deck), δ 7.02 (s, 4H, non-coordinated deck) ppm. *Infrared* (KBr): ν(SO) 1266 cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 599 $[M-CF_3SO_3]^+$; 481 $[M-CF_3SO_3-S]^+$; 450 $[M-2CF_3SO_3]^+$.

[Ru(η^4-C_4Me_4S-2-OMe)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3] 94.

A fresh solution of Na[OMe] was prepared (0.1 g Na, 25 cm^3 methanol) and degassed by three repetitions of freeze-pump-thaw cycles. [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ (0.053 g, 0.07 mmol) was added to the solution and the mixture was stirred for *ca.* 15 min. Water (15 cm^3) was added and the product was isolated by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to *ca.* 30 cm^3 and dried over potassium carbonate. The clear yellow solution was then filtered through celite and the solvent removed by evaporation. This crude material was recrystallised from chloroform/hexane to produce a pale lemon yellow solid, which was collected by filtration, washed with hexane (25 cm^3) and then dried *in vacuo*. *Yield*: 0.030 g, 0.05 mmol, 67 %. *Anal.*: Found: C, 49.28, H, 4.94 %

(Calc. for $RuC_{26}H_{31}S_2O_4F_3$: C, 49.58, H, 4.97 %). *^{1}H-NMR* [$CDCl_3$]: 2-methoxy-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.49 (s, 3H, Me), δ 1.67 (s, 3H, Me), δ 2.00 (s, 3H, Me), δ 2.25 (s, 3H, Me), δ 2.92 (s, 3H, OMe) ppm; [2.2]-*para*cyclophane resonances, δ 2.97 (m, 4H, methylene), δ 3.26 (m, 4H, methylene), δ 4.82, 5.28 (AA'BB', 4H, coordinated arene), δ 6.87, 6.86 (AA'BB', 4H, non-coordinated arene) ppm. *Infrared* (KBr): ν(SO), 1266(s) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 481 $[M-CF_3SO_3]^+$.

[Ru(η^4-C_4Me_4S-2-CN)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3] 95.

A suspension of [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ (0.067 g, 0.09 mmol) in water (10 cm^3) was stirred with an excess of KCN (0.1 g) for 2 h. The resulting yellow/orange mixture was then filtered through celite, which was washed with water (2 x 10 cm^3). The product was isolated from the combined filtrate and washings by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to *ca.* 30 cm^3 and the solution dried over potassium carbonate. The clear yellow solution was then filtered through celite and the solvent removed by evaporation. The crude material was recrystallised from chloroform/hexane to produce a pale yellow solid, which was collected by filtration, washed with hexane (25 cm^3) and dried *in vacuo*. *Yield*: 0.022 g, 0.04 mmol, 41 %. *Anal.*: Found: C, 49.57, H, 4.44, N, 2.04 % (Calc. for $RuC_{26}H_{28}S_2NO_3F_3$: C, 49.98, H, 4.53 N, 2.24 %). *^{1}H-NMR* [$CDCl_3$]: 2-cyano-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.41 (s, 3H, Me), δ 1.80 (s, 3H, Me), δ 2.08 (s, 3H, Me), δ 2.46 (s, 3H, Me) ppm; [2.2]-*para*cyclophane resonances, δ 2.94 (m, 2H, upper deck methylene), δ 3.05 (m, 2H, upper deck methylene), δ 3.28 (m, 4H, lower deck methylene), δ 4.85, 5.48 (AA'BB', 4H,

coordinated arene), δ 6.88, 6.87 (AA'BB', 4H, uncoordinated arene) ppm. *^{13}C-{^{1}H}-NMR* [$CDCl_3$]: δ 13.8, 14.0, 17.0, 21.2 (thiopheneyl methyls); δ 64.7, 71.1, 87.3, 92.4 (thiopheneyl ring); δ 126.7 (-CN); δ 31.5, 34.3 (methylene); δ 83.1, 85.1, 117.7 (coordinated arene); δ 133.6, 133.5, 139.0 (non-coordinated arene) ppm. *Infrared* (KBr): ν(CN), 2222(w) cm^{-1}; ν(SO), 1269(s) cm^{-1}. *Mass spectrum* (FAB): m/z 476 $[M-CF_3SO_3]^+$; 450 $[M-CF_3SO_3-CN]^+$.

[Ru(η^4-C_4Me_4S-2-OEt)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3] 96.

A fresh solution of Na[OEt] was prepared (0.1 g Na, 25 cm^3 ethanol) and degassed by three repetitions of freeze-pump-thaw cycles. [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ (0.052 g, 0.07 mmol) was added to the solution and the mixture was stirred for *ca.* 30 min. Water (10 cm^3) was added and the product was isolated by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to *ca.* 30 cm^3 and dried over potassium carbonate. The clear yellow solution was then filtered through celite and the solvent removed by evaporation. This crude material was then recrystallised from chloroform/hexane to produce a pale yellow solid, which was collected by filtration, washed with hexane (25 cm^3) and then dried *in vacuo*. *Yield*: 0.027 g, 0.04 mmol, 60 %. *Anal.*: Found: C, 50.42, H, 4.42 % (Calc. for $RuC_{27}H_{33}S_2O_4F_3$: C, 50.38, H, 5.17 %). *^{1}H-NMR* [$CDCl_3$]: 2-ethoxy-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.06 (t, 3H, $^3J_{HH}$ = 7.0 Hz, $OCH_2C\underline{H_3}$), δ 1.48 (s, 3H, Me), δ 1.67 (s, 3H, Me), δ 1.99 (s, 3H, Me), δ 2.25 (s, 3H, Me), δ 3.72 (q, 2H, $^3J_{HH}$ = 7.0 Hz, $OC\underline{H_2}CH_3$), ppm; [2.2]-*para*cyclophane resonances, δ 2.97 (m, 4H, methylene), δ 3.26 (m, 4H, methylene), δ 4.80, 5.26 (AA'BB', 4H, coordinated arene), δ 6.87, 6.86 (AA'BB', 4H, non-coordinated

arene) ppm. *Infrared* (KBr): ν(SO), 1266(s) cm^{-1}. *Mass spectrum* (positive ion electrospray): m/z 495 $[M-CF_3SO_3]^+$.

[Ru(η^4-C_4Me_4S-2-SEt)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3] 97.

A suspension of [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ (0.056 g, 0.07 mmol) in water (10 cm^3) was stirred with an excess of NaSEt (0.1 g) 16 h. The yellow/orange mixture was filtered through celite, which was washed with water (2 x 10 cm^3), the washings and the filtrate were combined. The product was isolated from the aqueous solution by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to *ca.* 30 cm^3 and dried over potassium carbonate. The clear yellow solution was filtered through celite and the solvent removed by evaporation. This crude material was recrystallised from chloroform/hexane to produce a pale yellow solid, which was collected by filtration, washed with hexane (25 cm^3) and dried *in vacuo*. *Yield*: 0.029 g, 0.04 mmol, 59 %. *Anal.*: Found: C, 49.13, H, 5.02 % (Calc. for $RuC_{27}H_{33}S_3O_3F_3$: C, 49.15, H, 5.04 %). *^{1}H-NMR* [$CDCl_3$]: 2-ethylthiolate-2,3,4,5-tetramethylthiopheneyl resonances, δ 1.14 (t, 3H, $^3J_{HH}$ = 7.5 Hz, -$SCH_2C\underline{H_3}$), δ 1.42 (s, 3H, Me), δ 1.74 (s, 3H, Me), δ 2.02 (s, 3H, Me), δ 2.46 (s, 3H, Me), δ 2.32 (m , 2H, -$SC\underline{H_2}CH_3$) ppm; [2.2]-*para*cyclophane resonances, δ 2.89 (m, 2H, methylene), δ 3.04 (m, 2H, methylene), δ 3.26 (m, 4H, methylene), δ 4.75, 5.35 (AA'BB', 4H, coordinated arene), δ 6.87, 6.86 (AA'BB', 4H, non-coordinated arene) ppm. *Infrared* (KBr): ν(SO), 1267(s) cm^{-1}. *Mass spectrum* (FAB): m/z 512 $[M-CF_3SO_3]^+$; 451 $[M-CF_3SO_3-SEt]^+$.

[Ru(σ,η^3-$SC_3Me_3C(O)Me$)(η^6-[2.2]-*para*cyclophane)] 99.

A suspension of [Ru(η^5-C_4Me_4S)(η^6-[2.2]-*para*cyclophane)][CF_3SO_3]$_2$ (0.045 g, 0.06 mmol) in water (10 cm^3) was treated with an excess of KOH (0.02 g), which resulted in the immediate formation of a pale yellow solution. After stirring for 16 h a yellow/green mixture was formed and the product isolated by extraction with CH_2Cl_2 (3 x 30 cm^3). The extracts were combined and the volume was reduced to *ca.* 30 cm^3 and dried over potassium carbonate. The clear yellow solution was filtered through celite and the solvent removed by evaporation. The crude material was recrystallised from dichloromethane/hexane to produce an orange/yellow solid, which was collected by filtration and dried *in vacuo*. *Yield*: 0.020 g, 0.04 mmol, 71 %. *Anal.*: Found: C, 61.53, H, 6.09 % (Calc. for $RuC_{24}H_{28}SO$: C, 61.91, H, 6.06 %). *^{1}H-NMR* [$CDCl_3$]: $SC_3Me_3C(O)Me$ resonances, δ 1.44 (s, 3H, Me), δ 1.81 (s, 3H, Me), δ 1.99 (s, 3H, Me), δ 2.33 (s, 3H, Me) ppm; [2.2]-*para*cyclophane resonances, δ 2.83 (m, 4H, methylene bridge), δ 3.17 (m, 4H, methylene bridge), δ 4.25, 4.72 (AA'BB', 4H, coordinated arene), δ 6.75 (s, 4H, uncoordinated arene) ppm. *^{13}C-{^{1}H}-NMR* [$CDCl_3$]: δ 16.5, 22.8, 26.0, 28.3 (acyl-thiolate methyls), δ 74.2, 89.9, 99.2 (acyl-thiolate backbone), δ 207.0 (carbonyl); δ 31.5, 34.4 (methylene); δ 79.8, 83.9, 117.9 (coordinated arene); δ 132.7, 132.8, 139.3 (non-coordinated arene) ppm. *Infrared* (KBr): ν(CO), 1652(s) cm^{-1}. *Mass spectrum* (FAB): m/z 467 $[M+H]^+$; 342 $[M-C_3Me_3C(O)Me]^+$.

3.3.3 X-RAY CRYSTALLOGRAPHIC DATA

Table 3.3:
Crystal data and structure refinement for
[Ru(η^4-C_4Me_4S-2-OEt)([9]aneS_3)][PF_6] 85.

Empirical formula	$C_{16}H_{29}F_6OPRuS_4$
Formula weight	611.67
Temperature	100(2) K
Wavelength	0.71070 Å
Crystal system,	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.2692(2) Å
	b = 17.0596(6) Å
	c = 14.9350(4) Å
	α = 90 °
	β = 104.780(2) °
	γ = 90 °
Volume	2283.51(11) $Å^3$
Z	4
Calculated density	1.779 g cm^{-3}
Absorption coefficient	1.177 mm^{-1}
F(000)	1240
Crystal size	0.20 x 0.20 x 0.15 mm^3
Theta range for data collection	3.35 to 26.00 °
hkl index ranges	-11 → 11, -21 → 21, -18 → 18
Reflections collected	19911
Independent reflections	4421 [R(int) = 0.034]
Completeness to 2 theta = 26 °	95.3%
Absorption correction	Scalepack
Max. and min. transmission	0.8432 and 0.7986
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4421 / 0 / 318
Goodness-of-fit on F^2	1.128
Final R indices [I>2σ(I)]	R1 = 0.0723, wR2 = 0.1597
R indices (all data)	R1 = 0.0754, wR2 = 0.1614
Extinction coefficient	0.0033(6)
Largest diff. peak and hole	4.922 and -2.175 e $Å^{-3}$

Table 3.4:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ru(η^4-C_4Me_4S-2-OEt)([9]aneS_3)][PF_6] 85.

	x	y	z	U(eq)
Ru(1)	5209(1)	2259(1)	3988(1)	23(1)
S(1)	7543(2)	2368(1)	3573(1)	27(1)
S(2)	3070(2)	2595(1)	4373(1)	32(1)
S(3)	4900(2)	1004(1)	4555(1)	22(1)
S(4)	3739(2)	1853(1)	2559(1)	28(1)
P(5)	1182(2)	69(1)	7358(2)	32(1)
F(1)	1727(18)	722(9)	6687(10)	42(4)
F(2)	550(2)	-688(17)	7740(3)	116(12)
F(3)	2780(2)	-326(13)	7628(11)	53(5)
F(4)	-380(3)	458(17)	7150(2)	83(10)
F(5)	1900(2)	750(10)	8145(13)	73(5)
F(6)	590(3)	-589(14)	6680(2)	102(8)
O(1)	9658(6)	2885(3)	5131(4)	33(1)
C(1)	8322(8)	2432(4)	4855(6)	32(2)
C(2)	6980(8)	2781(5)	5111(6)	34(2)
C(3)	6256(8)	3373(4)	4454(5)	29(2)
C(4)	6353(8)	3199(4)	3551(5)	30(2)
C(5)	8780(9)	1613(5)	5235(6)	40(2)
C(6)	6979(11)	2838(5)	6059(8)	56(3)
C(7)	5475(9)	4084(5)	4690(7)	44(2)
C(8)	5977(10)	3724(5)	2735(6)	42(2)
C(9)	9589(8)	3692(4)	4849(6)	34(2)
C(10)	11044(8)	4078(5)	5320(6)	36(2)
C(11)	2831(10)	1846(5)	5201(6)	43(2)
C(12)	3142(9)	1032(5)	4929(6)	36(2)
C(13)	4338(9)	431(4)	3506(5)	32(2)
C(14)	3269(10)	829(5)	2721(5)	38(2)
C(15)	1957(9)	2344(5)	2492(6)	38(2)
C(16)	1515(8)	2349(5)	3383(6)	42(2)
F(1A)	1610(4)	570(2)	6780(3)	170(2)
F(2A)	850(3)	-397(13)	8213(14)	56(6)
F(3A)	2450(5)	-455(19)	7130(4)	131(17)
F(4A)	-170(4)	600(2)	7470(2)	83(11)
F(5A)	2090(3)	260(3)	8262(15)	138(15)
F(6A)	20(3)	-180(3)	6380(2)	104(11)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3.5:
Bond lengths (Å) and angles (°) for [Ru(η^4-C_4Me_4S-2-OEt)([9]aneS$_3$)] 85.

Ru(1)-C(4)	2.117(7)	S(4)-C(14)	1.831(8)
Ru(1)-C(3)	2.167(7)	O(1)-C(1)	1.429(9)
Ru(1)-C(2)	2.212(8)	O(1)-C(9)	1.437(9)
Ru(1)-S(2)	2.2737(19)	C(1)-C(2)	1.513(11)
Ru(1)-S(4)	2.326(2)	C(1)-C(5)	1.527(10)
Ru(1)-S(3)	2.3456(17)	C(2)-C(6)	1.419(13)
Ru(1)-S(1)	2.4046(18)	C(2)-C(3)	1.448(11)
S(1)-C(4)	1.792(8)	C(3)-C(4)	1.406(11)
S(1)-C(1)	1.869(8)	C(3)-C(7)	1.501(11)
S(2)-C(16)	1.831(8)	C(4)-C(8)	1.481(11)
S(2)-C(11)	1.830(9)	C(9)-C(10)	1.504(10)
S(3)-C(13)	1.808(7)	C(11)-C(12)	1.496(12)
S(3)-C(12)	1.853(8)	C(13)-C(14)	1.492(10)
S(4)-C(15)	1.832(8)	C(15)-C(16)	1.490(12)
C(4)-Ru(1)-C(3)	38.3(3)	C(1)-O(1)-C(9)	117.7(5)
C(4)-Ru(1)-C(2)	66.1(3)	O(1)-C(1)-C(2)	114.9(6)
C(3)-Ru(1)-C(2)	38.6(3)	O(1)-C(1)-C(5)	104.5(6)
C(4)-Ru(1)-S(2)	115.1(2)	C(2)-C(1)-C(5)	115.8(7)
C(3)-Ru(1)-S(2)	92.6(2)	O(1)-C(1)-S(1)	114.1(5)
C(2)-Ru(1)-S(2)	103.5(2)	C(2)-C(1)-S(1)	98.8(5)
C(4)-Ru(1)-S(4)	99.5(2)	C(5)-C(1)-S(1)	109.0(6)
C(3)-Ru(1)-S(4)	131.7(2)	C(6)-C(2)-C(3)	120.6(8)
C(2)-Ru(1)-S(4)	164.4(2)	C(6)-C(2)-C(1)	119.2(8)
S(2)-Ru(1)-S(4)	87.83(7)	C(3)-C(2)-C(1)	111.9(7)
C(4)-Ru(1)-S(3)	156.9(2)	C(6)-C(2)-Ru(1)	126.5(6)
C(3)-Ru(1)-S(3)	140.4(2)	C(3)-C(2)-Ru(1)	69.0(4)
C(2)-Ru(1)-S(3)	103.3(2)	C(1)-C(2)-Ru(1)	98.6(5)
S(2)-Ru(1)-S(3)	86.82(7)	C(4)-C(3)-C(2)	111.8(7)
S(4)-Ru(1)-S(3)	87.88(6)	C(4)-C(3)-C(7)	123.2(7)
C(4)-Ru(1)-S(1)	46.2(2)	C(2)-C(3)-C(7)	125.0(7)
C(3)-Ru(1)-S(1)	69.9(2)	C(4)-C(3)-Ru(1)	68.9(4)
C(2)-Ru(1)-S(1)	67.8(2)	C(2)-C(3)-Ru(1)	72.4(4)
S(2)-Ru(1)-S(1)	160.94(7)	C(7)-C(3)-Ru(1)	125.6(5)
S(4)-Ru(1)-S(1)	98.12(7)	C(3)-C(4)-C(8)	127.1(7)
S(3)-Ru(1)-S(1)	111.37(6)	C(3)-C(4)-S(1)	109.8(5)
C(4)-S(1)-C(1)	92.7(3)	C(8)-C(4)-S(1)	120.6(6)
C(4)-S(1)-Ru(1)	58.4(2)	C(3)-C(4)-Ru(1)	72.8(4)
C(1)-S(1)-Ru(1)	83.0(2)	C(8)-C(4)-Ru(1)	132.9(6)
C(16)-S(2)-C(11)	100.3(4)	S(1)-C(4)-Ru(1)	75.4(3)
C(16)-S(2)-Ru(1)	107.2(3)	O(1)-C(9)-C(10)	108.4(6)
C(11)-S(2)-Ru(1)	105.0(3)	C(12)-C(11)-S(2)	113.5(6)
C(13)-S(3)-C(12)	101.2(4)	C(11)-C(12)-S(3)	110.5(6)
C(13)-S(3)-Ru(1)	102.4(2)	C(14)-C(13)-S(3)	114.9(5)
C(12)-S(3)-Ru(1)	106.5(3)	C(13)-C(14)-S(4)	113.9(6)
C(15)-S(4)-C(14)	101.6(4)	C(16)-C(15)-S(4)	113.8(5)
C(15)-S(4)-Ru(1)	102.9(3)	C(15)-C(16)-S(2)	112.5(6)
C(14)-S(4)-Ru(1)	105.4(3)		

Table 3.6:
Crystal data and structure refinement for
[Ru(η^4-C_4Me_4S-2-H)([9]aneS_3)][PF_6] 86.

Empirical formula	$C_{14}H_{25}F_6PRuS_4$
Formula weight	567.62
Temperature	100(2) K
Wavelength	0.71070 Å
Crystal system	Orthorhombic
Space group	Pcab
Unit cell dimensions	a = 15.1549(7) Å
	b = 16.3035(7) Å
	c = 16.7695(6) Å
	α = 90 °
	β = 90 °
	γ = 90 °
Volume	4143.4(3) $Å^3$
Z	8
Density (calculated)	1.820 g cm^{-3}
Absorption coefficient	1.287 mm^{-1}
F(000)	2288
Crystal size	0.30 x 0.30 x 0.05 mm^3
Theta range for data collection	3.67 to 26.00°
hkl index ranges	-18 → 18, -20 → 20, -20 → 20
Reflections collected	7677
Independent reflections	4059 [R(int) = 0.0428]
Completeness to theta = 26 °	99.7 %
Max. and min. transmission	0.9385 and 0.6988
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4059 / 0 / 240
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R1 = 0.0354, wR2 = 0.0724
R indices (all data)	R1 = 0.0526, wR2 = 0.0777
Extinction coefficient	0.00072(9)
Largest diff. peak and hole	0.605 and -0.567 e $Å^{-3}$

Table 3.7:

Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ru(η^4-C_4Me_4S-2-H)([9]aneS$_3$][PF$_6$] 86.

	x	y	z	U(eq)
Ru(1)	2411(1)	626(1)	804(1)	16(1)
S(1)	3009(1)	539(1)	-514(1)	23(1)
S(2)	2291(1)	2054(1)	910(1)	20(1)
S(3)	859(1)	572(1)	764(1)	19(1)
S(4)	2303(1)	567(1)	2161(1)	18(1)
P(6)	-107(1)	-1981(1)	1878(1)	21(1)
F(1)	-350(1)	-2690(1)	2510(1)	30(1)
F(2)	141(1)	-1267(1)	1261(1)	28(1)
F(3)	813(1)	-1830(1)	2340(1)	31(1)
F(4)	-1021(1)	-2134(1)	1429(1)	31(1)
F(5)	-574(1)	-1318(1)	2445(1)	30(1)
F(6)	366(2)	-2643(1)	1321(1)	39(1)
C(1)	2712(2)	-558(2)	-444(2)	23(1)
C(2)	2764(2)	-642(2)	463(2)	20(1)
C(3)	3518(2)	-221(2)	775(2)	19(1)
C(4)	3710(2)	513(2)	347(2)	21(1)
C(5)	1824(2)	-714(2)	-831(2)	28(1)
C(6)	2407(2)	-1420(2)	828(2)	25(1)
C(7)	4042(2)	-485(2)	1496(2)	24(1)
C(8)	4496(2)	1065(2)	423(2)	27(1)
C(9)	1099(2)	2279(2)	912(2)	24(1)
C(10)	571(2)	1617(2)	486(2)	23(1)
C(11)	491(2)	548(2)	1812(2)	21(1)
C(12)	1190(2)	172(2)	2349(2)	20(1)
C(13)	2166(2)	1633(2)	2522(2)	21(1)
C(14)	2567(2)	2246(2)	1951(2)	23(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3.8:
Bond lengths (Å) and angles (°) for [Ru(η^4-C_4Me_4S-2-H)([9]aneS_3][PF_6] 86.

Ru(1)-C(4)	2.119(3)	P(6)-F(6)	1.597(2)
Ru(1)-C(3)	2.173(3)	P(6)-F(2)	1.601(2)
Ru(1)-C(2)	2.209(3)	P(6)-F(5)	1.603(2)
Ru(1)-S(4)	2.2846(9)	P(6)-F(1)	1.612(2)
Ru(1)-S(2)	2.3428(9)	P(6)-F(3)	1.614(2)
Ru(1)-S(3)	2.3544(9)	C(1)-C(5)	1.515(5)
Ru(1)-S(1)	2.3914(9)	C(1)-C(2)	1.528(5)
S(1)-C(4)	1.793(4)	C(2)-C(3)	1.432(5)
S(1)-C(1)	1.848(4)	C(2)-C(6)	1.509(5)
S(2)-C(14)	1.822(4)	C(3)-C(4)	1.424(5)
S(2)-C(9)	1.844(4)	C(3)-C(7)	1.509(5)
S(3)-C(10)	1.820(4)	C(4)-C(8)	1.498(5)
S(3)-C(11)	1.844(3)	C(9)-C(10)	1.521(5)
S(4)-C(12)	1.832(3)	C(11)-C(12)	1.520(5)
S(4)-C(13)	1.852(3)	C(13)-C(14)	1.513(5)
P(6)-F(4)	1.596(2)		
C(4)-Ru(1)-C(3)	38.74(13)	C(13)-S(4)-Ru(1)	107.11(11)
C(4)-Ru(1)-C(2)	66.48(13)	F(4)-P(6)-F(6)	90.45(13)
C(3)-Ru(1)-C(2)	38.14(12)	F(4)-P(6)-F(2)	90.78(12)
C(4)-Ru(1)-S(4)	115.03(10)	F(6)-P(6)-F(2)	90.47(13)
C(3)-Ru(1)-S(4)	92.94(9)	F(4)-P(6)-F(5)	90.16(12)
C(2)-Ru(1)-S(4)	103.64(9)	F(6)-P(6)-F(5)	179.30(15)
C(4)-Ru(1)-S(2)	100.71(10)	F(2)-P(6)-F(5)	89.87(12)
C(3)-Ru(1)-S(2)	133.89(10)	F(4)-P(6)-F(1)	89.93(12)
C(2)-Ru(1)-S(2)	165.49(9)	F(6)-P(6)-F(1)	90.08(13)
S(4)-Ru(1)-S(2)	87.74(3)	F(2)-P(6)-F(1)	179.10(13)
C(4)-Ru(1)-S(3)	156.08(10)	F(5)-P(6)-F(1)	89.57(12)
C(3)-Ru(1)-S(3)	138.33(10)	F(4)-P(6)-F(3)	179.36(14)
C(2)-Ru(1)-S(3)	101.51(9)	F(6)-P(6)-F(3)	89.77(13)
S(4)-Ru(1)-S(3)	87.39(3)	F(2)-P(6)-F(3)	89.82(12)
S(2)-Ru(1)-S(3)	87.78(3)	F(5)-P(6)-F(3)	89.62(12)
C(4)-Ru(1)-S(1)	46.37(9)	F(1)-P(6)-F(3)	89.47(12)
C(3)-Ru(1)-S(1)	69.50(9)	C(5)-C(1)-C(2)	117.2(3)
C(2)-Ru(1)-S(1)	67.33(9)	C(5)-C(1)-S(1)	110.6(3)
S(4)-Ru(1)-S(1)	160.97(3)	C(2)-C(1)-S(1)	97.9(2)
S(2)-Ru(1)-S(1)	99.09(3)	C(3)-C(2)-C(6)	122.7(3)
S(3)-Ru(1)-S(1)	110.48(3)	C(3)-C(2)-C(1)	111.2(3)
C(4)-S(1)-C(1)	93.99(17)	C(6)-C(2)-C(1)	117.4(3)
C(4)-S(1)-Ru(1)	58.80(11)	C(3)-C(2)-Ru(1)	69.54(19)
C(1)-S(1)-Ru(1)	84.60(12)	C(6)-C(2)-Ru(1)	126.5(2)
C(14)-S(2)-C(9)	100.85(17)	C(1)-C(2)-Ru(1)	99.2(2)
C(14)-S(2)-Ru(1)	103.05(12)	C(4)-C(3)-C(2)	112.4(3)
C(9)-S(2)-Ru(1)	105.92(12)	C(4)-C(3)-C(7)	122.3(3)
C(10)-S(3)-C(11)	101.00(17)	C(2)-C(3)-C(7)	125.2(3)
C(10)-S(3)-Ru(1)	102.28(12)	C(4)-C(3)-Ru(1)	68.61(19)
C(11)-S(3)-Ru(1)	106.07(11)	C(2)-C(3)-Ru(1)	72.32(19)
C(12)-S(4)-C(13)	99.79(16)	C(7)-C(3)-Ru(1)	124.7(2)
C(12)-S(4)-Ru(1)	104.61(11)	C(3)-C(4)-C(8)	128.6(3)

C(3)-C(4)-S(1)	107.7(2)	C(9)-C(10)-S(3)	114.7(2)
C(8)-C(4)-S(1)	121.6(3)	C(12)-C(11)-S(3)	111.2(2)
C(3)-C(4)-Ru(1)	72.66(19)	C(11)-C(12)-S(4)	113.5(2)
C(8)-C(4)-Ru(1)	130.9(3)	C(14)-C(13)-S(4)	111.6(2)
S(1)-C(4)-Ru(1)	74.83(13)	C(13)-C(14)-S(2)	113.7(2)
C(10)-C(9)-S(2)	111.9(2)		

CHAPTER 4

SYNTHESIS, STRUCTURE AND REACTIVITY OF OSMIUM-THIOPHENE COMPLEXES.

4.1 INTRODUCTION

In contrast to the chemistry of ruthenium-thiophene complexes the chemistry associated with osmium-thiophene moieties (excluding that of cluster compounds) remains largely unexplored. The literature relating to these osmium-thiophene compounds and their reactivity has been summarised in Chapter 1 (Section 1.5). In order to partially redress this imbalance and to deepen the knowledge in this field several sandwich compounds of the type $[Os(\eta^5\text{-Th})(\eta^6\text{-}p\text{-cymene})]^{2+}$ (Th = C_4H_4S **100**, 2,5-$Me_2C_4H_2S$ **101**, C_4Me_4S **102**) have been prepared, one of which has been characterised crystallographically. The reactions of these compounds with nucleophiles was examined as were base hydrolysis reactions.

4.2 RESULTS AND DISCUSSION

4.2.1 SYNTHESIS AND CHARACTERISATION OF OSMIUM THIOPHENE COMPLEXES

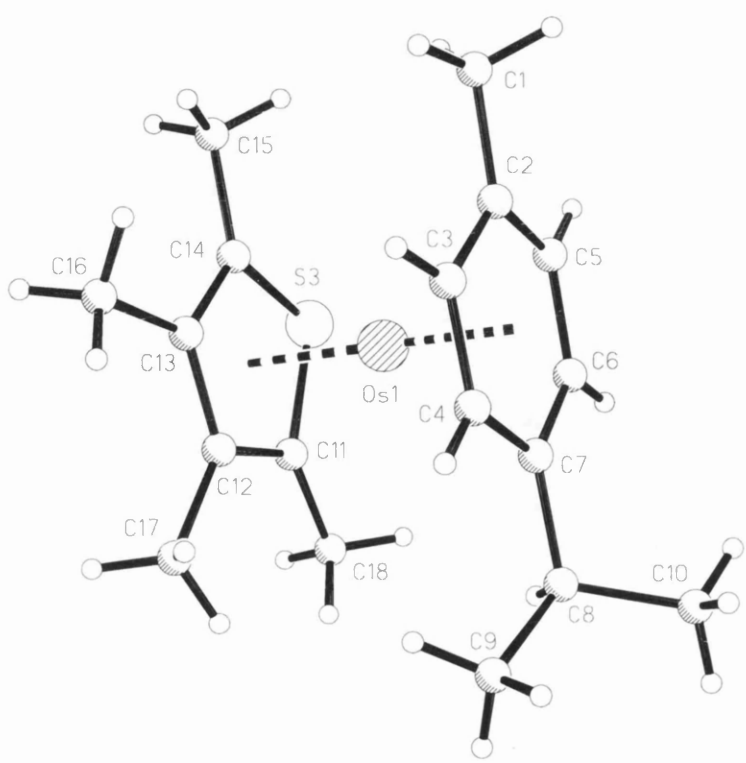
The reaction of $[\{Os(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$ **103** with silver triflate in dichloromethane proceeds smoothly to give a yellow solution of $[Os(\eta^6\text{-}p\text{-cymene})(CF_3SO_3)_2]_n$ **104**. Addition of a slight excess of a thiophene (thiophene, 2,5-dimethylthiophene, 2,3,4,5-tetramethylthiophene) followed by stirring for *ca.* 16 hours gives, after work-up, good yields (65-85%) of the cationic complexes $[Os(\eta^5\text{-Th})(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ (Th = C_4H_4S **100**, 2,5-$Me_2C_4H_2S$ **101**, C_4Me_4S **102**). Some of these triflate salts are moderately hydroscopic and thus it is advantageous to carry out anion metathesis of the triflate counterion for hexafluorophosphate, which yields materials that are

better suited to storage and handling. Microanalytical data for these complexes are wholly consistent with the proposed formulations, confirming the dicationic nature of these complexes, and the counterions give rise to characteristic infrared bands (see Experimental). The ^{1}H-NMR spectra of the three complexes are all easy to interpret, each showing two sets of ligand resonances for the p-cymene and thiophene ligands, integrating in a 1:1 ratio. The compound $[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ **102** was readily crystallised from an acetone/hexane solvent system and was conclusively identified by a single crystal structure determination (Figure 4.1 and Table 4.1). The sandwich structure is confirmed by the X-ray diffraction study and the two aromatic rings are essentially parallel and planar, with the angle formed at the metal by the centroids of the two rings being 176.9 °. Interestingly, the deviation of the sulfur atom from the [C(11)C(12)C(13)C(14)] plane is only 0.07 Å, which is much less than that observed in the Ru(II) compounds described in Chapters 2 and 3. Substituents on both the arene and thiophene ligands are displaced somewhat from the metal, with deviations in the range 0.9 - 5.6 °. The aromatic C-C bond lengths in the thiophene are indistinguishable from each other, but there is some evidence of bond length alternation in the arene ligand. While the Os-C bonds distance for the thiophene ligand span a small range 2.22 - 2.27 Å, the range observed for the arene ligand is greater, 2.21 - 2.28 Å. The Os-S distance, 2.347(2) Å, is significantly shorter than that found for several ruthenium compounds which contain η^5-bonded tetramethylthiophene, *e.g.* 2.442(1) Å in $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$ **61** and 2.414(4) - 2.432(4) Å in $[\{Ru(\eta^5\text{-}C_4Me_4S)(\mu\text{-}Cl)\}_3(\mu^3\text{-}S)]$ **45**[75]. However it is

Table 4.1:
Selected Bond lengths (Å) and angles (°) for
[Os(η^5-C_4Me_4S)(η^6-p-cymene)][CF_3SO_3]$_2$ 102.

Bond Lengths			
Os(1)-S(3)	2.347(2)	Os(1)-C(2)	2.290(8)
Os(1)-C(11)	2.224(8)	Os(1)-C(3)	2.220(8)
Os(1)-C(12)	2.271(8)	Os(1)-C(4)	2.253(9)
Os(1)-C(13)	2.272(8)	Os(1)-C(5)	2.213(8)
Os(1)-C(14)	2.232(8)	Os(1)-C(6)	2.224(7)
S(3)-C(11)	1.769(9)	Os(1)-C(7)	2.277(8)
S(3)-C(14)	1.755(8)	C(2)-C(3)	1.436(11)
C(11)-C(12)	1.437(11)	C(3)-C(4)	1.397(13)
C(12)-C(13)	1.443(11)	C(4)-C(7)	1.453(11)
C(13)-C(14)	1.420(11)	C(6)-C(7)	1.424(11)
C(5)-C(6)	1.426(11)	C(2)-C(5)	1.419(11)
Bond Angles			
C(11)-S(3)-C(14)	92.3(4)	C(2)-C(3)-C(4)	121.2(7)
S(3)-C(11)-C(12)	110.3(6)	C(3)-C(4)-C(7)	121.5(8)
C(11)-C(12)-C(13)	113.2(7)	C(4)-C(7)-C(6)	117.3(7)
C(12)-C(13)-C(14)	112.0(7)	C(5)-C(6)-C(7)	120.1(7)
S(3)-C(14)-C(13)	112.1(6)	C(2)-C(5)-C(6)	122.5(7)
C(3)-C(2)-C(5)	116.9(7)		

Figure 4.1:
The crystal structure of the cation in [Os(η^5-C_4Me_4S)(η^6-p-cymene)] [CF_3SO_3]$_2$ 102, showing the atom labelling scheme.



essentially indistinguishable from the Ru-S distance in the symmetrical sandwich compound $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46**, av. 2.355(2) Å.[75]

Rauchfuss had previously shown that the compounds $[Ru(\eta^5\text{-}Th)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2$ (Th = 2,5-$Me_2C_4H_2S$, C_4Me_4S) can be reduced either chemically, using cobaltocene, or electrochemically to the Ru(0) derivatives, resulting in the formation of $[Ru(\eta^4\text{-}Th)(\eta^6\text{-}C_6Me_6)]$ compounds.[79] The electrochemical process takes place in two clearly defined quasi-reversible one-electron steps, separated by *ca.* 160 mV.[79] The electrochemical response of the new osmium complexes were examined by cyclic voltammetry at scan rates in the range 10 - 200 mV s^{-1} over the temperature range -40 to 30 °C, using acetonitrile as solvent and tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. Both the $[Os(\eta^5\text{-}C_4H_4S)(\eta^6\text{-}p\text{-cymene})]^{2+}$ and $[Os(\eta^5\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^6\text{-}p\text{-cymene})]^{2+}$ cations exhibit single irreversible reduction processes under these experimental conditions, at potentials of -0.20 and -0.31 volts respectively. In contrast the $[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})]^{2+}$ cation exhibits a quasi-reversible peak at -0.37 volts. The reversibility of this process increases with increasing scan rate, however even at 200 mV s^{-1} the ratio of peak currents is only 0.52 (Figure 4.2). In contrast to the results reported earlier on $[Ru(\eta^5\text{-}C_4H_4S)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2$ **105**[79] and $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$ **46**[78], two separate one-electron reduction processes are never resolved. It is also interesting to note that the reductions of the $[Os(\eta^5\text{-}Th)(\eta^6\text{-}p\text{-cymene})]^{2+}$ cations occur much more readily than that observed for the structurally related $[Os(\eta^5\text{-}C_4Me_4N)(\eta^6\text{-}p\text{-cymene})]^{+}$ cation, -2.3 V.[150]

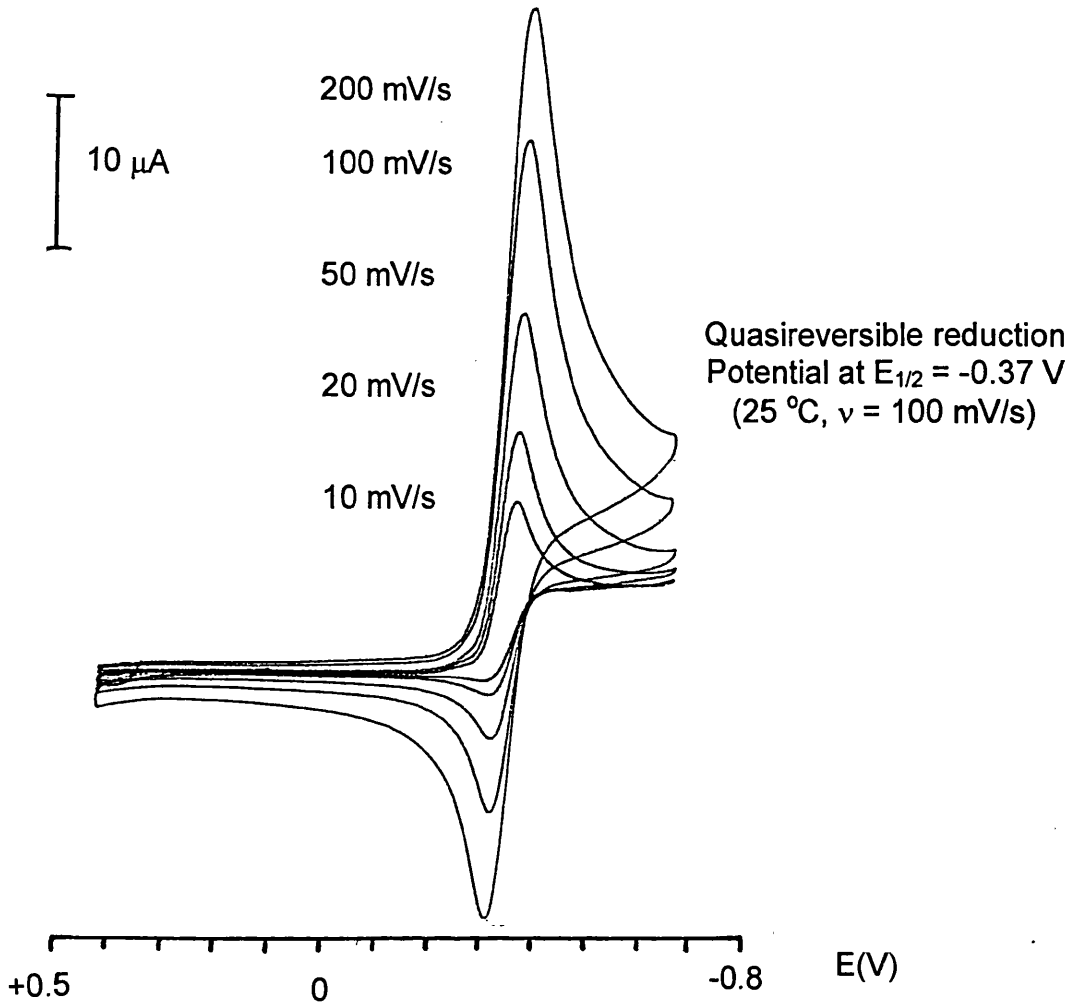


Figure 4.2: The cyclic voltammogram of [Os(η^5-C_4Me_4S)(η^6-p-cymene)][CF_3SO_3]$_2$ 102, (suppporting electrolyte, 0.2 M [Bu_4N][PF_6] in acetonitrile).

4.2.2 THE REACTIONS OF THE [OS(η^5-TH)(η^6-P-CYMENE)]$^{2+}$ CATIONS

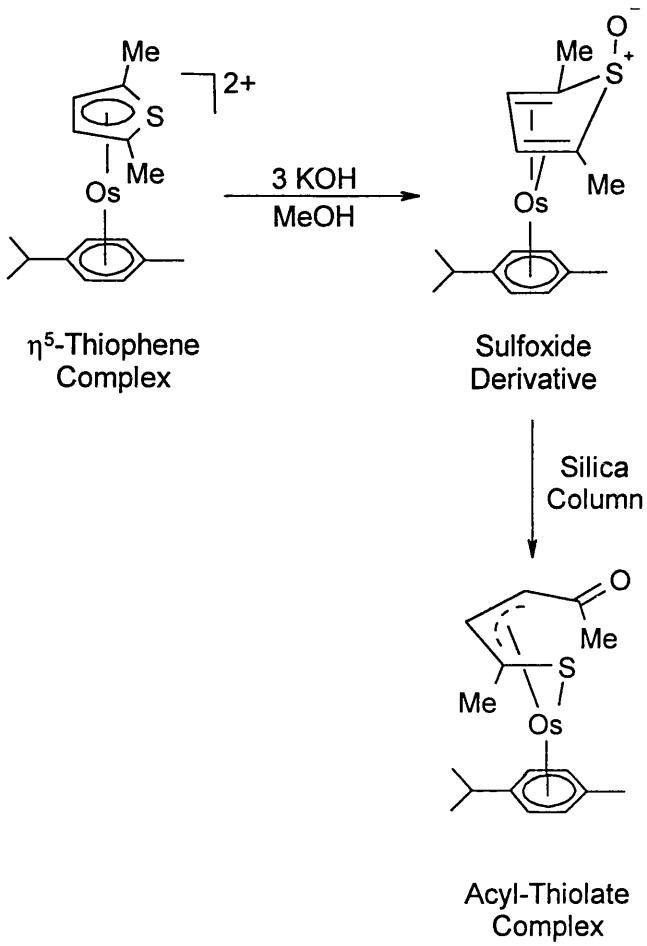
The chemical reduction of [Os(η^5-C_4Me_4S)(η^6-*p*-cymene)][CF_3SO_3]$_2$ **102** was attempted by the reaction of this complex with 2 equivalents of [Co(Cp)$_2$] in THF at –78 °C. However the reaction proved unsuccessful, as the product which was isolated by extraction into ether was too unstable to allow full and conclusive characterisation. Nevertheless the ^{1}H-NMR data obtained for this extract appear to show that the thiophene has been reduced in preference to the arene ligand, presumably forming [Os(η^4-C_4Me_4S)(η^6-*p*-cymene)] **106**.

Though attempts were made to stabilise this species by low temperature *in situ* reaction with $[Fe(CO)_5]$ and Me_3NO, no tractable materials were ever obtained.

The reaction of $[Os(\eta^5\text{-Th})(\eta^6\text{-}p\text{-cymene})]^{2+}$ cations with a number of nucleophiles (H^-, MeO^-, CN^-) in a range of solvents (tetrahydrofuran, methanol and ethanol) generally gave yellow-brown solids on work-up. ^{1}H-NMR studies on these materials clearly indicated that nucleophilic addition reactions have occurred, however the data indicates that both rings have been attacked although it appears from the product distribution that the attack generally occurs preferentially at the thiophene ligand. This is indicated by the appearance of thiophene methyl doublets in the compounds derived from the reaction of $[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})]^{2+}$ with hydride ion. Due to the complexity of the mixtures obtained it was not possible to separate and purify the compounds derived from these reactions satisfactorily.

In contrast to the complexity of the reactions described above the reactions of $[Os(\eta^5\text{-Th})(\eta^6\text{-}p\text{-cymene})]^{2+}$ cations with KOH proceed smoothly to give single products. A typical example was the reaction of the $[Os(\eta^5\text{-2,5-}Me_2C_4H_2S)(\eta^6\text{-}p\text{-cymene})]^{2+}$ cation and KOH in methanol, which after work-up gives a yellow oil. The ^{1}H-NMR spectrum of this material exhibits the five easily attributable signals for the *p*-cymene ligand and in addition to these one singlet, at δ 1.82 ppm, for the two equivalent methyl groups of the thiophene derived ligand, and a second singlet, at δ 4.85 ppm, for the protons of the heterocyclic ring. These observations are consistent with the formation of a symmetrical product. The infrared spectrum of this material contains a band at 998 cm^{-1}, due to a ν(S-O) stretch, (similar to that observed for $[Ru(\eta^4\text{-2,5-}Me_2C_4H_2S\text{-1-O})(\eta^6\text{-}p\text{-cymene})]$

107, 1011 cm^{-1})[82] but does not contain any bands due to a counterion. The compound can be extracted into hexane, consistent with it being neutral, and

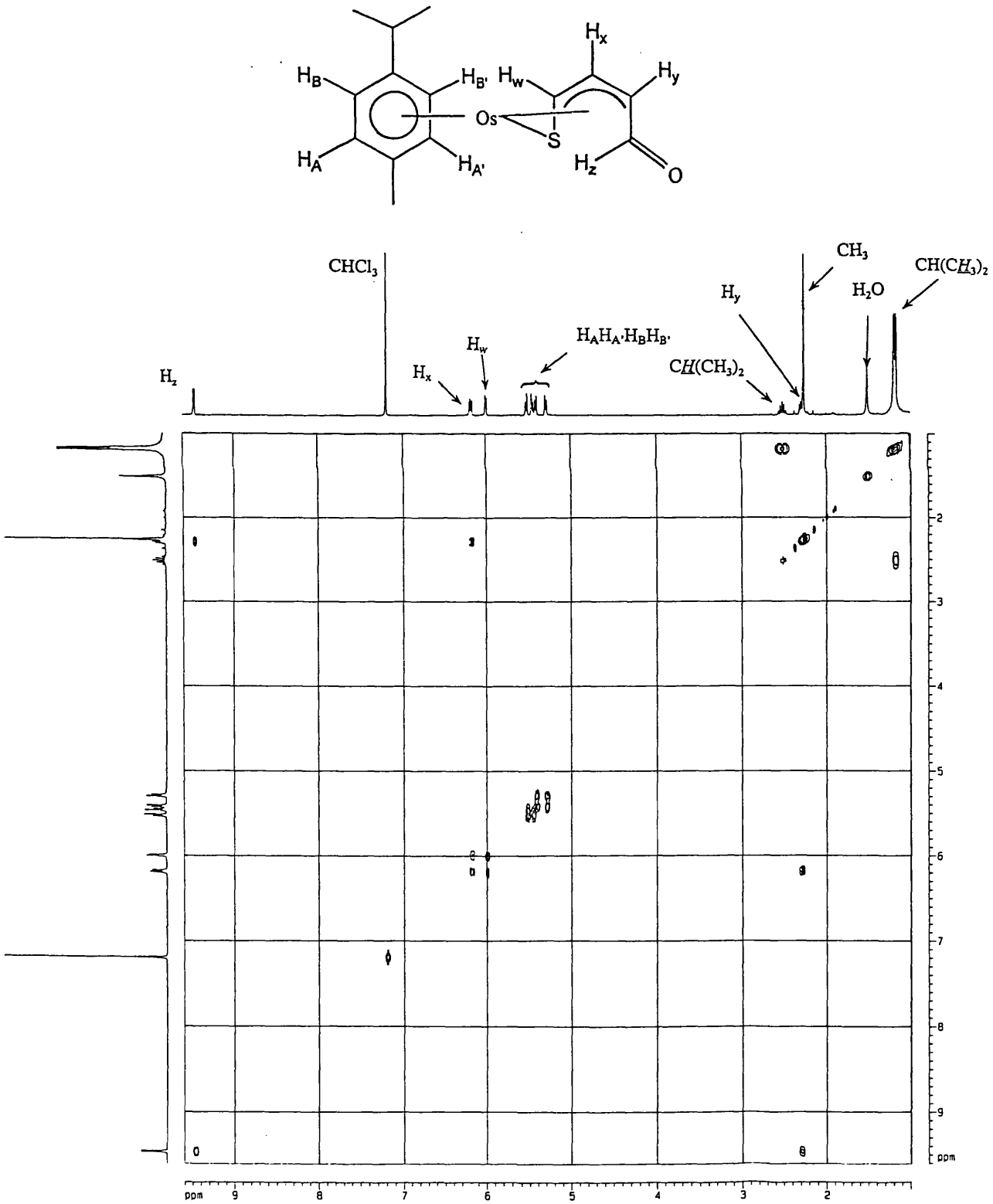


Scheme 4.1: Base Hydrolysis of [Os(η5-Me2C4H2S)(η6-p-cymene)][CF3SO3]2 101.

hence it is deduced that this species is [Os(η^4-2,5-$Me_2C_4H_2S$-1-O)(η^6-*p*-cymene)] **108** (Scheme 4.1) analogous to the observations made in related ruthenium chemistry described previously by Rauchfuss and co-workers.[82] The sample also exhibited a number of signals due to small amounts of impurities and in an attempt to remove these, the sample was chromatographed on a silica column. When the proton spectrum of the chromatographed material was run it was immediately apparent that a chemical transformation had taken place. The signals for the *p*-cymene ligand are now far more complex, the methyls of the isopropyl group are now diastereotropic, appearing as two doublets at δ 1.29 and 1.30 ppm, both these resonances coupling to the septet

at δ 2.57 ppm, and the remaining methyl giving a signal at δ 2.46 ppm. The AA'BB' coupling pattern of the ring protons on the *p*-cymene ligand now appears as two AX patterns (four doublet resonances at δ 5.10, 5.20, 5.35 and 5.45 ppm) as a result of the loss of symmetry. The sulfur-containing ligand exhibits two signals from the methyl groups, at δ 2.09 and 2.23 ppm, with the remaining protons of this ligand resonating at δ 2.23 and 6.09 ppm. In addition, the $^{13}C-\{^1H\}$-NMR spectrum of the chromatographed sample contains sixteen resonances, consistent with the loss of symmetry, and most notably exhibits a carbonyl signal, at δ 206.8 ppm. Infrared spectroscopy confirms the presence of the carbonyl functionality, ν(CO) 1654 cm^{-1}. Thus it was concluded that the final product is the acyl thiolate complex $[Os(\sigma,\eta^3\text{-}SCMeC_2H_2C(O)Me)(\eta^6\text{-}p\text{-cymene})]$ **109** (Scheme 4.1), which is formed from $[Os(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}1\text{-}O)(\eta^6\text{-}p\text{-cymene})]$ **108** by C-S bond cleavage. It is believed that this process was catalysed by the acidic sites on the silica. Thiophene and tetramethylthiophene analogues of $[Os(\sigma,\eta^3\text{-}SCMeC_2H_2C(O)Me)(\eta^6\text{-}p\text{-cymene})]$ **109** were obtained simiarly and display the characteristic loss of symmetry in their NMR spectra. This is illustrated in Figure 4.3, which shows both ^1H-NMR and the 2D ^1H-^1H-COSY spectra of $[Os(\sigma,\eta^3\text{-}SCHC_2H_2C(O)H)(\eta^6\text{-}p\text{-cymene})]$ **110** together with assignments. These compounds $[Os(\sigma,\eta^3\text{-}SCRC_2R'_2C(O)R)(\eta^6\text{-}p\text{-cymene})]$ ($SCRC_2R'_2C(O)R$ = $SCHC_2H_2C(O)H$ **110**, $SCMeC_2H_2C(O)Me$ **109**, $SCMeC_2Me_2C(O)Me$ **111**) are analogous to compounds described for ruthenium by Rauchfuss and co-workers.[82] Interestingly, while these ruthenium compounds were described as being obtained in two isomeric forms the osmium analogues showed no tendency to

Figure 4.3:
^{1}H and 2D ^{1}H-^{1}H-COSY NMR spectra of [Ru(σ, η^3-SCHC$_2$H$_2$C(O)H)(η^6-p-cymene)] 110, recorded in a CDCl$_3$ solution.



isomerise, even at elevated temperatures. Instead, these complexes decomposed at high temperature, depositing an organic polymeric film in the process. In the absence of any isomerism it can only be concluded that the structure of the new osmium compounds is equivalent to that of the 'thermodynamic' isomer isolated by Rauchfuss's group.[82]

4.2.3 SUMMARY.

The reactions of $[\{Os(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$ with silver triflate and thiophenes give a series of mixed sandwich complexes of the type $[Os(\eta^5\text{-}Th)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$. While these complexes do not react cleanly with nucleophiles to form thiopheneyl derivatives, they do react with the hydroxide ion in methanol, *via* base hydrolysis, to yield acyl thiolate complexes of the type $[Os(\sigma,\eta^3\text{-}SCRC_2R'_2C(O)R)(\eta^6\text{-}p\text{-cymene})]$. These complexes are similar to those previously described for ruthenium by Rauchfuss and co-workers. It can be speculated that the differences in reactivity are due to differences in the site of initial attack. The hydroxide ion attacks specifically at the sulfur of the thiophene, thus directing the reaction toward the formation of the observed products, while nucleophilic reagents like H^-, OMe^-, CN^- attack a range of carbon atoms, with little control or selectivity, resulting in the complex mixture of products observed in this study.

4.3 EXPERIMENTAL

4.3.1 INSTRUMENTAL

The ^{1}H and ^{13}C-{^{1}H}-NMR spectra were recorded using Bruker spectrometers (AMX 300, AMX 400 or Avance 500) referenced internally against the respective deuterated solvents ($(CD_3)_2CO$, ^{1}H-NMR, δ 2.04 ppm; $CDCl_3$, ^{1}H-NMR, δ 7.27, ^{13}C-{^{1}H}-NMR, δ 77.0 ppm). Infrared spectra were recorded on a Nicolet-205 spectrometer between 4000 and 400 cm^{-1} in the solid state, as KBr discs, or in solution (CH_2Cl_2) using CaF_2 solution cell. Elemental analyses were carried out by the departmental service at UCL. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded by the ULIRS at the London School of Pharmacy (assignments based on the ^{192}Os isotope). Electrochemical measurements were made utilising a PAR 174A polargraphic analyser and a PAR 175 waveform generator in conjunction with a Bryans Instruments 60000 series X-Y/t chart recorder. Platinum wires were used as the working, counter and reference electrodes. Cyclic voltammograms were recorded in the temperature range -40 °C to 30 °C at scan rates in the range 10-200 mV s^{-1} in acetonitrile solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte. Potentials are referenced against the ferrocene/ferrocenium couple (+0.55 V). The X-ray structural determination was carried on at low temperature on a Nonius Kappa CCD equipped diffractometer at KCL. The data was processed routinely, crystal parameters, fractional coordinates and bond lengths and angles are reported in tables at the end of the experimental section.

4.3.2 MATERIALS

Acetonitrile was pre-dried by standing over 4 Å molecular sieves, and distilled from CaH_2 under a nitrogen atmosphere. Methanol was dried and distilled from CaH_2. The compounds $[\{Os(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$[151] and tetramethylthiophene[152] were prepared according to literature methods. Thiophene and 2,5-dimethylthiophene were obtained commercially and dried and distilled prior to use. All other details of material purification and general experimental procedures are as described in Chapter 2 (Section 2.3.2).

4.3.3 SYNTHESIS

$[Os(\eta^5\text{-}C_4H_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$ 100.

A dichloromethane (20 cm^3) solution of $[Os\{(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$ (0.131 g; 0.17 mmol) was stirred with silver trifluoromethanesulfonate (0.171 g; 0.67 mmol) in the dark for 2 h. The yellow suspension was filtered to remove the precipitated silver chloride. The yellow filtrate was stirred with an excess of thiophene (1 cm^3) for 16 h. Removal of the solvent and residual thiophene by vacuum distillation left a brown oil, which was extracted with ethanol. The ethanolic solution was filtered through Celite and the filtrate treated with an excess of ethanolic $NH_4[PF_6]$. After storing at -20 °C for 4 h a light chestnut coloured solid was collected by filtration, washed with dichloromethane (10 cm^3) and diethylether (10 cm^3), and dried *in vacuo*. *Yield* 0.154 g, 0.20 mmol, 67 %. *Anal.:* Found C, 24.18, H, 2.52 % (Calc. for $OsC_{14}H_{18}F_{12}P_2S$: C, 24.07, H, 2.60 %). *^{1}H-NMR* $[(CD_3)_2CO]$: *p*-cymene resonances, δ 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), δ 2.74 (s, 3H, CH_3), δ 3.07 (sp, $^3J_{HH}$ = 7.0 Hz, 1H, $CH(CH_3)_2$), δ 7.31 (AA'BB', 4H, ring) ppm; thiophene resonance, δ 7.75 ppm

(m, 4H) ppm. *Infrared* (KBr): $\nu(PF_6)$ 834 cm^{-1}. *Mass spectrum* (FAB): m/z 410 $[M-2PF_6]^+$. *Cyclic voltammetry* (25 °C, ν = 100 mV s^{-1}) E_f = –0.20 V (irreversible).

$[Os(\eta^5\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ 101.

In a similar manner to that described above $[\{Os(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$ (0.098 g; 0.12 mmol) was reacted with first 4 equivalents of silver trifluoromethanesulfonate (0.129 g; 0.50 mmol) and then an excess of 2,5-dimethylthiophene (0.5 cm^3). After stirring for 16 h the solution was concentrated to *ca.* 10 cm^3 and cooled to 0 °C. A pale cream precipitate was formed and collected by filtration, washed with cold dichloromethane (10 cm^3) and diethylether (10 cm^3), and subsequently dried *in vacuo*. *Yield* 0.157 g, 0.21 mmol, 86 %. *Anal.:* Found C, 29.27, H, 2.90 % (Calc. for $OsC_{18}H_{22}F_6O_6S_3$: C, 29.42, H, 3.02 %). *^{1}H-NMR* $[(CD_3)_2CO]$: *p*-cymene resonances, δ 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), δ 2.69 (s, 3H, CH_3), δ 3.09 (sp, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), δ 7.30 (AA'BB', 4H, ring) ppm; DMT resonances, δ 2.74 (s, 6H, CH_3), δ 7.61 (s, 2H) ppm. *Infrared* (KBr): ν(SO) 1270 cm^{-1}. *Mass spectrum* (FAB): m/z 587 $[M-CF_3SO_3]^+$, 438 $[M-2CF_3SO_3]^+$. *Cyclic voltammetry* (25 °C, ν = 100 mV s^{-1}) E_f = –0.31 V (irreversible).

$[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ 102.

This complex was prepared by an analogous method to that described above. *Yield* 78 %. *Anal.:* (Found C, 31.26, H, 3.16 %. Calc. for $OsC_{20}H_{26}F_6O_6S_3$: C, 31.49, H, 3.44 %). *^{1}H-NMR* $[(CD_3)_2CO]$: *p*-cymene resonances, δ 1.42 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), δ 2.59 (s, 3H, CH_3), δ 3.09 (sept, $^3J_{HH}$ = 6.9 Hz, 1H,

C*H*(CH_3)$_2$), δ 7.17 (AA'BB', 4H, ring) ppm; TMT resonances, δ 2.62 (s, 6H, CH_3), δ 2.69 (s, 6H, CH_3) ppm. *Infrared* (KBr): ν(SO) 1273 cm^{-1}. *Mass spectrum* (FAB): m/z 466 $[M-2CF_3SO_3]^+$. *Cyclic voltammetry* (25 °C, ν = 100 mV s^{-1}) $E_{½}$ = –0.37 V (quasireversible).

[Os(σ,η^3-$SC_3H_3C(O)H$)(η^6-*p*-cymene)] 110.

An excess of KOH (0.031g, 0.55 mmol) was added to a solution of [Os(η^5-C_4H_4S)(η^6-*p*-cymene)][PF_6]$_2$ (0.101g, 0.16 mmol) in methanol (15 cm^3) and the mixture stirred for 4 h. After this time the methanol was removed under reduced pressure and the yellow oily residue was extracted into dichloromethane (3 x 15 cm^3), filtered through Celite, and washed through with fresh dichloromethane (10 cm^3). The volume was reduced to *ca.* 5 cm^3 and the solution was loaded onto a short silica column. Eluting with dichloromethane/methanol (100:1) led to the recovery of a yellow band. Evaporation of the solvent gave an air sensitive yellow/tan viscous oil which was dried *in vacuo*. *Yield* 0.042 g, 0.10 mmol, 64 %. *Anal.:* Found C, 40.04, H, 4.73 % (Calc. for $OsC_{14}H_{18}OS$: C, 39.60, H, 4.27 %). *^{1}H-NMR* [$CDCl_3$]: *p*-cymene resonances, δ 1.25 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), δ 1.26 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), δ 2.34 (s, 3H, CH_3), δ 2.59 (sp, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(CH_3)$_2$), δ 5.37 (d, $^2J_{HH}$ = 5.4 Hz, 1H, ring), δ 5.49 (d, $^3J_{HH}$ = 5.4 Hz, 1H, ring), δ 5.53 (d, $^3J_{HH}$ = 5.4 Hz, 1H, ring), δ 5.60 (d, $^3J_{HH}$ = 5.4 Hz, 1H, ring) ppm; $SC_3H_3C(O)H$ resonances, δ 2.37 (m, 1H), δ 6.07 (d, $^3J_{HH}$ = 3.5 Hz, 1H), δ 6.26 (dd, 1H), δ 9.54 ppm (d, $^3J_{HH}$ = 4.2 Hz, 1H) ppm. *Infrared* (CH_2Cl_2): ν(CO) 1667 cm^{-1}. *Mass spectrum* (EI): m/z 426 $[M]^+$, 398 $[M-CO]^+$, 358 $[M-C_4H_4O]^+$.

[Os(σ,η^3-SCMeC$_2$H$_2$C(O)Me)(η^6-*p*-cymene)] 109.

An analogous procedure to that described above was used for the preparation of [Os(σ,η^3-SCMeC$_2$H$_2$C(O)Me)(η^6-*p*-cymene)]. However to obtain a sample of the highest purity the silca column must first be washed with dichloromethane, prior to eluting with the dichloromethane/methanol mixture. *Yield* 61 %. *Anal.:* Found C, 42.76, H, 4.73 % (Calc. for OsC$_{16}$H$_{22}$OS: C, 42.46, H, 4.90 %). *^{1}H-NMR* [CDCl$_3$]: *p*-cymene resonances, δ 1.29 (d, ^{3}J$_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.30 (d, ^{3}J$_{HH}$ = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), δ 2.46 (s, 3H, CH$_3$), δ 2.57 (sp, ^{3}J$_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), δ 5.10 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring), δ 5.20 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring), δ 5.35 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring) δ 5.45 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring) ppm; SCMeC$_2$H$_2$C(O)Me resonances, δ 2.09 (s, 3H, CH$_3$), δ 2.22 (d, ^{3}J$_{HH}$ = 6.1 Hz, 1H), δ 2.23 (s, 3H, CH$_3$), δ 6.09 ppm (d, ^{3}J$_{HH}$ = 6.1 Hz, 1H). *^{13}C-{^{1}H}-NMR* [CDCl$_3$]: δ 19.1, 23.5, 24.2, 26.8, 30.7, 31.6 ppm (aliphatic); δ 55.3, 73.5, 73.6, 75.4, 75.8, 79.6 ppm (unsaturated); δ 89.3, 90.7, 100.8 ppm (quaternary); δ 206.8 ppm (carbonyl). *Infrared* (KBr): ν(CO) 1654 cm^{-1}. *Mass spectrum* (EI): m/z 454 [M]$^+$, 438 [M-O]$^+$, 426 [M-CO]$^+$, 411 [M-C$_2$H$_3$O]$^+$, 358 [M-C$_6$H$_8$O]$^+$.

[Os(σ,η^3-SC$_3$Me$_3$C(O)Me)(η^6-p-cymene)] 111.

An analogous procedure to that described above was used for the preparation of [Os(η^6-p-cymene)(SC$_3$Me$_3$C(O)Me)]. *Yield* 76 %. *Anal.:* Found C, 44.56, H, 6.13 % (Calc. for OsC$_{18}$H$_{26}$OS.MeOH: C 44.51, H 5.90 %). *^{1}H-NMR* [CDCl$_3$, -20 °C]: *p*-cymene resonances, δ 1.24 (d, ^{3}J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), δ 1.27 (d, ^{3}J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), δ 2.49 (s, 3H, CH$_3$), δ 2.59 (sp, ^{3}J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), δ 4.98 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring), δ 5.25 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring), δ 5.36 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring), δ 5.47 (d, ^{3}J$_{HH}$ = 5.4 Hz, 1H, ring) ppm;

$SC_3Me_3C(O)Me$ resonances, δ 1.63 (s, 3H, CH_3), δ 2.01 (s, 3H, CH_3), δ 2.07 (s, 3H, CH_3), δ 2.23 ppm (s, 3H, CH_3) ppm. *Infrared* (CH_2Cl_2): ν(CO) 1652 cm^{-1}. *Mass spectrum* (EI): m/z 482 $[M]^+$, 439 $[M-C_2H_3O]^+$, 358 $[M-C_8H_{12}O]^+$.

4.3.3 X-RAY CRYSTALLOGRAPHIC DATA

Table 4.2:
Crystal data and structure refinement for
$[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$ 102.

Empirical formula	$C_{20}H_{26}F_6O_6OsS_3$
Formula weight	762.79
Temperature	100(2) K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.3702(17) Å
	b = 26.414(5) Å
	c = 12.256(3) Å
	α = 90 °
	β = 109.38(3) °
	γ = 90 °
Volume	2556.1(9) $Å^3$
Z	4
Density (calculated)	1.982 g cm^{-3}
Absorption coefficient	5.312 mm^{-1}
F(000)	1488
Crystal size	0.22 x 0.04 x 0.02 mm^3
Theta range for data collection	3.01 to 26.00 °
hkl Index ranges	-9 → 10, -32 → 32, -14 → 15
Reflections collected	11403
Independent reflections	4826 [R(int) = 0.1037]
Completeness to theta = 26 °	96.2 %
Absorption correction	Scalepack
Max. and min. transmission	0.9012 and 0.3878
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4826 / 0 / 326
Goodness-of-fit on F^2	1.047
Final R indices [$I>2\sigma(I)$]	R1 = 0.0547, wR2 = 0.1477
R indices (all data)	R1 = 0.0685, wR2 = 0.1565
Extinction coefficient	0.0030(4)
Largest diff. peak and hole	3.332 and -3.772 e $Å^{-3}$

Table 4.3:
Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ru(η^5-C_4Me_4S)(η^6-p-cymene)][CF_3SO_3]$_2$ 102.

	x	y	z	U(eq)
Os(1)	4047(1)	1143(1)	1731(1)	11(1)
S(1)	484(3)	2110(1)	4421(2)	17(1)
S(2)	3508(3)	4436(1)	3779(2)	16(1)
S(3)	1334(3)	1063(1)	1879(2)	14(1)
F(1)	2111(7)	2173(2)	6655(5)	37(1)
F(2)	456(8)	1526(2)	6160(5)	37(1)
F(3)	2861(7)	1531(2)	5832(5)	36(1)
F(4)	2119(8)	3579(2)	2780(7)	51(2)
F(5)	2971(9)	4070(3)	1686(6)	57(2)
F(6)	682(7)	4248(2)	2071(5)	41(2)
O(1)	-1018(8)	2332(2)	4553(5)	23(1)
O(2)	1743(8)	2466(2)	4321(5)	31(2)
O(3)	164(8)	1684(2)	3638(5)	27(1)
O(4)	2529(9)	4397(3)	4546(6)	32(2)
O(5)	3487(8)	4930(2)	3270(6)	26(1)
O(6)	5120(8)	4180(2)	4155(6)	26(1)
C(1)	3606(12)	1438(3)	-1094(7)	21(2)
C(2)	4528(11)	1160(3)	-3(7)	15(2)
C(3)	5904(11)	1388(3)	898(7)	18(2)
C(4)	6805(12)	1117(3)	1890(8)	19(2)
C(5)	3996(10)	673(3)	225(7)	15(2)
C(6)	4857(10)	397(3)	1253(6)	11(2)
C(7)	6302(10)	610(3)	2103(7)	15(2)
C(8)	7156(10)	291(3)	3183(7)	17(2)
C(9)	8418(11)	592(4)	4184(8)	27(2)
C(10)	8045(11)	-161(4)	2852(8)	25(2)
C(11)	3054(11)	1057(3)	3194(7)	14(2)
C(12)	3940(10)	1532(3)	3358(7)	14(2)
C(13)	3280(10)	1875(3)	2397(7)	15(2)
C(14)	1870(10)	1667(3)	1514(7)	15(2)
C(15)	777(11)	1925(3)	434(8)	24(2)
C(16)	3914(11)	2407(3)	2357(7)	19(2)
C(17)	5393(11)	1664(3)	4457(7)	20(2)
C(18)	3293(11)	630(3)	4028(7)	21(2)
C(19)	1536(11)	1823(3)	5831(8)	24(2)
C(20)	2279(12)	4061(4)	2506(9)	33(2)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 4.4:
Bond lengths (Å) and angles (°) for
[Ru(η^5-C_4Me_4S)(η^6-p-cymene)][CF_3SO_3]$_2$ 102.

Os(1)-C(5)	2.213(8)	F(2)-C(19)	1.355(10)
Os(1)-C(3)	2.220(8)	F(3)-C(19)	1.350(10)
Os(1)-C(11)	2.224(8)	F(4)-C(20)	1.334(13)
Os(1)-C(6)	2.224(7)	F(5)-C(20)	1.316(13)
Os(1)-C(14)	2.232(8)	F(6)-C(20)	1.358(11)
Os(1)-C(4)	2.253(9)	C(1)-C(2)	1.495(11)
Os(1)-C(12)	2.271(8)	C(2)-C(5)	1.419(11)
Os(1)-C(13)	2.272(8)	C(2)-C(3)	1.436(11)
Os(1)-C(7)	2.277(8)	C(3)-C(4)	1.397(13)
Os(1)-C(2)	2.290(8)	C(4)-C(7)	1.453(11)
Os(1)-S(3)	2.347(2)	C(5)-C(6)	1.426(11)
S(1)-O(1)	1.444(6)	C(6)-C(7)	1.424(11)
S(1)-O(3)	1.444(6)	C(7)-C(8)	1.532(11)
S(1)-O(2)	1.447(6)	C(8)-C(10)	1.531(11)
S(1)-C(19)	1.824(9)	C(8)-C(9)	1.548(12)
S(2)-O(4)	1.441(7)	C(11)-C(12)	1.437(11)
S(2)-O(6)	1.442(6)	C(11)-C(18)	1.491(11)
S(2)-O(5)	1.443(6)	C(12)-C(13)	1.443(11)
S(2)-C(20)	1.846(10)	C(12)-C(17)	1.526(11)
S(3)-C(14)	1.755(8)	C(13)-C(14)	1.420(11)
S(3)-C(11)	1.769(9)	C(13)-C(16)	1.509(11)
F(1)-C(19)	1.335(11)	C(14)-C(15)	1.501(11)

C(5)-Os(1)-C(3)	66.6(3)	C(14)-Os(1)-C(4)	143.3(3)
C(5)-Os(1)-C(11)	134.9(3)	C(5)-Os(1)-C(12)	172.1(3)
C(3)-Os(1)-C(11)	155.0(3)	C(3)-Os(1)-C(12)	120.6(3)
C(5)-Os(1)-C(6)	37.5(3)	C(11)-Os(1)-C(12)	37.3(3)
C(3)-Os(1)-C(6)	79.4(3)	C(6)-Os(1)-C(12)	137.4(3)
C(11)-Os(1)-C(6)	110.5(3)	C(14)-Os(1)-C(12)	63.6(3)
C(5)-Os(1)-C(14)	117.4(3)	C(4)-Os(1)-C(12)	106.0(3)
C(3)-Os(1)-C(14)	115.7(3)	C(5)-Os(1)-C(13)	148.0(3)
C(11)-Os(1)-C(14)	69.5(3)	C(3)-Os(1)-C(13)	104.0(3)
C(6)-Os(1)-C(14)	145.6(3)	C(11)-Os(1)-C(13)	64.6(3)
C(5)-Os(1)-C(4)	77.9(3)	C(6)-Os(1)-C(13)	174.4(3)
C(3)-Os(1)-C(4)	36.4(3)	C(14)-Os(1)-C(13)	36.8(3)
C(11)-Os(1)-C(4)	125.0(3)	C(4)-Os(1)-C(13)	113.5(3)
C(6)-Os(1)-C(4)	66.6(3)	C(12)-Os(1)-C(13)	37.0(3)

C(5)-Os(1)-C(7)	66.7(3)	C(14)-S(3)-Os(1)	64.0(3)
C(3)-Os(1)-C(7)	67.1(3)	C(11)-S(3)-Os(1)	63.6(3)
C(11)-Os(1)-C(7)	106.4(3)	C(5)-C(2)-C(3)	116.9(7)
C(6)-Os(1)-C(7)	36.9(3)	C(5)-C(2)-C(1)	121.2(8)
C(14)-Os(1)-C(7)	175.5(3)	C(3)-C(2)-C(1)	121.7(7)
C(4)-Os(1)-C(7)	37.4(3)	C(5)-C(2)-Os(1)	68.7(4)
C(12)-Os(1)-C(7)	112.0(3)	C(3)-C(2)-Os(1)	68.8(4)
C(13)-Os(1)-C(7)	140.2(3)	C(1)-C(2)-Os(1)	129.9(6)
C(5)-Os(1)-C(2)	36.7(3)	C(4)-C(3)-C(2)	121.2(7)
C(3)-Os(1)-C(2)	37.1(3)	C(4)-C(3)-Os(1)	73.1(5)
C(11)-Os(1)-C(2)	167.8(3)	C(2)-C(3)-Os(1)	74.1(5)
C(6)-Os(1)-C(2)	67.0(3)	C(3)-C(4)-C(7)	121.5(8)
C(14)-Os(1)-C(2)	105.4(3)	C(3)-C(4)-Os(1)	70.5(5)
C(4)-Os(1)-C(2)	65.8(3)	C(7)-C(4)-Os(1)	72.2(5)
C(12)-Os(1)-C(2)	151.2(3)	C(2)-C(5)-C(6)	122.5(7)
C(13)-Os(1)-C(2)	118.3(3)	C(2)-C(5)-Os(1)	74.6(5)
C(7)-Os(1)-C(2)	78.9(3)	C(6)-C(5)-Os(1)	71.7(4)
C(5)-Os(1)-S(3)	105.2(2)	C(7)-C(6)-C(5)	120.1(7)
C(3)-Os(1)-S(3)	154.8(2)	C(7)-C(6)-Os(1)	73.6(4)
C(11)-Os(1)-S(3)	45.4(2)	C(5)-C(6)-Os(1)	70.8(4)
C(6)-Os(1)-S(3)	109.1(2)	C(6)-C(7)-C(4)	117.3(7)
C(14)-Os(1)-S(3)	45.0(2)	C(6)-C(7)-C(8)	117.0(7)
C(4)-Os(1)-S(3)	168.7(2)	C(4)-C(7)-C(8)	125.6(7)
C(12)-Os(1)-S(3)	69.7(2)	C(6)-C(7)-Os(1)	69.6(4)
C(13)-Os(1)-S(3)	69.7(2)	C(4)-C(7)-Os(1)	70.4(5)
C(7)-Os(1)-S(3)	133.4(2)	C(8)-C(7)-Os(1)	129.2(5)
C(2)-Os(1)-S(3)	123.1(2)	C(10)-C(8)-C(7)	109.3(7)
O(1)-S(1)-O(3)	114.4(4)	C(10)-C(8)-C(9)	110.3(7)
O(1)-S(1)-O(2)	115.6(4)	C(7)-C(8)-C(9)	113.6(7)
O(3)-S(1)-O(2)	115.4(4)	C(12)-C(11)-C(18)	128.2(8)
O(1)-S(1)-C(19)	103.1(4)	C(12)-C(11)-S(3)	110.3(6)
O(3)-S(1)-C(19)	103.3(4)	C(18)-C(11)-S(3)	121.0(6)
O(2)-S(1)-C(19)	102.4(4)	C(12)-C(11)-Os(1)	73.1(4)
O(4)-S(2)-O(6)	115.6(4)	C(18)-C(11)-Os(1)	129.0(6)
O(4)-S(2)-O(5)	114.7(4)	S(3)-C(11)-Os(1)	70.9(3)
O(6)-S(2)-O(5)	116.0(4)	C(11)-C(12)-C(13)	113.2(7)
O(4)-S(2)-C(20)	103.6(5)	C(11)-C(12)-C(17)	123.1(7)
O(6)-S(2)-C(20)	102.6(4)	C(13)-C(12)-C(17)	123.7(7)
O(5)-S(2)-C(20)	101.3(5)	C(11)-C(12)-Os(1)	69.6(4)
C(14)-S(3)-C(11)	92.3(4)	C(13)-C(12)-Os(1)	71.5(4)

C(17)-C(12)-Os(1)	128.8(5)	F(1)-C(19)-F(3)	107.7(7)
C(14)-C(13)-C(12)	112.0(7)	F(1)-C(19)-F(2)	106.5(8)
C(14)-C(13)-C(16)	123.3(7)	F(3)-C(19)-F(2)	107.3(7)
C(12)-C(13)-C(16)	124.6(7)	F(1)-C(19)-S(1)	111.6(6)
C(14)-C(13)-Os(1)	70.1(4)	F(3)-C(19)-S(1)	112.1(6)
C(12)-C(13)-Os(1)	71.4(4)	F(2)-C(19)-S(1)	111.3(6)
C(16)-C(13)-Os(1)	129.5(5)	F(5)-C(20)-F(4)	108.5(9)
C(13)-C(14)-C(15)	127.2(7)	F(5)-C(20)-F(6)	108.6(9)
C(13)-C(14)-S(3)	112.1(6)	F(4)-C(20)-F(6)	106.1(8)
C(15)-C(14)-S(3)	120.4(6)	F(5)-C(20)-S(2)	111.8(7)
C(13)-C(14)-Os(1)	73.2(4)	F(4)-C(20)-S(2)	111.9(7)
C(15)-C(14)-Os(1)	128.4(6)	F(6)-C(20)-S(2)	109.7(7)
S(3)-C(14)-Os(1)	71.0(3)		

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COMPOUND NUMBERING

1 $[Ru(\eta^5,\eta^1\text{-}C_5H_4CH_2C_4H_3S)(PPh_3)_2][BPh_4]$

2 $[Ru(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)(dppe)][BF_4]$

3 $[Ru(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)\{(S,S)\text{-Chiraphos}\}][BF_4]$

4 $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(PPh_3)(NO)][BF_4]$

5 $[Ir(\eta^1\text{-}C_4H_4S)_2(PPh_3)_2(H)_2][PF_6]$

6 $[Ir(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)(PPh_3)_2(H)][PF_6]$

7 $[Re(2,3\text{-}\eta^2\text{-}C_4H_4Se)(\eta^5\text{-}C_5Me_5)(CO)_2]$

8 $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(CO)_2]$

9 $[Re(\eta^1\text{-}2,5\text{-}Me_2C_4H_2Se)(\eta^5\text{-}C_5Me_5)(CO)_2]$

10 $[Re(2\text{-}MeC_4H_3Se)(\eta^5\text{-}C_5Me_5)(CO)_2]$

11 $[Re(\eta^5\text{-}C_5H_5)(2\text{-}MeC_4H_3Se)(CO)_2]$

12 $[Cr(\eta^5\text{-}C_4H_4S)(CO)_3]$

13 $[Cr(CO)_6]$

14 $[Cr(\eta^5\text{-}2,5\text{-}Li_2H_2C_4S)(CO)_3]$

15 $[Cr(\eta^5\text{-}2,5\text{-}D_2H_2C_4S)(CO)_3]$

16 $[Mn(CO)_5Cl]$

17 $[Mn(CO)_5(CF_3SO_3)]$

18 $[Mn(\eta^5\text{-}C_4H_4S)(CO)_3][CF_3SO_3]$

19 $[Mn(\eta^4\text{-}C_4H_4S\text{-}2\text{-}CN)(CO)_3]$

20 $[Mn(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)(CO)_3]$

21 $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]_2$

22 $[Rh(\sigma,\eta^3\text{-}SC_3Me_3C(O)Me)(\eta^5\text{-}C_5Me_5)]$

23 $[Rh(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OH)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]$

24 $[Fe(\eta^5\text{-}C_4Me_4S)_2][PF_6]_2$

25 $[Fe(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5H_5)][PF_6]$

26 $[Fe(\eta^5\text{-}C_6H_5Cl)(\eta^5\text{-}C_5H_5)][PF_6]$

27 $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$

28 $[Rh(\eta^5\text{-}C_5Me_5)(CH_3CN)_3][PF_6]_2$

29 $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][PF_6]_2$

30 $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$

31 $[Ir(\eta^5\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)][PF_6]_2$

32 $[Rh(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)]$

33 $[Rh(\eta^5\text{-}C_4Me_4S)(\eta^5\text{-}C_5Me_5)][CF_3SO_3]_2$

34 $[Ir(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^5\text{-}C_5Me_5)]$

35 $[Re(\eta^1\text{-}C_4H_4S)(\eta^5\text{-}C_5Me_5)(CO)_2]$

36 $[\{Re(\eta^5\text{-}C_5Me_5)(CO)_2\}(\eta^1,\eta^4\text{-}C_4H_4S)\{Fe(CO)_3\}]$

37 $[(\eta^5\text{-}C_5H_5)(CO)_2Mo{=}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$

38 $[\{Ir(\eta^5\text{-}C_5Me_5)\}(\eta^4\text{-}S\text{-}\mu^3\text{-}2,5\text{-}Me_2C_4H_2S)\{Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2\}]$

39 $[\{Ir(\eta^5\text{-}C_5Me_5)\}(\eta^4\text{-}S\text{-}\mu^3\text{-}2,5\text{-}Me_2C_4H_2S)\{Fe_2(CO)_7\}]$

40 $[\{Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$

41 $[Ru(\eta^5\text{-}C_4H_4S)(\eta^5\text{-}C_5H_5)][BF_4]$

42 $[Ru(\eta^5\text{-}C_5H_5)(CH_3CN)_3][BF_4]$

43 $[Ru(\eta^5\text{-}C_5Me_5)(CH_3CN)_3][PF_6]$

44 $[\{Ru(\eta^5\text{-}C_4Me_4S)Cl(\mu\text{-}Cl)\}_2]$

45 $[\{Ru(\eta^5\text{-}C_4Me_4S)(\mu\text{-}Cl)\}_3(\mu^3\text{-}S)][PF_6]$

46 $[Ru(\eta^5\text{-}C_4Me_4S)_2][BF_4]_2$

47 $[Ru(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_4Me_4S)]$

48 $[\{Ru(\eta^5\text{-}C_4Me_4S)\}(\eta^4\text{-}\mu^2\text{-}C_4Me_4S)\{Fe(CO)_4\}]$

49 $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2]_n$

50 $[Ru(\eta^6\text{-}p\text{-cymene})(CF_3SO_3)_2]_n$

51 $[Ru(\eta^6\text{-}C_6Me_6)(CF_3SO_3)_2]_n$

52 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}NH_2)(\eta^6\text{-}p\text{-cymene})][PF_6]$

53 (-)-$[Ru(\eta^5\text{-}2\text{-}MeC_4H_3S)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2$

54 $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2$

55 $[Ru(\eta^4\text{-}C_4H_4S\text{-}2\text{-}H)(\eta^6\text{-}C_6Me_6)][PF_6]$

56 $[Ru(\eta^4\text{-}C_4Me_4S)(\eta^6\text{-}C_6Me_6)]$

57 $[Ru_3(\eta^4\text{-}\mu_2\text{-}C_4Me_4S)_2(\eta^6\text{-}C_6Me_6)_3]$

58 $[Os(\eta^5\text{-}2\text{-}MeC_4H_3S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$

59 $[Os(NH_3)_5(CF_3SO_3)][CF_3SO_3]_2$

60 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(CO)]$

61 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPhMe_2)]$

62 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(P(OMe)_3)]$

63 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NC_5H_5)]$

64 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(NC_5H_4CN)]$

65 $[Ru(\eta^5\text{-}C_4Me_4S)(CF_3SO_3)_2(CO)]$

66 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PMe_3)]$

67 $[Ru(\eta^5\text{-}C_4Me_4S)Cl_2(PPh_3)]$

68 $[Ru(\eta^5\text{-}C_4Me_4S)(H_2O)_3][CF_3SO_3]_2$

69 $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PPhMe_2)]$

70 $[Ru(bipy)_3][PF_6]_2$

71 $[Ru(\eta^5\text{-}C_4Me_4S)Cl(bipy)][PF_6]$

72 $[Ru(\eta^5\text{-}C_4Me_4S)(bipy)(PPhMe_2)][PF_6]_2$

73 $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$

74 $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]_2$

75 $[Ru(\eta^6\text{-}p\text{-cymene})\{\kappa^3\text{-}HB(Pz)_3\}][PF_6]$

76 $[Ru(\eta^5\text{-}C_4Me_4S)\{\kappa^2\text{-}HC(3,5\text{-}Me_2Pz)_3\}Cl][PF_6]$

77 $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(\mu\text{-}Cl)][PF_6]$

78 $[Ru_2(\eta^6\text{-}p\text{-cymene})(\mu\text{-}3,5\text{-}Me_2Pz)(\mu\text{-}OH)_2][BF_4]$

79 $[Ru(\eta^5\text{-}C_4Me_4S)(\kappa^3\text{-}[9]aneS_3)][PF_6]_2$

80 $[Ru_2(\kappa^3\text{-}[9]aneS_3)_2(\mu\text{-}Cl)_3][PF_6]$

81 $[Ru_2(\eta^5\text{-}C_4Me_4S)_2(\mu\text{-}Cl)_3][PF_6]$

82 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$

83 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)\{\kappa^3\text{-}HC(Pz)_3\}][PF_6]$

84 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)(\kappa^3\text{-}[9]aneS_3)][PF_6]$

85 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\kappa^3\text{-}[9]aneS_3)][PF_6]$

86 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)(\kappa^3\text{-}[9]aneS_3)][PF_6]$

87 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}CN)(\kappa^3\text{-}[9]aneS_3)][PF_6]$

88 $[Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}2\text{-}H)(\eta^6\text{-}C_6Me_6)][PF_6]$

89 $[Ru(CH_3CN)_3(\kappa^3\text{-}[9]aneS_3)][CF_3SO_3]_2$

90 $[Ru(\eta^6\text{-}C_6Me_6)([9]aneS_3)][PF_6]_2$

91 $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}S(CHCH_2)CH_2CH_2S\}(\sigma\text{-}SCHCH_2)]$

92 $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}S(CHCH_2)CH_2CH_2SCH_2CH_2S\}][PF_6]$

93 $[Ru(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]_2$

94 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OMe)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$

95 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}CN)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$

96 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$

97 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}SEt)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})][CF_3SO_3]$

98 $[Ru(\eta^4\text{-}C_4Me_4S\text{-}1\text{-}O)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]$

99 $[Ru(\sigma,\eta^3\text{-}SC_3Me_3C(O)Me)(\eta^6\text{-}[2.2]\text{-}\textit{para}\text{cyclophane})]$

100 $[Os(\eta^5\text{-}C_4H_4S)(\eta^6\text{-}p\text{-cymene})][PF_6]_2$

101 $[Os(\eta^5\text{-}2,5\text{-}Me_2C_4H_2S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$

102 $[Os(\eta^5\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]_2$

103 $[\{Os(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)\}_2]$

104 $[Os(\eta^6\text{-}p\text{-cymene})(CF_3SO_3)_2]_n$

105 $[Ru(\eta^5\text{-}C_4H_4S)(\eta^6\text{-}C_6Me_6)][CF_3SO_3]_2$

106 $[Os(\eta^4\text{-}C_4Me_4S)(\eta^6\text{-}p\text{-cymene})]$

107 $[Ru(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}1\text{-}O)(\eta^6\text{-}p\text{-cymene})]$

108 $[Os(\eta^4\text{-}2,5\text{-}Me_2C_4H_2S\text{-}1\text{-}O)(\eta^6\text{-}p\text{-cymene})]$

109 $[Os(\sigma,\eta^3\text{-}SCMeC_2H_2C(O)Me)(\eta^6\text{-}p\text{-cymene})]$

110 $[Os(\sigma,\eta^3\text{-}SCHC_2H_2C(O)H)(\eta^6\text{-}p\text{-cymene})]$

111 $[Os(\sigma,\eta^3\text{-}SCMeC_2Me_2C(O)Me)(\eta^6\text{-}p\text{-cymene})]$