THE CONVERSION OF REFINERY MATERIALS INTO USEFUL INORGANIC AND ORGANOMETALLIC PRECURSORS

BY

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Declaration

I declare that the thesis, **THE CONVERSION OF ANGLO PLATINUM REFINERY MATERIALS INTO USEFUL INORGANIC AND ORGANOMETALLIC PRECURSORS** is my own work and has never been presented for the award of any degree at any university before and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

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Haleden Chiririwa

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Finally, my family for their continuous encouragement, support and guidance throughout my studies without which I wouldn't have achieved what I have today.

Abstract

Anglo American Platinum Platinum Corporation Ltd. currently stores some of its recovered osmium as the relatively stable potassium osmate salt $K_2[OsO_2(OH)_4]$ and ruthenium in the metallic form, however, ammonium hexachlororuthenate $(NH_4)_2[RuCl_6]$ and an acidic ruthenium solution $H_2[RuCl_6]$ are respectively an intermediate salt and solution produced in the final refining of the ruthenium. To date the development of the chemistry of these starting materials to provide useful inorganic and organometallic precursors has not been extensively reported. This is partly due to the relative cost of osmium starting materials and the inertness of most osmium complexes and also the toxicity of OsO_4. Most known ruthenium compounds are usually made from $RuCl_3.3H_2O$.

In the present project locally available refinery materials have been converted into a range of known osmium and ruthenium compounds including clusters such as $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$, $[\{Os(CO)_3Cl_2\}_2]$ and $H_4Ru_4(CO)_{12}$ together with the well known Grubbs' catalyst starting material $RuCl_2(PPh_3)_3$ as well as other useful complexes such as $[\{RuCl_2(C_8H_{12})\}_n]$, $OsHCl(CO)(PPh_3)_3$, $OsCl_2(PPh_3)_3$, and $Os(CO)_3(PPh_3)_2$.

The development of the synthesis of convenient osmium and ruthenium precursors as well as potential catalysts has been proven to be possible based on standard (literature) synthetic methods using the Anglo Platinum refinery material. Some procedures are new and some are modified literature procedures.

Abbreviations

°C	degrees celcius
COD	1,5 cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dec	decomposition
Eqn	equation
eqv	equivalent
g	gram
h	hour
Hz	hertz
IR	infrared
L	ligand
m	medium (in IR)
MIBK	Methyl Isobutyl Ketone
min	minute
m.p	melting point
NMR	nuclear magnetic resonance
NTs	N-Tosylimino
ppm	parts per million
R	alkyl group
s	strong (in IR)
temp	temperature
THF	tetrahydrofuran
tlc	thin layer chromatography
w	weak (in IR)
X	halogen atom

List of compounds prepared in this thesis

Compound	***Name***
1	ammonium hexachloroosmate
2	dodecacarbonyltriosmium
3	hexacarbonyltetrachlorodiosmium
4	carbonylchlorohydridotris(triphenylphosphine)osmium
5	carbonyldihydridotris(triphenylphosphine)osmium
6	tricarbonylbis(triphenylphosphine)osmium
7	dodecacarbonyltriruthenium
8	dodecacarbonyltetra(μ-hydrido)-tetraruthenium
9	dichlorotris(triphenylphosphine)ruthenium
10	dichloro(cycloocta-1,5-diene)ruthenium
11	ammonium hexachlororuthenate
12	(pentamethylcyclopentadienyl)dichlororuthenium dimer
13	dihydrogen hexachloroosmate
14	dihydrogen hexabromoosmate
15	sodium hexachloroosmate
16	dichlorotris(triphenylphosphine)osmium
17	dibromotris(triphenylphosphine)osmium
18	ammonium hexabromoosmate
19	(pentamethylcyclopentadienyl)dibromoosmium dimer
20	(pentamethylcyclopentadienyl)dicarbonylruthenium dimer
21	(cyclopentadienyl)dicarbonylruthenium dimer

Conference proceedings

Poster entitled " Conversion of potassium osmate into versatile inorganic and organometallic precursors." H. Chiririwa and J. R. Moss, presented at the 37th National Convention of the South African Chemical Institute (SACI), Pretoria, South Africa (2004)

Poster entitled " Conversion of potassium osmate into versatile inorganic and organometallic precursors." H. Chiririwa and J. R. Moss, presented at the Cape Organometallic Symposium, Cape Town Waterfront, South Africa (2004)

Poster entitled " Conversion of Anglo Platinum Refinery Materials into useful into inorganic and organometallic precursors." H. Chiririwa and J. R. Moss, presented at the Inorganic Chemistry Conference, Pietermaritzburg, South Africa (2005)

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Chapter 1

An Introduction into the Extraction and Refining of Platinum Group Metals

1.1 General introduction

The Platinum Group Metals (PGM's) consist of a family of six greyish to silver-white metals with close chemical and physical affinities.[1] They belong to the transition elements group (VIII) in the periodic table to which the ferrous metals iron (Fe), cobalt (Co) and nickel (Ni) belong. The six metals of the platinum group occur in nature in close association with one another and with nickel and copper. Of the few deposits known, those in South Africa and Russia are by far the largest. Together South Africa and Russia account for 90% of world PGM production.[1-3] Platinum and palladium have the greatest economic importance and are found in largest quantities. The other four, namely rhodium, ruthenium, iridium and osmium are only produced as co-products of platinum and palladium. The rationale behind the utilization of PGM's and their complexes as catalysts is their ability to catalyse reactions under milder conditions with higher selectivities as compared to other metals, their higher stability in various oxidation states, functional group tolerance, and their highly understood synthetic chemistry.[3]

1.1.2 Major resources[4,5]

Country	Region	Major product	Main by-products
South Africa	Bushveld Complex	Pt	Pd, Rh
Russia	Noril'sk, Siberia	Cu, Ni	Pd, Pt
Canada	Sudbury, Ontario	Pd	Pt, Ni
USA	Stillwater, Montana	Ni	Cu, Pd
Zimbabwe	Great Dyke	Pt	Pd, Ni

1.1.3 Regions mined by Anglo Platinum in South Africa[6]

The Bushveld Complex

This was formed some 2,000 million years ago and is an irregularly shaped saucer 370 km across and its center is buried underneath the ground but the rim is exposed to the surface. It has series of layers three of which contain significant quantities of PGM's,

1. The Merensky Reef which has been a principal source of PGM's since 1925
2. The Upper Group 2 (UG2) Reef and
3. The Platreef.

The last two reefs were not exploited on a large scale until the early 1990's.

The chemical similarities of these elements leads to their tendency to be concentrated together as a result of natural geological processes and this meant that their discoveries as individual elements was inextricably linked. The high resistance of the PGM's to oxidation and corrosion led them to be classified as "Noble" elements together with gold and silver while their scarcity and consequent value causes them to be called "Precious" metals.[7,10]

Anglo Platinum is currently reviewing a number of options to enable it to maximize future production from the Merensky Reef. Declining Merensky production has been greatly offset by the increase in output from the UG2 project.[5]

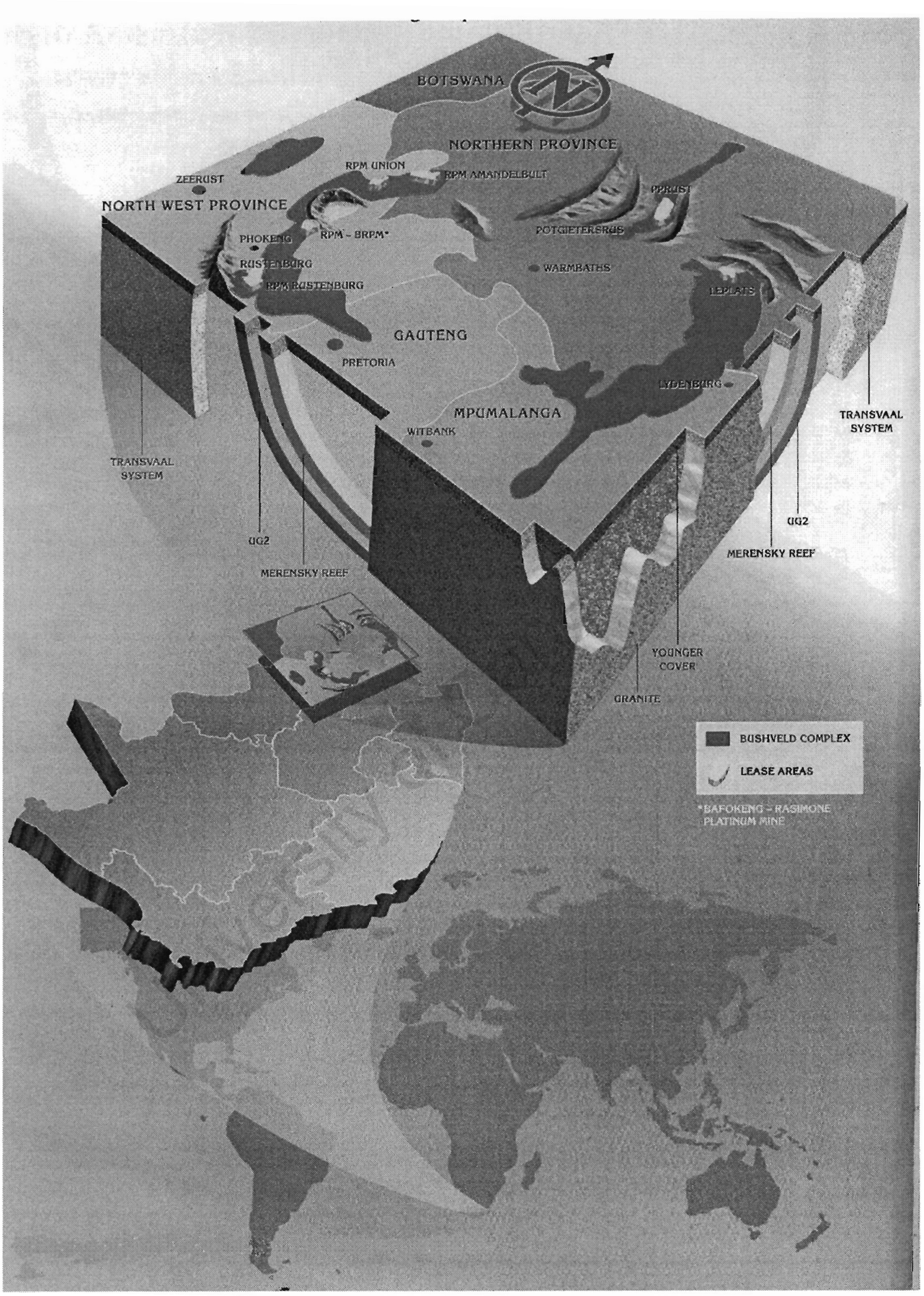

Figure 1.1 Location of Anglo Platinum managed operations in South Africa[8]

	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
Atomic Number	44	45	46	47	76	77	78	79
Atomic Mass	101.07	102.91	106.42	107.87	190.23	192.22	195.08	196.97
Melting Point (^{0}C)	2334	1964	1555	962	3033	2446	1768	1064
Boiling Point (^{0}C)	4150	3695	2963	2162	5012	4428	3825	2856
Density(g/cm^3)	12.3	12.4	12.02	10.5	*22.61	*22.65	21.45	19.31
Electronegativity	2.2	2.28	2.2	1.93	2.2	2.2	2.28	2.54
Vickers Hardness no	240	101	41		350	220	41	
Tensile Strength	165	71	17			112	14	

Table 1.1 Physical properties of the PGM's, gold and silver[9]

The mechanical properties of the six platinum metals differ greatly. Platinum and palladium are soft, ductile and resistant to oxidation and high temperature corrosion. They have wide spread catalytic uses and are often used in industry with the addition of other metals including other PGM's. Rhodium and iridium are difficult to work, but are valuable alone and in alloys. Their chemical compounds have many uses and rhodium is a particularly good catalyst. Ruthenium and osmium are hard, brittle and almost unworkable in the metallic state, with poor oxidation resistance, but are valuable as additions to metals, usually other PGM's and as catalysts.[7]

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* The measured densities of iridium and osmium show that osmium is slightly more dense than iridium, so osmium has generally been credited with being the heaviest known element. Calculations of the density from the space lattice are more reliable for these elements than actual measurements, give a density of 22.65 for iridium compared to 22.661 for osmium. At present, therefore, it is known that either iridium or osmium is the heaviest element, but the data do not allow selection between the two. (http://www.scescape.net)

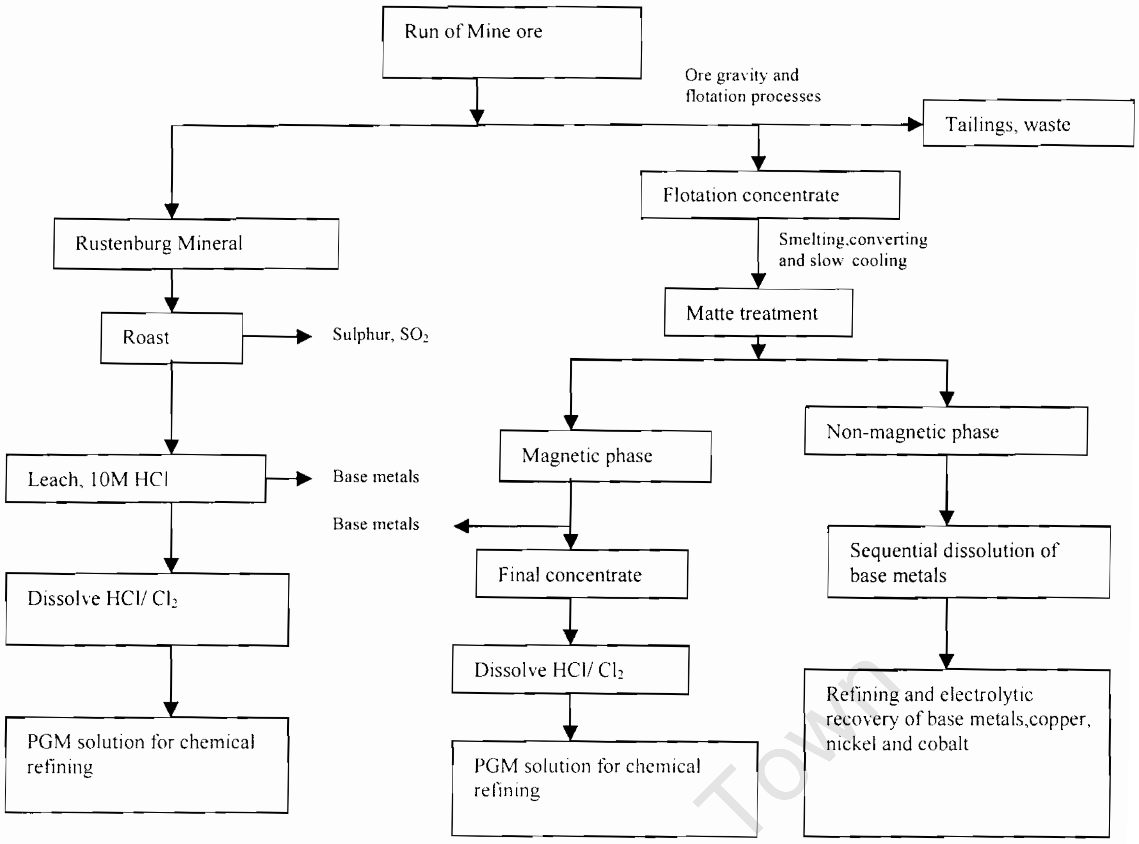

Figure 1.2 General overview of ore treatment at most refineries[4]

1.1.4 Ore extraction

With the exception of small alluvial deposits of platinum, palladium, and iridosmine (an alloy of iridium and osmium), virtually no ores exist in which the major metal is from the platinum group. Platinum minerals are usually highly disseminated in sulfide ores, particularly the nickel mineral pentlandite [$(Ni,Fe)_9S_8$]. The most common platinum-group minerals include laurite (RuS_2), irarsite [(Ir,Ru,Rh,Pt)AsS], osmiridium (Ir,Os), cooperite (PtS), and braggite [(Pt,Pd)S].

The Merensky and UG2 reefs are narrow and the working areas are too narrow to allow the use of mechanised equipment therefore the miners use hand held pneumatic drills to drill holes which are then filled with explosives. After blasting the ore is removed using scrapers and transported to the bottom of the shaft and hauled to the surface. Open–pit methods are used to mine the Platreef which is much wider than other reefs.[10]

1.1.4.1 Concentration

The ore is crushed and milled to reduce the size of the rock particles and to expose the minerals which contain the PGM's. The particles are mixed with water and reagents which include froth stabilizers, gangue depressants activators and pH or redox stabilizers. Air is pumped through the liquid, creating bubbles to which the PGM containing particles adhere. These float to the surface and are removed as a soapy froth.

Metal sulphide surfaces are more hydrophobic than metal oxide surfaces and will generally float more effectively than metal oxide minerals and also because the S^{2-} has a larger diameter than O^{2-} and metals prefer to coordinate to the sulphur atoms and there is a reduced tendency for water coordination at the surface. Copper sulphate is sometimes added to activate the surface since Cu^{2+} is octahedral and likes to coordinate to sulphur ligands. After being dried the concentrate is smelted in an electric furnace with temperatures exceeding 1500°C. During the process the matte containing the valuable metals is separated from the unwanted minerals , which form a slag and are discarded. The matte is then transferred to converters, where air is blown blown through it in order to remove iron and sulphur. Sometimes gravity separation is employed prior to flotation; this results in a concentrate containing up to 50 percent platinum metals, making smelting unnecessary.

1.1.5 Extraction and Refining

Platinum group metals are mined either on their own (which is only done in South Africa) or as a byproduct of nickel mining. The refining process described herein discusses the general process as performed at most refineries in South Africa.[6] There are a number of possible competitive refining flow sheets available for the PGM's and each of the major producers has evolved their current process over many years.

The PGM concentrate can be separated by a solvent extraction procedure as illustrated in scheme 1.5.

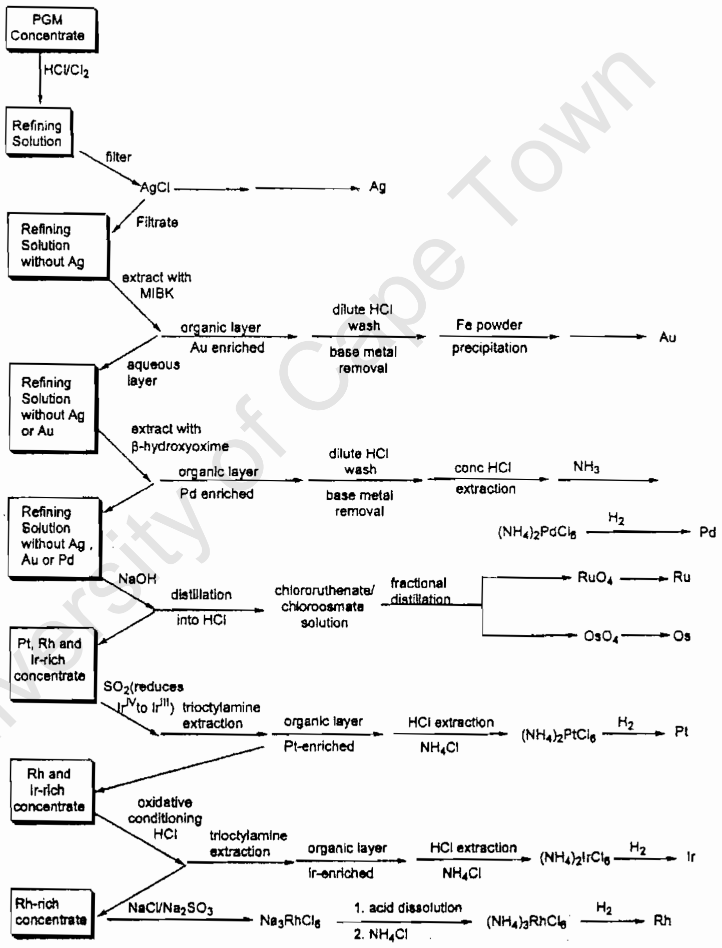

Figure 1.3 Refinement scheme for the chemical separation of PGM's[3]

1.1.5.1 Individual solubilization

The procedure for separating the platinum metals begins with a mineral concentrate obtained as described previously. This concentrate is leached with aqua regia, which dissolves the platinum and palladium and leaves the other metals as solids in the leach residue. The platinum is precipitated from solution with ammonium chloride, and the resulting crude platinum salt is recovered by filtration and then heated to decompose it to a powdered metallic form. The metal is redissolved in aqua regia, then reprecipitated with ammonium chloride and calcined to pure metal. The palladium, which remained in solution when the platinum was precipitated, is now precipitated by the addition of ammonia. After the palladium salts are recovered by filtration, they are redissolved and reprecipitated to form a pure salt, and this is converted to metallic form, usually by chemical reduction with formic acid.

The residue left over from leaching the original mineral concentrate contains rhodium, iridium, ruthenium, and osmium. This is treated with molten sodium bisulfate to convert the rhodium to rhodium sulfate.

The rhodium is then solubilized by water leaching, separated from the insolubles, and precipitated from solution by reduction with zinc powder. The crude rhodium metal product is converted to a soluble salt by treatment with chlorine and sodium chloride at high temperature, dissolved in water, precipitated with sodium nitrite, filtered, redissolved, and reprecipitated with ammonium chloride. This final precipitate is reduced to a pure metal powder.

The residue from rhodium sulfate leaching is fused with alkali nitrate salts to convert ruthenium to soluble sodium ruthenate. After filtration, the solution of sodium ruthenate is treated with chlorine gas to distill off the ruthenium as the volatile compound ruthenium tetroxide.

The ruthenium-bearing distillate is then treated with reducing agents to precipitate the ruthenium as a fine metal powder. Osmium is recovered in a similar fashion, although, unlike ruthenium, it can also be recovered by distillation from acidic solutions.

The final residue is treated with sodium peroxide to convert iridium to a form soluble in hydrochloric acid, from which it can be precipitated with ammonium chloride and calcined to metal powder.

1.1.5.2 Simultaneous solubilization

Simultaneous solubilization of all platinum metals can be accomplished by fusing the mineral concentrate obtained from copper and nickel sulfide ores with aluminum metal, dissolving the aluminum, and treating the residue with hydrochloric acid and chlorine.

This dissolves all platinum-group metals, which are subsequently separated by solvent extraction. The individual metal solutions are then treated by conventional techniques to recover the various metals in a pure state.

1.1.6 Consolidation

Irrespective of the chemical separation processes used, the platinum metals are recovered in a finely divided metallic powder form. They can be converted to massive metal form by electron-beam melting. The lower-melting-point metals palladium and platinum can be fused by induction melting techniques.

1.1.7 Assaying

Assaying ores and concentrates for platinum-group metals is extremely difficult, since the concentration of any particular metal may be less than one part per million. Initial concentration is achieved by fire assay. The assay bead is dissolved in aqua regia and the metals separated and concentrated, often by solvent extraction. Dissolution of the bead is complicated by the presence of iridium, rhodium, or ruthenium, so that special solubilizing techniques may be required. The concentrated solutions are analyzed by atomic absorption spectroscopy or photometric techniques. Arc spectroscopy is sometimes employed directly on the bead obtained from fire assay.

Osmium is the hardest of the group and has the highest melting point, but its ready oxidation is a limitation to its use as a metal. Iridium is the most corrosion-resistant of the platinum metals, while rhodium is valued for retaining its properties at high temperatures.

The separation chemistry of the platinum-group metals is among the most complex and challenging of metal separations and involves separating and purification of the six PGM's, plus gold and small amounts of silver.

The soluble metals- gold, palladium and platinum, which dissolve in hydrochloric acid and chlorine gas are the first to be extracted and the insoluble PGM comes out next with rhodium usually last.

1.1.8 Summary of extraction of refinery materials at most refineries

The insoluble residue from treatment of platinum metal concentrates with aqua regia is smelted with lead carbonate and then treated with nitric acid to remove silver as the nitrate.

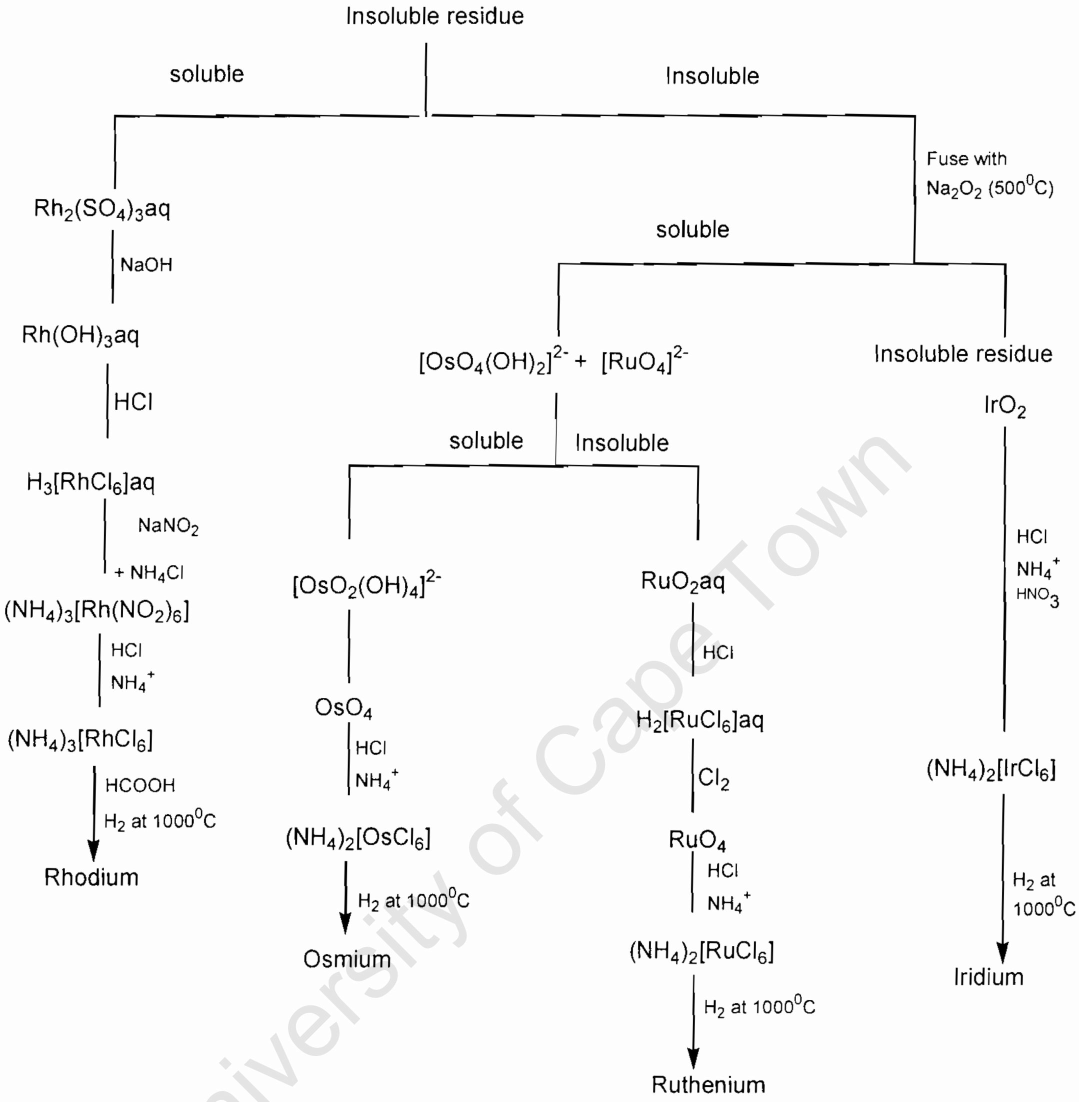

Figure 1.4 General treatment of the residues at most refineries [11]

The resulting mass is extracted with water and the insoluble fraction treated for iridium and rhodium while the soluble portion contains perosmate and ruthenate ions, $[OsO_4(OH_2)]^{2-}$ and $[RuO_4]^{2-}$ the osmium may at this stage be removed by distillation with nitric acid, which gives the tetroxide or alcohol may be added to the alkaline solution precipitating the ruthenium as hydrated dioxide and reduces the perosmate to the purple potassium osmate $K_2[OsO_2(OH)_4]$. The latter can be precipitated by addition of concentrated potassium hydroxide to give the tetroxide, or treated with an alcohol, hydrochloric acid, an ammonium chloride mixture to give ammonium hexachloroosmate (IV) $(NH_4)_2[OsCl_6]$.[6,11]

1.1.9 Scope of this thesis

This thesis presents an overview of the work done using Anglo Platinum refinery materials in the synthesis of osmium and ruthenium complexes. The organisation of this thesis begins in Chapter 1 with a description of the sources of the platinum group metals, goes through their basic refining and separation methodologies. To put the work in perspective a short review of the literature reports on homogeneous catalysis by some organometallic complexes of osmium and ruthenium that have been prepared from the Anglo Platinum refinery materials will be given in Chapter 2 together with the wide variety of organic transformations that are catalysed by these metal complexes. The literature survey was evaluated with respect to first reports of osmium complexes that were first used as homogeneous catalysts, relevant growth from the days of Manchot *et al.* in the 1940's, Vaska in the 1960's, Bradford and Nyholm in the 1970's and to Sanchez-Delgado and coworkers who have since done a lot of osmium chemistry from the 1980's to the late 1990's. Recent osmium complexes that are of importance in homogeneous catalysis that have been synthesised up to the present day are also reviewed. A similar review of analogous ruthenium complexes is also discussed. Reviews of the topics were undertaken with respect to work linked to or done in this thesis.

Syntheses and characterisation of the various known osmium and ruthenium complexes is presented in Chapter 3. Most of the syntheses have been modified as the literature procedures mainly use commercially available starting materials ($RuCl_3.3H_2O$ and OsO_4) whereas most of the complexes discussed in this thesis have been prepared from Anglo Platinum refinery materials. From the literature survey it appears that no work has been reported about the preparation of the various osmium and ruthenium complexes using refinery materials.

Chapter 4 is a discussion pertaining to the experimental work presented in Chapter 3 and also includes some attempted syntheses which were not successful.

Chapter 5 gives a final overview of the research and contains conclusions of the thesis and future work that could be done with the abundant supply of the refinery materials from Anglo Platinum.

In this thesis, figures, schemes and equations are integrated within the text followed by a detailed listing of the references for each chapter.

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Chapter 2

A review of homogeneous catalysis by osmium and ruthenium complexes

2.1 Introduction

Platinum group metal catalysts are widely used in chemical processes for reactions ranging from gas phase oxidation through selective hydrogenation of chemical, petrochemical and pharmaceutical feedstocks to fuel cells for power generation.[1] All six of the platinum group elements have significant catalytic properties, however platinum, palladium, rhodium and ruthenium are the most widely used.[2] Although platinum group metals are more expensive in initial cost than base metal catalysts, they often prove to be more reactive and require less severe reaction conditions. In addition the spent catalyst can be recovered and the precious metal reprocessed into fresh catalyst.

Homogeneous catalysis has penetrated almost all the areas of industrial activity. It is practised in hydrogenation, oxidation, oligomerisation, polymerisation, reactions with carbon monoxide, hydrocyanation, isomerisation, metathesis, hydrogenolysis, carbon-carbon and carbon-heteroatom coupling. The science of homogenous catalysis has made dramatic breakthroughs in the past 20 years, especially in the areas of asymmetric catalysis, oxidation catalysis, carbonylation reactions, and olefin metathesis reactions. All these areas involve the utilisation of platinum group metal complexes as catalysts or as catalyst precursors.

A homogeneous catalytic cycle or process can be written as outlined below:

$$A + B \rightleftharpoons C$$

Homogeneous reactions are complex and proceed through multiple reaction steps linked in a closed cycle. The catalytic cycle describes a number of different organometallic species, all of which are essential to the catalytic cycle

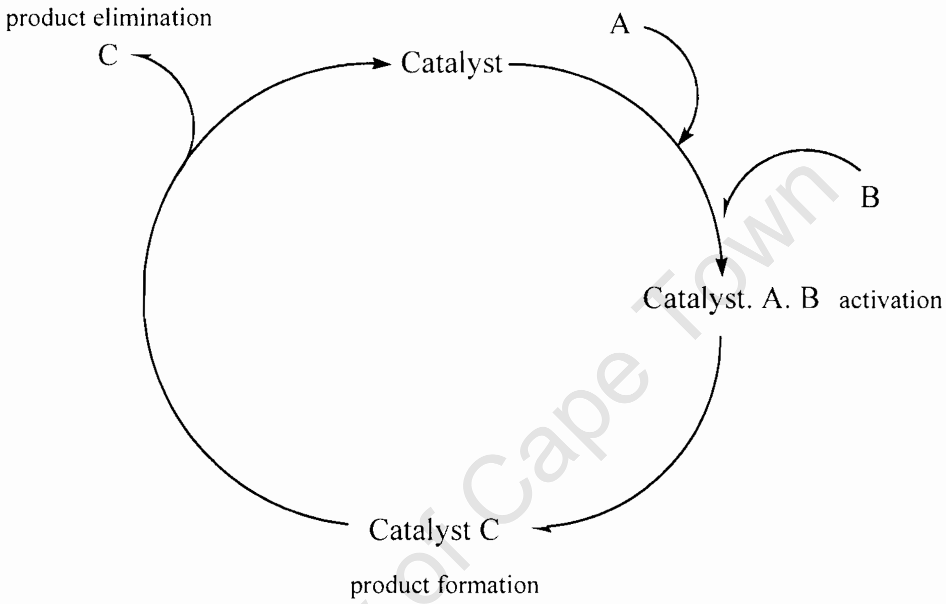


Figure 2.1 Catalytic cycle

The principles of homogeneous catalysis are based on coordinative unsaturation, oxidative addition and insertion reactions, reductive elimination as well as attacks by electrophiles and nucleophiles on coordinated ligands.

The main prerequisites of a homogenous catalyst are that:

a) it should not react in an irreversible way with the substrate,

b) it should provide a low-energy path for the formation of the intermediates,

c) the intermediates should not be kinetically too stable.

2.2 Homogeneous versus heterogeneous catalysts

Advantages of homogeneous catalysts over heterogeneous catalysts are faster kinetics, good accessibility of catalytic sites, stereoselectivity, the possibility of gaining an understanding of the catalytic process and also a possibility of inducing a catalyst to a product or process.

Heterogeneous catalysts have multiple active sites and result in multiple products and broad molecular weights in the case of polymers and a description of mechanistic studies is a very difficult task unlike in homogeneous catalysis where catalytic species are similar and catalytic transitions are also identical which makes it an easier task to work out the mechanism of the reaction.

Table 2.1 Characteristics of homogeneous and heterogeneous catalysts[3]

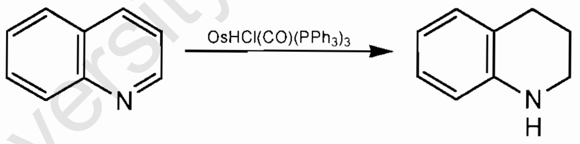
Homogeneous catalysts	Heterogeneous catalysts
Difficult separation	Easy separation
Low thermal stability	High thermal stability
High activity	Lower activity
Well defined catalyst	Poorly defined catalyst
No diffusion limitation	Limited by diffusion processes

Homogeneous catalysis by platinum group metals has been traditionally dominated by ruthenium, rhodium and palladium. In the past few years, a number examples of organic transformations catalysed by osmium have emerged in the literature, and show that this relatively unexplored area offers considerable potential to be exploited in the near future.[13]

2.3 Homogeneous catalysis by osmium complexes

The trinuclear cluster $Os_3(CO)_{12}$ is a very useful precatalyst for alkene isomerisation, alkyne cyclotrimerisation,[4] C-N bond activation,[5] hydroformylation,[6-7] water-gas shift,[6-8] and CO hydrogenation[9] reactions in solution. An unsaturated dihydrido derivative $Os_3H_2(CO)_{10}$ has also been reported by Shapley to hydrogenate olefins in solution.[10]

For various reasons, the catalytic applications of osmium complexes has been studied much less than other PGM complexes. But in the past few years, a number of interesting examples of organic transformations that are catalysed by osmium complexes have emerged in the literature mostly from the Sanchez-Delgado group indicating that this relatively undeveloped field offers catalytic potential to be exploited in the future. The ability of $OsHCl(CO)(PPh_3)_3$ to function as a catalyst in the hydrogenation of C=C bonds was first briefly mentioned by Vaska[11] and Mitchell[12]. Olefin hydrogenation by the same complex has also been reported in patent literature.[13] $OsHCl(CO)(PPh_3)_3$ has also been shown to be an efficient catalyst precursor for homogeneous hydrogenation of the heterocyclic ring in quinoline and benzothiophene as shown in eqns.1 and 2.[13]



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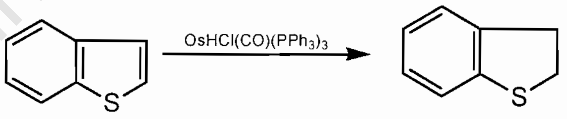
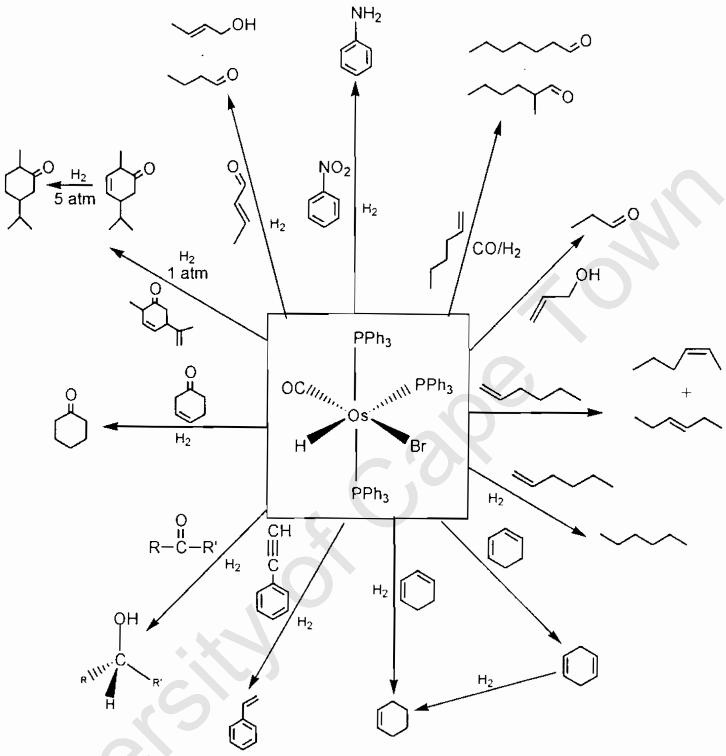


(2)

The other very important mononuclear complex of osmium is $OsHBr(CO)(PPh_3)_3$ which was first reported by Vaska in 1961.[14] This complex was obtained by the reaction of the osmium(IV) halides with triphenylphosphine and an alcohol acting as the reacting solvent and the preparation was conducted in vessels open to the atmosphere.

The versatile reactivity of this compound, its selectivity properties and structure have now been well developed by Sanchez-Delgado and coworkers[15-18] and demonstrates that homogeneous catalysis by osmium complexes is more promising than hitherto realised provided that the ligands and reactions conditions are chosen appropriately. They have also illustrated that the complex is easy to prepare, handle and recycle.



Scheme 2.1[13]

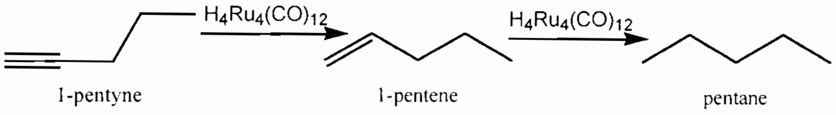
Olefin hydrogenation by use of $[OsH(Cl)(CO)(PPh_3)_3]$ as well as hydroformylation catalysed by an unspecified osmium salt complexed by phosphine ligands have also been claimed in patent literature.[19]

In 1986 Sanchez-Delgado and coworkers demonstrated that tetranuclear osmium clusters $H_3Os_4(CO)_{12}(I)$, $H_4Os_4(CO)_{12}$, $[H_2Os_4(CO)_{12}(I)]^-$ and $[H_3Os_4(CO)_{12}]^-$ are efficient catalyst precursors for the hydrogenation of styrene to ethylbenzene under moderate reaction conditions. The complexes are also known to be thermally and oxidatively highly stable.[20]

In 1996 Min-Kyo Cheong and Moo-Jin Jun reported the homogeneous hydrogenation of propionaldehyde to propan-1-ol using the osmium(II) complexes containing chelating phosphine ligands, $OsHCl(CO)(PPh_3)(L\text{-}L)$ [L-L=$Ph_2P(CH_2)_nPPh_2$ (n=1, 2, 3), $Ph_2PCH{=}CHPPh_2$, $Ph_2PFe(C_5H_4)_2PPh_2$] and $[OsH(Cl)(CO)(PPh_3)_3]$ as catalysts[21]. All the compounds showed good catalytic activity under reaction conditions conducted at 110°C and hydrogen pressure of 20 atm. All the other complexes showed higher catalytic activity than $OsHCl(CO)(PPh_3)_3$ which does not have a chelate ring which suggests that for the osmium complexes the bidentate ligand does not easily dissociate due to the chelate effect in the initial steps.The complex which had the largest chelate ring involving a ferrocene moiety, was found to have the highest catalytic activity since the dissociation of the monomeric phosphine ligand from the catalyst precursor was easier than for other complexes with smaller chelate rings in the initial step of the reaction mechanism.[21]

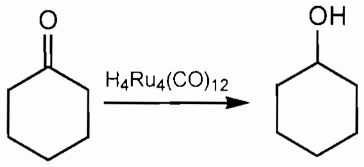
2.4 Homogeneous catalysis by dodecacarbonyltetrahydridotetraruthenium

A toluene solution of $H_4Ru_4(CO)_{12}$, at 80°C under H_2 at atmospheric pressure catalyses the hydrogenation of 1- and 2-pentyne to 1- and 2-pentene and finally the pentenes are converted to pentane.[22]



The most active species is the $H_4Ru_4(CO)_{12}$ which coordinates to the organic substrate by cleavage of Ru-CO bonds. This system can be improved by using higher hydrogen pressures in order to enhance the rate of hydrogenation compared to the rate of pentene isomerisation.[23]

Cyclohexanone is reduced to cyclohexanol in the presence of $H_4Ru_4(CO)_{12}$ in THF under fairly severe conditions, 100°C and 100 atm of H_2.[24] Other solvents were also tried for the system but these gave a range of products e.g high hydrogenation rates accompanied by lower selectivities were obtained in alcohols, and with methyl alcohol the only product formed is methyl ether. In hydrocarbons very good selectivity was combined with a very low reaction rate.



After the hydrogenation of cyclohexanone in THF the catalyst could be recovered unchanged and this suggests that the catalyst retains the initial arrangement of the metal atoms in the molecule throughout the reaction.[24] The solvent assists the reaction by involvement in the catalytically active intermediate. It was also noted that activity was decreased by the partial replacement of CO groups in the $H_4Ru_4(CO)_{12}$ with phosphine, thus progressive replacement of the carbonyl ligands by phosphines caused a decrease in hydrogenating activity.[24]

Catalytic reduction of nitrobenzene to aniline using carbon monoxide and water occurs in the presence of $H_4Ru_4(CO)_{12}$.[25]

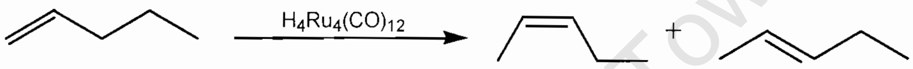
$$RNO_2 + 3CO + H_2O \xrightarrow{H_4Ru_4(CO)_{12}} RNH_2 + 3CO_2$$

$H_4Ru_4(CO)_{12}$ is a catalyst precursor in alkaline aqueous ethoxyethanol solution for the water gas shift reaction. Aqueous triethylamine has also been used in the reaction.[26]

$$H_2O + CO \xrightarrow{H_4Ru_4(CO)_{12}} H_2 + CO_2$$

The catalyst species present under the reaction conditions is believed to be the carbonyl hydride anion $[Ru_4H_3(CO)_{12}]^-$. A possible catalytic cycle involves initial nucleophilic attack of H_2O or OH^- on the coordinated CO, followed by rearrangement and decarboxylation to give hydridic species from which H_2 is eliminated in a CO-assisted rate-limiting step.

$H_4Ru_4(CO)_{12}$ catalyses double bond migration in pent-1-ene at 50°C, giving cis-pent-2-ene 60% and trans-pent-2-ene 40%.[27]

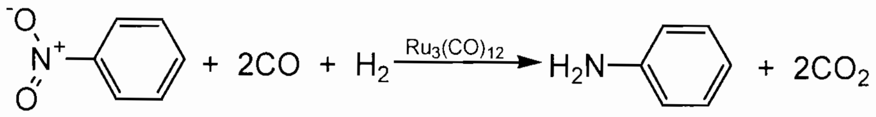


The initial conversion of pent-1-ene is largely decreased with increasing CO partial pressure and also hydrogen, weak acids and polar substances. A metal hydride addition-elimination mechanism involving σ alkyl intermediates has been suggested. The carbonyl groups can be substituted by phosphine or phosphite ligands and the effect causes a decrease in conversion of pent-1-ene. Solvent also has an effect on isomerisation of pent-1-ene as coordination of alkenes occurs by displacement of solvent.[28]

2.5 Homogeneous catalysis by dodecacarbonyltriruthenium

$Ru_3(CO)_{12}$ catalyses the hydrogenation of CO to methanol and methyl formate under severe conditions of temperature and pressure (225-275°C, 100-180 atm). Under mild conditions carboxylic acid solutions of $Ru_3(CO)_{12}$ react with mixtures of CO and H_2 to give methanol. The mechanism involves a mononuclear hydrido-ruthenium species. The carboxylic acid acylates a coordinated formaldehyde intermediate forming a glycol precursor. The intermediates in the cycle are dinuclear hydrido-ruthenium complexes containing O-donor ligands.[25]

Solutions of $Ru_3(CO)_{12}$ are also catalyst precursors for the reduction of nitrobenzene to aniline by carbon monoxide and hydrogen.[29]



The possibility that the first steps of the reduction sequence may be carried out by hydrogen requires the use of a metal catalyst which is capable to activate molecular hydrogen and to form a rather labile hydrido compound. In consideration to the labile character of second-row transition metals, the ruthenium carbonyls appear to be better catalysts for the reduction of nitrobenzene by making use of the $CO \rightarrow CO_2$ pathway than both iron and osmium.[29]

The role of carbon monoxide is not only to avoid the decomposition of the catalyst at high temperatures under hydrogen pressure, but carbon monoxide directly participates in the reduction of nitrobenzene. The reaction mechanism that was proposed by L'Eplattenier and coworkers[29] suggests that a phenylnitrene intermediate stabilised by bonding to ruthenium in a binuclear complex undergoes either hydrogenolysis to give aniline or CO insertion and hydrogenolysis to give aniline.

Catalytic reduction of nitrobenzene to aniline can also be carried out using phase transfer catalysis as was reported by Alper and Amaratunga.[30]

$$RNO_2 \xrightarrow[CH_3OCH_2CH_2OH,\ PhCH_2N(C_2H_5)^+Cl^-]{Ru_3(CO)_{12},\ CO,\ NaOH,\ C_6H_6} RNH_2$$

Amines were obtained in high yields at room temperature and atmospheric pressure with benzyltriethylammonium chloride as the phase transfer catalyst in an aqueous base organic solvent system. The purpose of the phase transfer catalyst was to accelerate the rate at which the benzyltriethylammonium carbonylruthenate cluster intermediate was formed. They also noted that the concentration of the sodium hydroxide (5M) was very critical since low or very high concentrations resulted in lower yields of anilines.

The reaction was also noted to occur even in the absence of 2-methoxyethanol but this also had the effect of lowering the yield. Also of importance was that nitro compounds with hindering groups, such as 2,6-dimethylnitrobenzene resulted in lower yields. [30]

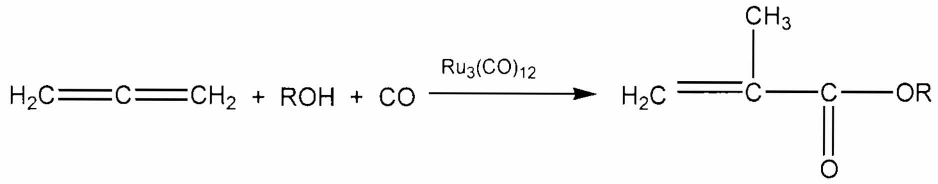
$Ru_3(CO)_{12}$ is a catalyst precursor for the hydroformylation of linear and branched olefins as well as of cyclohexene. The reaction is slow and accompanied by hydrogenation of the olefin substrate.[31]

$Ru_3(CO)_{12}$ is a catalyst precursor for the water gas shift reaction.[32] There are a broad range of catalysts for this reactions which have been studied and the activity of the $Ru_3(CO)_{12}$ has been noted to be very different in acidic or alkaline environment.[72]

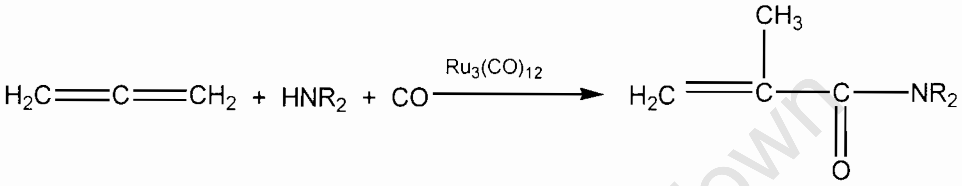
$$H_2O + CO \overset{Ru_3(CO)_{12}}{\rightleftharpoons} H_2 + CO_2$$

The principal species under the reaction conditions are the trinuclear anion $HRu_3(CO)_{11}^-$ and the tetranuclear anion $H_3Ru_4(CO)_{12}^-$. The catalytic mechanism is reported to involve nucleophilic attack of water on the coordinated CO followed by decarboxylation to give hydridic species from which H_2 is eliminated in a rate limiting step.[31]

In 2002 Zhou *et al.* reported that $Ru_3(CO)_{12}$ effectively catalyses intermolecular alkoxy- and amino-carbonylation of allenes under mild conditions producing a variety of methacrylates and methacrylamides, in good yields with an atom economy of 100%.[69]



$$H_2C{=}C{=}CH_2 + ROH + CO \xrightarrow{Ru_3(CO)_{12}} H_2C{=}C(CH_3){-}C({=}O){-}OR$$

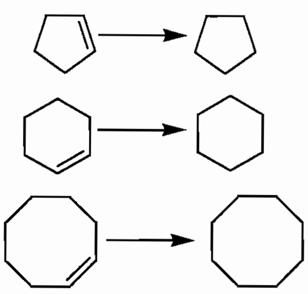


$$H_2C{=}C{=}CH_2 + HNR_2 + CO \xrightarrow{Ru_3(CO)_{12}} H_2C{=}C(CH_3){-}C({=}O){-}NR_2$$

The methacrylates and methacrylamides are obtained in quantitative yields and no polymeric products are detected at all.[70] Reactions at very high or low temperature decrease the yield together with solvents like THF or dioxane.

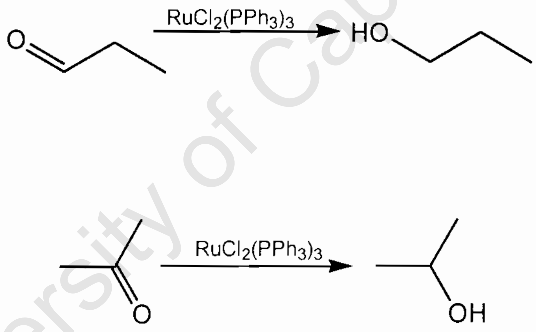
2.6 Homogeneous catalysis with dichlorotris(triphenylphosphine)ruthenium(II)

The ruthenium(II) complex $RuCl_2(PPh_3)_3$ catalyses the hydrogenation of both olefins and acetylenes such as hept-1-ene and hex-1-yne at 25°C and 1 atm in benzene-ethanol (1:1) solutions.[33] Other substances that have been catalysed by the complex include the cyclic hydrocarbons as shown below.[34]



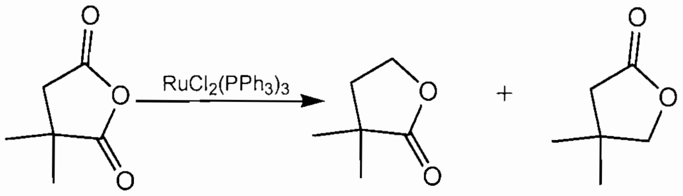
The active species is the hydride [$RuHCl(PPh_3)_3$] and the alcohol acts as a reducing agent in the formation of this intermediate.[34]

$RuCl_2(PPh_3)_3$ also catalyses the homogeneous hydrogenation of aldehydes to alcohols.[35] α, β- Unsaturated aldehydes are selectively hydrogenated to the corresponding unsaturated alcohol. Few examples of the reductions are known and most of them involve use of cobalt,[36] rhodium[37] or iridium[38]. Aliphatic as well as aromatic aldehydes are reduced rapidly at 100°C and 70 atm H_2 with selectivities close to 100% and it was noted that no hydrogenation occurs at 25°C under hydrogen at atmospheric pressure.



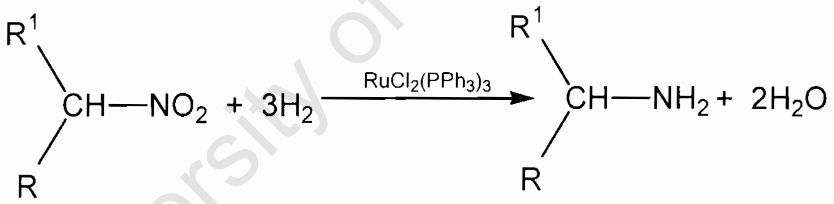
Spectroscopic evidence indicated that stoichiometric decarbonylation of the aldehyde occurs during the hydrogenation cycle and the active species being the ruthenium-hydride complexes. It was also noted that addition of small amounts of water increased the rate of the reaction.[35]

Decarbonylation of cyclic anhydrides to lactones is also catalysed by $RuCl_2(PPh_3)_3$.[39] The metal hydride reduction of unsymmetrical cyclic anhydrides to lactones usually occurs at the more hindered carbonyl group. However symmetrical cyclic anhydrides can be converted in good yield into the corresponding lactones by reduction from the less hindered side.[40]



The highest degree of regioselectivity seems to occur when there are two subtituents on the hindered carbon atom adjacent to the carbonyl group. When there is one substituent the regioselectivity is much less pronounced. In cases where each carbon atom adjacent to the carbonyl groups is fully substituted reduction occurs from the less hindered side.[41]

$RuCl_2(PPh_3)_3$ has also been used in the selective hydrogenation of nitroalkanes to amines, in good yields and conversions.[42]



$$\overset{R^1}{\underset{R}{CH}}-NO_2 + 3H_2 \xrightarrow{RuCl_2(PPh_3)_3} \overset{R^1}{\underset{R}{CH}}-NH_2 + 2H_2O$$

The preferred reaction conditions for the amine synthesis (50-150 atm of H_2, 90-130°C, excess alkali) favour the formation of the intermediate hydrochlorotris(triphenylphosphine)ruthenium(II) complex and the basic conditions favour the deprotonation of the nitroalkane to its anionic form.[43]

Nitroalkane hydrogenation catalysed by solutions of $RuCl_2(PPh_3)_3$ has advantages over other methods for reducing nitroalkanes in that this method has good yields of alkylamine obtained, improved catalyst turnover and there is also no need for stringent reaction conditions.[42]

The complex $RuCl_2(PPh_3)_3$ is an active catalyst for the exchange of D_2 with compounds containing active hydrogen atoms such as acetic acid and methanol at ambient conditions.[44]

$$RH + D_2 \xrightarrow{RuCl_2(PPh_3)_3} RD + HD$$

Other analogous compounds of $Pt^{0,II}$, $Pd^{0,II}$, Ni^{II} and Fe^{II} are inactive. The catalytic activity is strongly dependent on the identity of the metal atom i.e its position in the periodic table, oxidation state, d^n configuration and the nature of the ligands.[44]

$RuCl_2(PPh_3)_3$ catalyses the hydrogenation of oxygen to form water in toluene solutions under ambient conditions.[45]

$$H_2 + 0.5O_2 \xrightarrow{RuCl_2(PPh_3)_3} H_2O$$

Water was identified as the only product of the reaction, by gas chromatography and through absorption by $CuSO_4$.

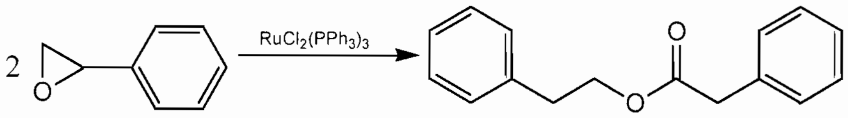
$RuCl_2(PPh_3)_3$ catalyses transfer hydrogenolysis of CCl_4 to $CHCl_3$ by propan-2-ol, benzyl alcohol or cyclohexanol.[46]

$$2R^1R^2CHOH + CCl_4 \xrightarrow{RuCl_2(PPh_3)_3} R^1R^2CO + CHCl_3 + R^1R^2CHCl + H_2O$$

$RuCl_2(PPh_3)_3$ also catalyses the addition of CCl_4 to olefins to give 1,1,1,3-tetrachloro adducts and hydrogenolysis of the latter to give the corresponding trichloro compounds.[47]

$$R^1CH{=\!=}CHR^2 + CCl_4 \longrightarrow R^1CHClCH(CCl_3)R^2$$

$RuCl_2(PPh_3)_3$ catalyses the dimerisation of terminal epoxides to carboxylic esters at 180°C.[48]



Dimerisation takes place at the terminal carbon atom and this indicated that the hindered, rather than the unhindered, epoxide C-O bond is cleaved and only the terminal hydrogen atoms are essential in catalysis.

The epoxide adds oxidatively to the bisphosphine complex formed by dissociation of triphenylphosphine in $RuCl_2(PPh_3)_3$.

$$RuCl_2(PPh_3)_3 \rightleftharpoons RuCl_2(PPh_3)_2 + PPh_3$$

Dissociation is then followed by electrophilic addition of a second epoxide molecule to the CO group of the resulting acyl hydride to an alkyl hydride followed by reductive elimination to give the ester and regeneration of the catalyst.

$RuCl_2(PPh_3)_3$ is an effective catalyst for the alcoholysis of diarylsilanes.[49]

$$Ph_2SiH_2 + MeOH \xrightarrow[C_6H_6,\ 20^0C]{RuCl_2(PPh_3)_3} Ph_2SiH(OMe) + H_2$$

It also catalyses the addition of diarylsilanes to ketones.[49]

$$Ph_2SiH_2 + Me_2CO \xrightarrow[C_6H_6,\ 20^0C]{RuCl_2(PPh_3)_3} Ph_2SiH(OCMe)$$

$RuCl_2(PPh_3)_3$ catalyses hydrogen transfer from triethylsilane to polychloroalkanes.[50]

$$Et_3SiH + CCl_4 \xrightarrow{RuCl_2(PPh_3)_3} CHCl_3 + Et_3SiCl$$

Secondary amines R_2NH have been reported to disproportionate to RNH_2 and R_3N in the presence of $RuCl_2(PPh_3)_3$.[51]

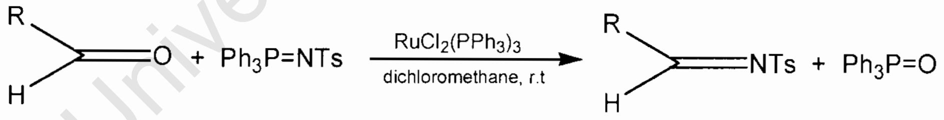
Since their discovery about 40 years ago, the ruthenium(II) triphenylphosphine complexes $RuX_2(PPh_3)_3$ (X= Cl or Br) have attracted a lot of attention.[52,53] Molecular ruthenium complexes have promoted a large variety of improved catalytic reactions. In the field of alkene metathesis alkylidene ruthenium complexes have proven to have high catalytic activity associated to high tolerance towards a variety of functional groups.[52,53] The reaction of the complex $RuCl_2(PPh_3)_3$ with diazoalkanes has allowed the synthesis of the alkylidene ruthenium complex $RuCl_2(=CHR)(PR_3)_2$ and Grubbs has shown that the complex $RuCl_2(=CHPh)(PCy_3)_2$ is an efficient catalyst for alkene metathesis.[52,55] The first Grubbs catalyst was prepared in 1992 but it had limited activity and this led to further refinements in 1996 and led to the design of the $16e^-$ alkylidene-ruthenium catalyst precursors of the general formula $RuX_2(=CHR)(L^1)(L^2)$[55-57] or a simple representation as $RuCl_2(=CHC_6H_5)\ (PCy_3)_2$.

Three years later Grubbs introduced an even better ruthenium catalyst, the second-generation Grubbs catalyst where one of the tricyclohexylphosphines is replaced with an N-heterocycle ligand.[58] Since its introduction, Grubbs catalyst has found a variety of uses in organic synthesis such as the synthesis of epothilones, preparation of carbohydrate-containing polymers and many more examples continue to appear in literature. The major advantage of the ruthenium catalysts is that they are easier to handle and reactions can be run at mild conditions. Recently Grubbs has developed functional group tolerant catalysts that have led to new applications in ring closing metathesis, cross metathesis and material synthesis.[73]

The catalytic activation of inert C-H bonds has also been promoted by ruthenium catalysts and there is now a possibility of insertion of a variety of molecules for the functionalisation of aromatic compounds and alkenes.[59]

Ruthenium catalysts also promote the selective anti-Markovnikov additions of alkyne vinylidene-ruthenium intermediates.[60-62] Ruthenium catalysts also control regioselective oxidative couplings of unsaturated substrates generating C-C bond formation reactions[63,64] which include carbonylation reactions.[65] They constitute a family of versatile catalyst precursors as they promote combinations of molecules with atom economy.[66-68] The versatility arises due to electron richness and steric hindrance that is brought about by the C_5R_5 ligand and also from the lability of the L_2 and X ligands.

Recently in 2004 Jain and co-workers reported a novel imido-transfer reaction of aldehydes using $RuCl_2(PPh_3)_3$ as the catalyst under mild reaction conditions and good yields of products were obtained.[71]



Aromatic aldehydes with electron withdrawing groups were found to be more reactive and required shorter reaction times.[71]

The mechanism of the reaction has not been yet understood at the moment but they believe it to involve the formation of a ruthenium-imido intermediate followed by the transfer of the imido group to the carbonyl moiety giving the corresponding aldimide.

2.7 Concluding remarks

It is very evident from the literature survey that homogeneous catalysis by ruthenium and osmium complexes is more promising than hitherto realised.[13] A number of interesting examples of organic transformations catalysed by osmium complexes have been reported, showing that this relatively unexploited field can be further pursued in the near future, such as hydrogenation, oligomerisation, hydrosilylation and hydroformylation.

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Chapter 3

Experimental

3.1 General experimental details

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques unless otherwise stated. Nitrogen gas was purified through columns of active molecular sieves (5Å) and a BASF catalyst before use on the Schlenk line.

3.2 Solvents and reagents

All solvents were distilled prior to use by standard literature procedures and were stored under nitrogen in Teflon sealed storage bottles. Table 3.1 summarises the drying agents used in the purification of used solvents.

Solvent	**Drying Agent**	**Distillation**	**Colour**
Dichloromethane	CaH_2	Yes	None
Diethylether	Na / benzophenone	Yes	Blue
Ethanol	CaO / Mg / MgO	Yes	None
Heptane	Na	Yes	None
Methanol	Mg turnings / I_2	Yes	None
Pentane	Na / benzophenone	Yes	None
Tetrahydrofuran	Na / benzophenone	Yes	Blue
Toluene	Na	Yes	None

Table 3.1 Purification of solvents

The starting materials potassium osmate $K_2[OsO_2(OH)_4]$, ammonium hexachlororuthenate(IV) $(NH_4)_2[RuCl_6]$ and an acidic ruthenium solution dihydrogen hexachlororuthenate $H_2[RuCl_6]$ containing about 38g/l of ruthenium metal were all obtained from Anglo Platinum Corporation and these are refinery materials. Ruthenium trichloride $RuCl_3.3H_2O$ was obtained on loan from Johnson Matthey. Triphenylphosphine was purchased from Lancaster and used as received. 1,2,3,4,5-pentamethylcyclopentadiene, *t*–butyl alcohol, 2-methoxyethanol, 2-(2-methoxyethoxyethanol), cycloocta-1,5-diene and dicyclopentadiene were purchased from Aldrich. Dicyclopentadiene was freshly distilled prior to use to give cyclopentadiene. Concentrated hydrochloric and hydrobromic acids were puchased from Merck. Iron(II) chloride and sodium chloride were purchased from Saarchem.

3.3 Instrumentation

Melting points were determined on the Kofler hotstage microscope (Reichart Thermovar) and are uncorrected. Microanalysis data was obtained from the University of Cape Town's Microanalytical Laboratory using a Carlo Erba EA1108 elemental analyser. Infrared Spectra were recorded on a Perkin-Elmer 1000 FT-IR spectrometer, at the University of Cape Town, in solution cells with NaCl windows in hexane, dichloromethane, chloroform or as KBr discs for solids. All data are given in wavenumbers (cm^{-1}). The electronic spectra were recorded on a Varian Cary 100 Conc ultraviolet and visible spectrophotometer in the absorbance mode using deionised water in 10 mm cells. Carbonylation reactions were carried out in a 200ml Parr autoclave. Because of the highly toxic nature of carbon monoxide and flammable nature of hydrogen gas, procedures were carried out in a well-ventilated fumehood. The autoclave room was also well-ventilated and also equipped with a Dräger Multiwarn II, which is a portable gas measuring instrument for the continous monitoring of the concentrations of several gases in the ambient air.

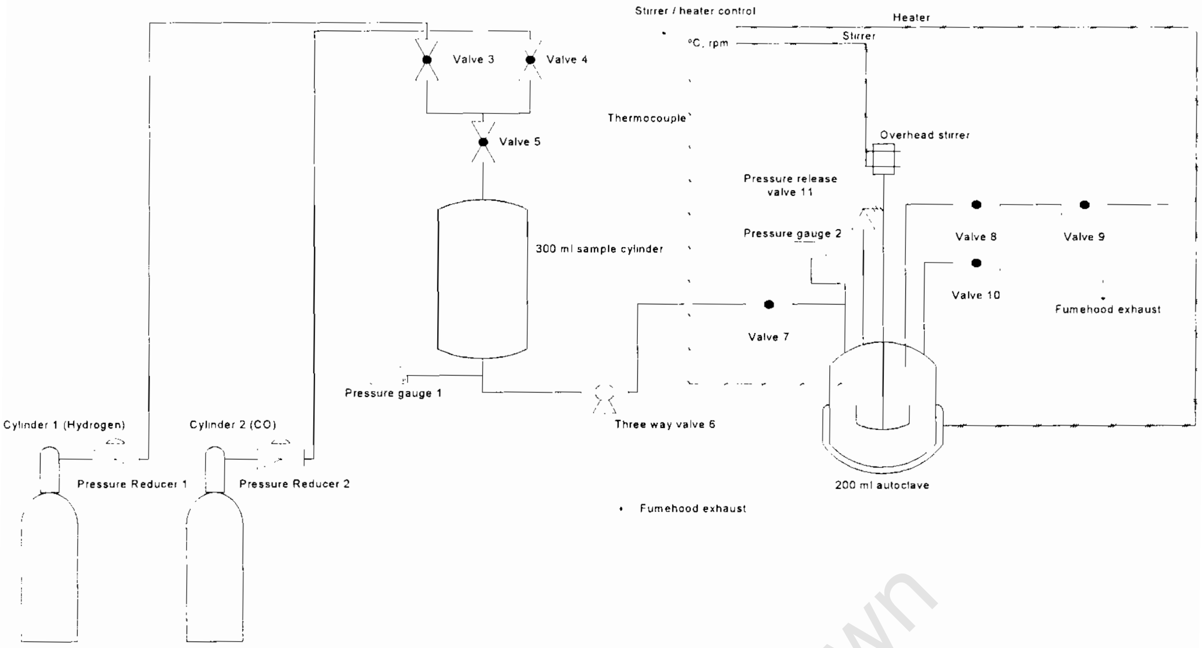
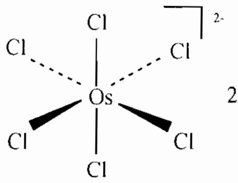


Figure 3.1 Schematic representation of the 200ml Parr Autoclave

3.4 Experimental details

3.4.1 Compounds prepared from potassium osmate(VI) $K_2[OsO_2(OH)_4]$

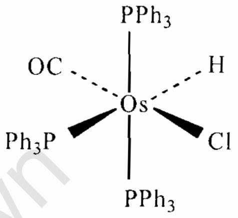
3.4.1.1 Synthesis of $(NH_4)_2[OsCl_6]$ [1]



A modified literature procedure by Dwyer and Hogarth was followed.[1] Potassium osmate (5.00 g, 13.57 mmol) was added to a mixture of iron(II) chloride (50.00 g, 251.50 mmol) and concentrated hydrochloric acid (300 ml, 37%). After heating on a steam bath for 4 h with constant stirring the solution formed a blood-red yellowish colour and was taken off the steam bath, before addition of ammonium chloride

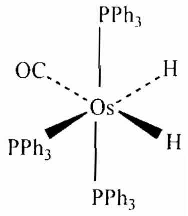
(10.75 g, 200.97 mmol) in water (50 ml). Precipitation of the complex began immediately and the mixture was allowed to cool to room temperature after which it was cooled to -15°C overnight. The precipitate was filtered using a Buchner funnel and washed with 80% ethanol (5 x 50 ml), absolute ethanol (5 x 50 ml) and dried *in vacuo* for 4 h affording red microcrystals in quantitative yield. (6.02 g, 99%), m.p 169-170°C subl. (lit.[1] m.p 170°C subl). Anal. Calc for $N_2H_8OsCl_6$: H, 1.86%; N,6.38%. Found: H, 1.67%; N, 6.36%.

3.4.1.2 Synthesis of OsHCl(CO)PPh$_3$)$_3$ [4]



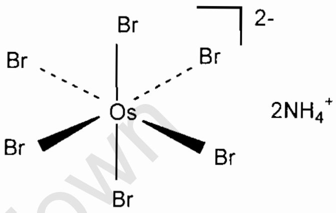
A modified literature procedure by Robinson *et al.* was followed.[2] Ammonium hexachloroosmate(IV) (1.00 g, 2.28 mmol), triphenylphosphine (7.13 g, 27.18 mmol), water (40 ml) and 2-(2-methoxyethoxyethanol) (95 ml) were added to a 250 ml beaker. The osmium salt dissolved in the water and the resulting lemon green solution was heated with stirring and the solution was heated gently until a maximum temperature of 190°C was reached. Heating was stopped (after *ca* 4 h) but stirring was continued until the solution reached room temperature and by this time there was visible precipitation of product. The white precipitate was filtered on a sintered glass filter and thoroughly washed with methanol (5 x 20 ml) and dried *in vacuo* for 2 h to give the product as white prisms.(1.29 g, 54%). Anal. Calc. for $C_{55}H_{46}ClOsP_3$: C, 63.40%; H, 4.40%; Found: C, 62.95%; H, 3.99%. IR ν_{co}(in CH_2Cl_2) 1912 (s) cm^{-1}. m.p. 180-181 °C (lit[2] 179-183°C)

3.4.1.3 Synthesis OsH$_2$(CO)(PPh$_3$)$_3$ [5]



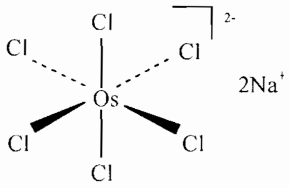
Ammonium hexachloroosmate(IV) (1.00 g, 2.28 mmol), triphenylphosphine (7.13 g, 27.18 mmol), water (40 ml) and 2-methoxyethanol (95 ml) were added to a 250 ml beaker. The osmium salt dissolved in the water and the resulting lemon green solution was heated under reflux with stirring for 1 h, during which period the colour changes to pale and a white precipitate separates. The mixture was then allowed to cool to room temperature after which the precipitate was filtered, washed with ethanol (5 x 20 ml), water (5 x 20 ml), ethanol (5 x 20 ml) and hexane (5 x 20 ml) and dried *in vacuo* for 2 h. (0.46 g, 73%). Anal. Calc. for $C_{55}H_{47}OOsP_3$: C, 63.60%; H, 4.70%; Found: C, 63.95%; H, 4.99%. IR v_{co}(in dichloromethane) 1934 (s) and v_{OsH}(in dichloromethane) 1915 (w) cm^{-1} m.p. 201-204°C (lit.[2] 202-204°C).

3.4.1.4 Synthesis of $(NH_4)_2[OsBr_6]$ [18]



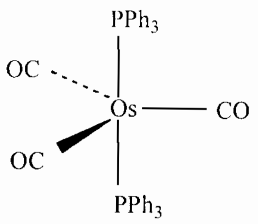
A modified literature procedure was followed.[1] Potassium osmate (0.31 g, 0.83 mmol), hydrobromic acid (10 ml, 48%) and water (10 ml) were refluxed in air for 2 h. The resulting hot solution was transferred from the round bottomed flask into a beaker and the flask rinsed with additional hydrobromic acid (10 ml). Ammonium bromide (3.00 g, 30.64 mmol) was then added and the resulting mixture was allowed to cool to room temperature before absolute ethanol (15 ml) was added whilst stirring. The solution changed from blood-red to a green black colour and was left to cool at -15°C overnight. A dark yellow solution was decanted and the black solid that had settled at the bottom of the beaker was filtered on a sintered glass filter and washed with absolute ethanol (5 x 20 ml) and dried *in vacuo* for 2 h affording black microcrystals (0.43 g, 73%). Anal. Calc. for: $N_2H_8OsBr_6$: H, 1.13%; N 3.96% Found: H, 1.25 % N, 3.89%.

3.4.1.5 Synthesis Na_2OsCl_6 [15]



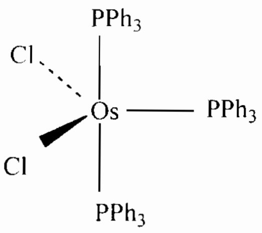
A modified literature procedure by Dwyer and Hogarth was followed.[1] Potassium osmate (5.00 g, 13.57 mmol) was weighed into a conical flask and addition of concentrated hydrochloric acid (150 ml, 37%) resulted in a red solution. Iron(II) chloride (50.00 g, 251.50 mmol) was added giving a dark orange solution which was then heated on a steam bath for 4 h with constant stirring. Sodium chloride (11.70 g, 200 mmol) was added to the solution and a reddish precipitate appeared on cooling to room temperature. The precipitate was filtered under reduced pressure and washed with 80% ethanol (5 x 50 ml), absolute ethanol (5 x 50 ml) and dried *in vacuo* for 4 h yielding very dark red microcrystals (3.78 g, 61%).

3.4.1.6 Attempted synthesis of $Os(CO)_3(PPh_3)_2$ [6]



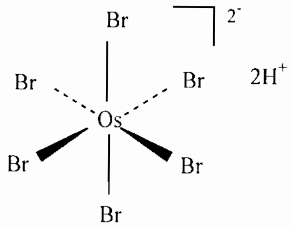
A modified literature procedure was used.[3] Triphenylphosphine (0.99 g, 3.75 mmol) and 2-methoxyethanol (37.50 ml) were boiled in a 2-necked flask for 20 min after which a solution of sodium hexachloroosmate (0.34 g, 0.60 mmol) in 2-methoxyethanol (18 ml) and formaldehyde (8 ml, 37% w/v) was added in succession. During refluxing, the colour of the reaction mixture changed from reddish brown to yellow and finally to an off-white colour. The mixture was refluxed for 1 h after which it was allowed to cool to room temperature whilst still stirring in the oil bath. The white powder was then filtered on a sintered glass filter and washed with ethanol (3 x 20 ml), water (3 x 20 ml) , ethanol (3 x 20 ml) and hexane (3 x 20 ml) before drying *in vacuo* for 2 h affording white microcrystals. Anal. Calc. for $C_{39}H_{30}O_3OsP_2$: C, 58.54%; H, 3.85%; Found: C, 58.47%; H, 3.46%. m.p. 190°C dec. IR ν_{co} (in dichloromethane): 2044 (vs) 1973 (s) and 1914 (s).

3.4.1.7 Synthesis of $OsCl_2(PPh_3)_3$ [16]



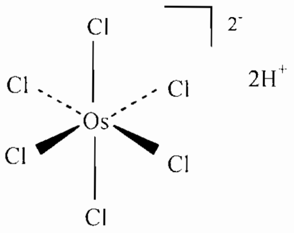
A literature procedure by Hoffman and Caulton was used.[4] Ammonium hexachloroosmate(IV) (137 mg, 0.31mmol), triphenylphosphine (414 mg, 1.58 mmol) was placed in a 2-necked round bottomed flask and charged with a solvent mixture made of *t*-butyl alcohol (25 ml) and water (10 ml). On initial addition of water the contents which were light green in colour later turned orange. When the reflux temperature reached 105°C the solution had become dark green (after *ca* 30 min). The solution was refluxed for 122 h under nitrogen and after cooling to room temperature, the pale green solid was filtered and washed with water (3 x 5 ml), methanol (3 x 5 ml) and hexane (3 x 5 ml). The solid was then dried *in vacuo* for 2 h (0.23g, 71%). Anal. Calc. for $C_{54}H_{45}Cl_2OsP_3$: C, 61.83%; H, 4.30%; Found: C, 61.75%; H,4.28%. m.p 131-133°C. (lit 132-134°C). IR (KBr): 1480 (s), 1432 (s), 1189 (m), 1158(m), 1119 (m), 1086 (s), 1027 (m), 998 (m), 745 (s), 694 (br, s), 549 (s), 518 (br,s). δ_P ^1H ($CDCl_3$) 29.24 (s).

3.4.1.8 Synthesis $H_2[OsBr_6]$ [14]



Potassium osmate (1.06 g, 2.88 mmol) and hydrobromic acid (40 ml, 48%) were refluxed in air in a round bottomed fllask for 5 h and subsequently allowed to cool to room temperature and cooled at -15°C overnight. The crystals were filtered on a sintered glass filter and thoroughly washed with absolute ethanol (5 x 40 ml) and dried *in vacuo* for 2 h affording black microcrystals. (1.70 g, 88%). The microcrystals are very soluble in cold water giving blood red solutions and are insoluble in other inorganic and organic solvents.

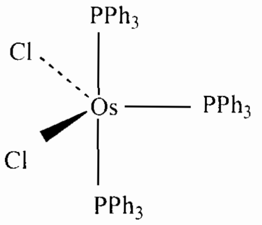
3.4.1.9 Synthesis $H_2[OsCl_6]$ [13]



A similar methodology used to prepare dihydrogen hexabromoosmate was used here replacing hydrobromic acid with concentrated hydrochloric acid (40 ml, 37%). Filtration afforded purple reddish microcrystals in quantitative yield. (1.02 g, 93%). The microcrystals are soluble in cold water giving yellowish green solutions and are insoluble in other inorganic and organic solvents.

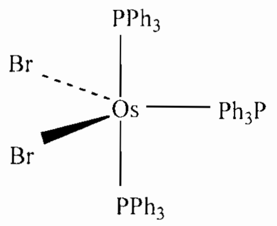
The dihydrogen hexabromoosmate $H_2[OsBr_6]$ and dihydrogen hexachloroosmate $H_2[OsCl_6]$ prepared from potassium osmate(VI) $K_2[OsO_2(OH)_4]$ were very difficult to characterise and were thus characterised by their colours[15], their solubility properties , and they were used to prepare known compounds dichlorotris(triphenylphosphine)osmium(II) $OsCl_2(PPh_3)_3$ and dibromotris(triphenylphosphine)osmium(II) $OsBr_2(PPh_3)_3$. Their electronic properties were also compared to those of similar salts.

3.4.1.9.1 Alternative synthesis of $OsCl_2(PPh_3)_3$ [16]



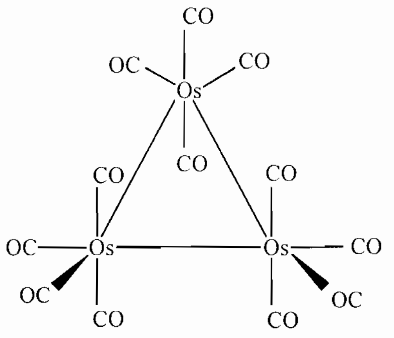
Dihydrogen hexachloroosmate (150 mg, 0.37 mmol), triphenylphosphine (450 mg, 1.72mmol) were placed in a round bottomed flask with a nitrogen inlet and water (15 ml) was added dissolving the dihydrogen hexachloroosmate giving a yellowish green solution. On addition of *t*-butyl alcohol the solution became orange and was refluxed at 105°C for 12 h under nitrogen. The reaction was allowed to cool to room temperature whilst stirring in the oil bath. The pale-green solid was filtered on a sintered glass filter and washed with water (3 x 5 ml), methanol (3 x 5 ml) and hexane (3 x 5 ml). The solid was then dried *in vacuo* for 2 h affording a dark green solid (0.25 g, 64%). Anal. Calc. for $C_{54}H_{45}Cl_2OsP_3$: C, 61.83%; H, 4.30%; Found: C, 61.65%; H,4.18%. m.p. 131-133 °C (lit.[4] 132-134 °C). IR (KBr): 1480 (s), 1432 (s), 1189 (m), 1158 (m), 1119 (m), 1086 (s), 1027 (m), 998 (m), 745 (s), 694 (br, s), 549 (s), 518 (br,s). δ_P ^{1}H ($CDCl_3$) 29.24 (s).

3.4.1.9.2 Synthesis of $OsBr_2(PPh_3)_3$ [17]



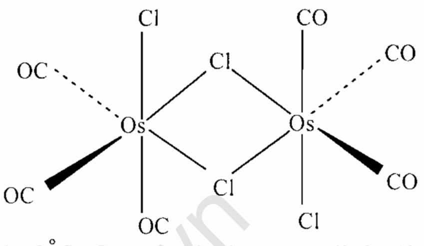
Dihydrogen hexabromoosmate (150 mg, 0.22 mmol), triphenylphosphine (450 mg, 172 mmol) were placed in a Schlenk tube. On addition of water (10 ml) the dihydrogen hexabromoosmate dissolved giving a blood red solution which was then refluxed under nitrogen for 12 h and allowed to cool to room temperature whilst cooling in the oil bath. The product was filtered on a sintered glass filter and washed with water (4 x 10 ml), methanol (3 x 10 ml) and hexane (4 x 10 ml) and dried *in vacuo* for 2 h affording a dark green solid (0.13 g, 59%). Anal. Calc. for $C_{54}H_{45}Br_2OsP_3$: C, 58.10%; 3.96%; Found: C, 59.20%; H, 3.79%. m.p 154 °C dec. IR (KBr): 1480 (s), 1431 (s), 1189 (m), 1153 (m), 1122 (m), 1082 (s), 1028 (m), 997 (m), 741 (s), 694 (br, s), 544 (s), 517 (s).

3.4.2 Synthesis of $Os_3(CO)_{12}$ [2]



The literature procedure by Johnson and Lewis, which used OsO_4 was modified.[5] Ammonium hexachloroosmate(IV) (2.00 g, 4.56 mmol) together with a zinc granule (0.56 g, 8.57 mmol) were added to a 200 ml Parr autoclave. Dry methanol (30 ml) was then added and the red mixture was purged 3 times with carbon monoxide (10 atm) of before being finally pressurised with carbon monoxide (50 atm) and heated at 125 °C for 24 h. The autoclave was turned off and allowed to cool to room temperature after which the gases were vented off slowly. The product that was obtained was filtered using a Buchner funnel and washed with acetone (5 x 10 ml) affording large yellow hexagonal crystals (0,86g, 64% yield). m.p. 223-225°C. (lit.[5] 224°C) The IR spectrum v_{co} (in dichloromethane): 2068 (s), 2034 (s), 2013 (m), and 1999 (m) cm^{-1}. (lit.[5] 2070 (s), 2036 (s), 2013 (s) and 2003 (m) cm^{-1}).

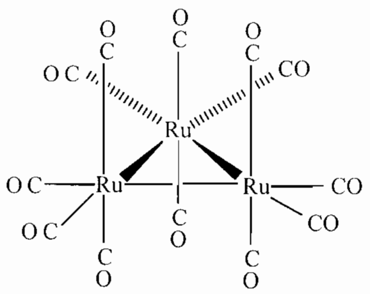
3.4.2.1 Synthesis of $[Os(CO)_3Cl_2]_2$ [3]



The literature procedure reported by Bruce *et al.* was followed.[6] Dodecacarbonyltriosmium (200 mg, 0.22 mmol), concentrated hydrochloric acid (37%, 0.21 ml) and cyclohexane (30 ml) were sealed in a tube wrapped with aluminium foil and heated at 170°C for 44 h in an oil bath placed behind a safety shield. The solvent was removed *in vacuo* affording light yellow microcrystals in good yields (199 mg, 87%) m.p. 264-266°C (lit.[6] 266°C). IR v_{co}(in CH_2Cl_2) showed bands at 2136 (s) and 2061 (s) cm^{-1}.(lit.[14] 2136 (s) and 2061 (s) cm^{-1}) IR v_{co}(in chloroform) 2135 (s) and 2063 (s) IR v_{co}(in tetrachlorocarbon) 2135 (m) and 2058 (s) (lit.[6] 2134 (s) and 2059 (s) cm^{-1}).

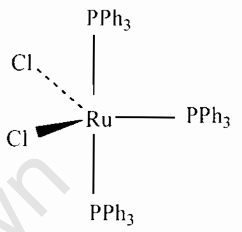
3.4.3 Compounds prepared using ruthenium trichloride trihydrate

3.4.3.1 Synthesis of $Ru_3(CO)_{12}$ [7]



The literature procedure by Johnson *et al.* was used.[7] Ruthenium trichloride trihydrate (2.50 g, 9.56 mmol) and dry methanol (100 ml) were added to a 200 ml Parr autoclave which was then purged 3 times with carbon monoxide (30 atm) before pressurising with carbon monoxide (50 atm) and heating the purple mixture at 125°C for 8 h. After cooling and depressurisation the crystals were filtered using a Buchner funnel from the mother liquor, washed with cold methanol (2 x 15 ml), dried *in vacuo* for 2 h and recrystallized from hot toluene affording orange crystals (1.703 g, 83%) m.p. 149-150°C dec. (lit.[7] 150°C dec.) IR v_{co} (in *n*-hexane) 2060 (s), 2030 (s), 2011 (m). (lit.[7] 2060 (s), 2030 (s), 2010 (m)).

3.4.3.2 Synthesis of $RuCl_2(PPh_3)_3$ [9]

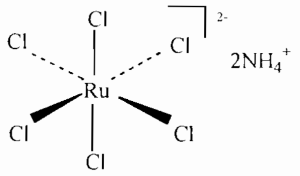


The literature procedure by Hallman *et al.* was used in this synthesis.[8] Ruthenium trichloride trihydrate (0.25 g, 0.96 mmol) was dissolved in methanol (62.5 ml) in a Schlenk tube and the mixture refluxed under nitrogen for 5 min. After cooling, triphenylphosphine (1.50 g, 5.73 mmol) was added and the solution was again refluxed under nitrogen for 3 h at 65°C. On cooling, the product was filtered under nitrogen, washed several times with degassed ether, and dried under vacuum yielding a brown product (0.735 g, 80%). Anal. Calc. for $C_{56}H_{45}Cl_2P_3Ru$: C,65.99 %; H, 4.6 %. Found: C, 65.59%; H, 4.85%. m.p 131-133°C. (lit.[8] 132-134°C).

3.4.3.3 Synthesis of $[RuCl_2(C_8H_{12})]_n$ [10]

The literature procedure by Singleton *et al.* was followed.[9] A flask containing a magnetic stirring bar and fitted with a reflux condenser was charged with a mixture of ruthenium trichloride trihydrate (1.00 g, 3.83 mmol) and cycloocta-1,5-diene (1 ml, 8mmol) in absolute ethanol (8 ml) and heated under reflux with stirring for 24 h. On completion of the reaction, the solution was cooled to room temperature and filtered under reduced pressure. Washing with diethylether (5 x 10 ml) gave a dark brown solid product in good yields (0.913 g, 85%). Anal. Calc. for $C_8H_{12}Cl_2Ru$: C, 34.30%; H, 4.29%. Found: C, 34.31%; H, 4.04%.

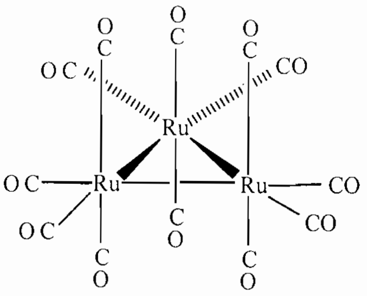
3.4.3.4 Synthesis of $(NH_4)_2[RuCl_6]$ [11]



Ruthenium trichloride trihydrate (0.50 g, 1.91 mmol) was placed into a conical flask. Concentrated hydrochloric acid (50 ml, 37% w/v) was added and the mixture turned to a dark orange colour. A six-fold excess of ammonium chloride (3.00 g, 56.13 mmol) in water (15 ml) was added and the mixture was heated on a steam bath for 4 h. The resulting solution was cooled to room temperature and decanted. The product was filtered and washed with absolute ethanol (30 × 4 ml) and dried *in vacuo* for 2 h affording dark purple crystals (0.56 g, 84%). Anal.Calc.for $N_2H_8RuCl_6$: H, 2.29%; N, 8.00%. Found: H, 2.09%; N, 8.36%.

3.4.4 Compounds prepared using ammonium hexachlororuthenate

3.4.4.1 Synthesis of $Ru_3(CO)_{12}$ [7]



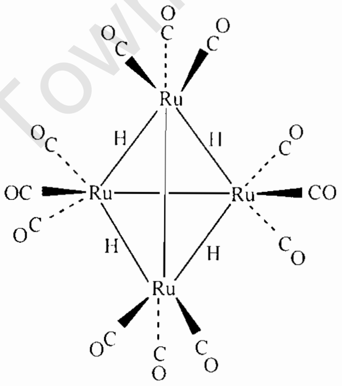
The literature procedure by Hallman *et al.* using was modified.[8] Ammonium hexachlororuthenate (5.00 g, 14.29 mmol) was combined with dry methanol (100 ml) in a 200 ml Parr autoclave and the mixture turned to a purple colour. The autoclave was sealed and purged three times with carbon monoxide (30 atm) before being finally pressurised with carbon monoxide (50 atm) and heated at 125°C for 8 h. Following cooling (~2 h) and depressurisation, the product was filtered from the mother liquor using a Buchner funnel and recrystallised from hot toluene before drying *in vacuo* for 2 h affording orange red crystals (2.29 g, 75%). IR ν_{CO} (in *n*-hexane) of the orange red crystals exhibited sharp bands at 2060 (s), 2030 (s), and 2011 (m) cm^{-1}. (lit.[8] 2060 (s), 2030 (s), 2010 (m)).

3.4.4.2 Synthesis of $[RuCl_2(C_8H_{12})]_n$ [10]

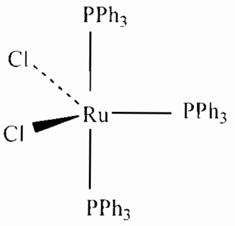
The literature procedure by Singleton *et al.* was modified.[9] Ammonium hexachlororuthenate(IV) (2.00 g, 5.72 mmol), water (20 ml), ethanol (40 ml) and cycloocta-1, 5-diene (6 ml, 48 mmol) were refluxed in air for 22 h. At this time the product had precipitated out of solution and was allowed to cool to room temperature while stirring in the oil bath. The product solid was filtered using a Buchner funnel, washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown solid (1.20 g, 75%). Anal. Calc. for $C_8H_{12}Cl_2Ru$: C, 34.30%; H, 4.29%. Found: C, 34.31%; H, 4.04%.

3.4.4.3 Synthesis of $H_4Ru_4(CO)_{12}$ [8]

Ammonium hexachlororuthenate (1.50 g, 4.29 mmol) was combined with cyclohexane (50 ml) in a 200ml Parr autoclave and the mixture turned to a purple colour. The autoclave was sealed and purged three times with carbon monoxide (20 atm) before being pressurised with carbon monoxide (45 atm) and hydrogen (25 atm) giving a total pressure of 70 atm and heated at 125°C for 8 h after which it was allowed to stir overnight. Following depressurisation, the crystals were filtered using a Hirsch funnel and washed with methanol (3 x 10 ml) and dried *in vacuo* for 2 h affording yellow crystals (0.49 g, 61%). Anal. Calc. for $C_{12}O_{12}H_4Ru_4$: C, 19.35%; H, 0.54%. Found: C, 19.65%; H, 0.50%. IR ν_{CO} (in cyclohexane): 2080 (s), 2066 (vs), 2029 (sh), 2024 (s) and 2009 (w) cm^{-1}. (lit.[10] 2081 (s), 2067 (vs), 2030 (sh), 2024 (s) and 2009 (w) cm^{-1}).



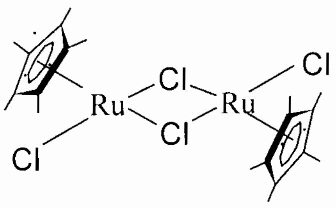
3.4.4.4 Synthesis of $RuCl_2(PPh_3)_3$ [9]



The literature procedure by Hallman *et al.* was modified.[8] Ammonium hexachlororuthenate(IV) (2.00 g, 5.72 mmol), water (20 ml), methanol (40 ml) were placed in a Schlenk tube and refluxed under nitrogen for 40 min and then cooled for 15 min. An excess of triphenylphosphine (12.00 g, 45.75 mmol) was added and the mixture was refluxed again for 3 h and allowed to cool to room temperature whilst stirring in the oil bath. The precipitate was filtered using a Buchner funnel and washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown solid (8.00 g, 70%). m.p. 132-133°C. (lit.[8] 132-134°C) Anal. Calcd. for $C_{56}H_{45}Cl_2P_3Ru$: C,65.99%; H, 4.6%. Found: C 65.58%; H, 4.51%. IR (KBr): 1481 (s), 1432 (s), 1191 (m), 1088 (s), 1027 (m), 998 (m), 744 (s), 695 (vs), 542 (s), 520 (s).

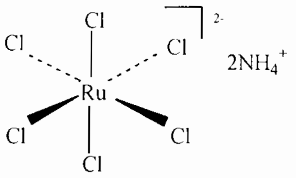
3.4.5 Compounds prepared using dihydogen hexachlororuthenate

3.4.5.1 Synthesis of a $[Cp^*RuCl_2]_2$ [20]



The literature procedure by Grubbs *et al.* was modified.[11] An aqueous solution of dihydrogen hexachlororuthenate (10 ml, 0.3 g Ru), 1,2,3,4,5-pentamethylcyclopentadiene (0.57 g, 4.19 mmol), ethanol (10 ml) were refluxed under nitrogen for 6 h. The brown solution was allowed to cool to room temperature before being cooled to -15°C and cooled to -78°C overnight. The precipitate was filtered on a sintered glass filter, washed with absolute ethanol (5 x 10 ml), pentane (5 x 10 ml) and dried *in vacuo* for 2 h affording chocolate brown microcrystals (0.47 g, 41%) (crystals do not melt below 350°C). Anal. Calc. for $C_{20}H_{30}Cl_4Ru_2$: C, 39.10%; H, 4.87%. Found: C, 40.11%; H, 4.87%. IR (KBr): 2984 (m), 2910 (m), 1478 (m), 1469 (br,s), 1372 (s), 1151 (w), 1075 (w), 1024 (s), 434 (m).(lit.[11] 2958 (w), 1436 (br, s), 1376 (s), 1151 (w), 1075 (w), 1024 (s), 436 (m) cm^{-1}.

3.4.5.2 Synthesis of $(NH_4)_2[RuCl_6]$ [11]

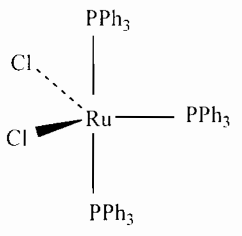


An aqueous solution of dihydrogen hexachlororuthenate (40 ml, 1.52 g Ru) was heated on a steam bath for 2 h and a twelve-fold excess of ammonium chloride (18.24 g, 0.34 mol) in water (85 ml) was added. The mixture was placed on the steam bath for another 1 h after which it was allowed to cool to room temperature and then cooled to -15°C overnight. The precipitate was washed with absolute ethanol (5 x 30 ml) and filtered using a Buchner funnel and the product dried *in vacuo* for 3 h affording reddish brown microcrystals (4.10 g, 78%). Anal. Calcd. for $N_2H_8RuCl_6$: N 8.00%; H, 2.31%. Found: N 8.21%; H, 2.60%.

3.4.5.3 Synthesis of $[RuCl_2(C_8H_{12})]_n$ [10]

A modified literature procedure by Singleton *et al.* was used.[9] Dihydrogen hexachlororuthenate (20 ml, 0.76 g Ru), cycloocta-1, 5-diene (1 ml, 8 mmol), ethanol (10 ml) were added to a two-necked round bottomed flask under nitrogen and mixture was refluxed for 26 h. On cooling to room temperature the solid was filtered using a Buchner funnel and washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown solid (1.90 g, 90%). Anal. Calcd. for $C_8H_{12}Cl_2Ru$: C, 34.30%; H, 4.29%. Found: C, 34.64%; H, 3.86%.

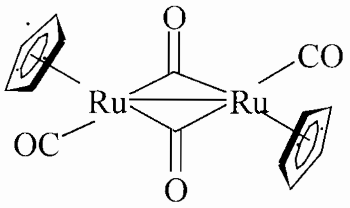
3.4.5.4 Synthesis of $RuCl_2(PPh_3)_3$ [9]



The literature procedure by Hallman *et al.* was modified.[8] Dihydogen hexachlororuthenate (10 ml, 0.38 g Ru), methanol (35 ml) were charged into a Schlenk tube and the mixture refluxed under nitrogen for 40 min and then allowed to cool for 15 min. An excess of triphenylphosphine (3.46 g, 13.21 mmol) was added and the mixture refluxed under nitrogen for 3 h and left to stir overnight in an oil bath. The product that had precipitated out was filtered using a Buchner funnel and washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown solid (2.78 g, 75%). m.p. 131-133°C . (lit.[8] 132-134°C) Anal. Calcd. for $C_{56}H_{45}Cl_2P_3Ru$: C,65.99%; H, 4.6%. Found: C 65.98%; H, 4.31%. IR (in KBr): 1481 (s), 1432 (s), 1191 (m), 1088 (s), 1027 (m), 998 (m), 744 (s), 695 (vs), 542 (s), 520 (s).

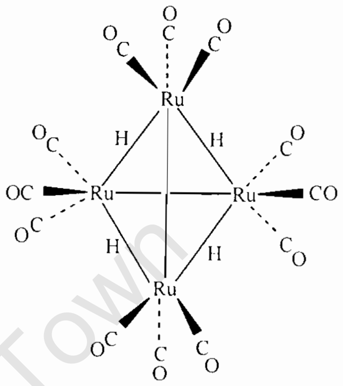
3.4.6 Compounds prepared using dodecacarbonyltriruthenium

3.4.6.1 Synthesis of $[CpRu(CO)_2]_2$ [21]



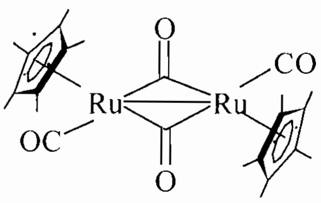
The literature procedure by Doherty and Knox was followed.[12] $Ru_3(CO)_{12}$ (prepared from the Anglo sample, section 3.4.3.1) (1.25 g, 1.96 mmol) was added to a 200 ml three-necked flask together with dried deoxygenated heptane (51.6 ml) and freshly distilled cyclopentadiene (2.58 g, 39.1 mmol) prepared by cracking dicyclopentadiene. The mixture was heated at reflux for 1 h and the stopper was removed from the flask and volume of solvent was reduced to *ca* 10 ml by continued reflux under a brisk flow of nitrogen as heptane boils away. The solution turns to a dark orange colour and to a chocolate brown colour after 1 h. An additional amount of heptane (44 ml) was added and reflux continued for a further 2 h. The reaction mixture was then cooled to room temperature and the mother liquor decanted from the resulting precipitate. The precipitate was then washed with hexane (3 x 10 ml) and dried *in vacuo* affording dark orange crystals (0.733 g, 64%). The IR ν_{co} (in dichloromethane) exhibited bands at 2002 (s), 1964 (s), and 1935 (m) and 1771 (s) cm^{-1}. (lit.[12] 2003 (s), 1966 (s), 1934 (m) and 1771 (s) cm^{-1}).

3.4.6.2 Synthesis of $H_4Ru_4(CO)_{12}$ [8]



The literature procedure by Bruce and Williams was followed.[10] Cyclohexane (25 ml) was added to dodecacarbonyltriruthenium (prepared from the Anglo sample, section 3.4.3.1) (0.50 g, 0.70 mmol) in a 200 ml Parr autoclave. After initial pressurisation with hydrogen (10 atm) and venting, the autoclave was charged with hydrogen (25 atm) and heated at 120°C for 2 h. After cooling and venting, the solution was removed from the autoclave and filtered using a Hirsch funnel. Removal of the solvent on the rotary evaporator afforded the product which was then dried *in vacuo* for 2 h affording yellow microcrystals (0.85 g, 73%). The IR ν_{co} (in cyclohexane) exhibited bands at 2080 (s), 2065 (vs), and 2029 (sh), 2023 (s) and 2007 (w) cm^{-1}. (lit.[10] 2081 (s), 2067 (vs), 2030 (sh), 2024 (s) and 2009 (w)).

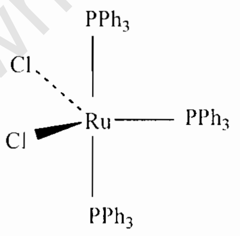
3.4.6.3 Synthesis of $[Cp^*Ru(CO)_2]_2$ [20]



The literature procedure by King *et al.* was followed.[13] Nitrogen was bubbled through *n*-decane (40 ml) for 10min. $Ru_3(CO)_{12}$ (prepared from the Anglo sample, section 3.4.3.1) (1.28 g, 2 mmol) and an excess of 1,2,3,4,5-

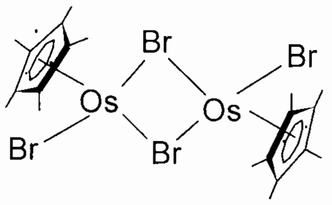
pentamethylcyclopentadiene (1.13 g, 8.31 mmol) was added giving an orange mixture. This was allowed to stir under nitrogen for 10 min before refluxing at 165°C for 3 h. The $Ru_3(CO)_{12}$ gradually dissolved upon heating and needle-like crystals precipitated out of solution. The mixture was allowed to cool to room temperature and the crystals were isolated by filtration using a Hirsch funnel, washed with cold hexane (3 x 10 ml) and dried *in vacuo* for 2 h affording orange crystals (0.65 g, 83%). m.p. 298-299°C dec. (lit.[13] 297°C dec.) Anal. Calcd. for $C_{24}H_{30}O_4Ru_2$: C,49.54%; H, 5.15%. Found: C 49.72%; 4.95%. The IR spectrum v_{co} (in dichloromethane) exhibited bands at 1926 (s) and 1746 (s) cm^{-1}. (lit.[13] 1925 (s) and 1744 (s) cm^{-1}). ^1H NMR ($CDCl_3$, 25°C) δ 1.84 (s, C_5Me_5).

3.4.6.4 Alternative synthesis of $RuCl_2(PPh_3)_3$ [9]



Dichloro(cycloocta-1,5-diene)ruthenium(II) (0.25 g, 0.89 mmol), triphenylphosphine (1.40 g, 5.34 mmol) and methanol (45 ml) were refluxed under nitrogen for 3 h and allowed to cool to room temperature whilst stirring in the oil bath. The product that had precipitated out was filtered on a sintered glass filter, washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown solid (0.57 g, 67%) m.p.131-132°C. (lit.[8] 132-134°C). IR (in KBr): 1480 (s), 1433 (s), 1191 (m), 1086 (s), 1024 (m), 996 (m), 743 (s), 692 (vs), 540 (s) and 519 (s).

3.4.7 Synthesis of $[Cp^*OsBr_2]_2$



A literature procedure by Gross *et al.*[16] was followed Dihydrogen hexabromoosmate (400 mg, 0.60 mmol), water (1 ml), 1,2,3,4,5-pentamethylcyclopentadiene (610 mg, 4.49 mmol) and absolute ethanol (15 ml) were refluxed under nitrogen for 2 h and allowed to cool to room temperature whilst stirring in the oil bath. The product that had precipitated out was filtered on a sintered glass filter, washed with diethylether (5 x 10 ml) and dried *in vacuo* for 2 h affording a brown-black solid (0.24 mg, 76%) m.p. 154-156°C. Anal. Calcd. for $C_{20}H_{30}Os_2Br_4$: C,24.74%; H, 3.10%. Found: C 24.93%; 3.19%. IR (KBr): 2924 (s), 2854 (s), 1980 (m), 1699 s), 1621 (m), 1446 (m), 1375 (m), 1020 (m), 897 (m), 696 (w). ^1H NMR ($CDCl_2$, 25^{0}C) δ 2.54 (s, C_5Me_5). (lit. ^1H NMR ($CDCl_2$, 25^{0}C) δ 2.56 (s, C_5Me_5).

3.5 References

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Chapter 4

Discussion pertaining to experimental section

4.1 Introduction

This project was divided into 2 main parts:

i) Syntheses of known osmium compounds using $K_2[OsO_2(OH)_4]$ and

ii) Syntheses of known ruthenium compounds using $(NH_4)_2[RuCl_6]$ and an acidic $H_2[RuCl_6]$ solution which contained *ca* 38g/L of ruthenium metal.

All the 3 materials used are refinery materials obtained from the Anglo Platinum Corporation. At the refinery, OsO_4 is produced but since this compound is toxic, volatile and difficult to store, it is converted to the stable salt potassium osmate $K_2[OsO2(OH)_4]$.

4.12 Synthesis of $(NH_4)_2[OsCl_6]$ [1]

The literature method that was reported by Dwyer and Hogarth[1] in 1957 in the synthesis of compound **[1]** used OsO_4 as the starting material as shown in eqn. (1) and the yields were between 91-94%.

$$OsO_4 + 7HCl + FeCl_2.4H_2O + 2NH_4Cl \longrightarrow \underset{\mathbf{1}}{(NH_4)_2OsCl_6} + FeCl_3.6H_2O + 4H_2O \quad (1)$$

We used instead potassium osmate $K_2[OsO_2(OH)_4]$ in a similar procedure. The method that we followed is shown in eqn. (2) and has not been reported before, as far as we were aware.

$$K_2OsO_2(OH)_4 + 7HCl + FeCl_2.4H_2O + 2NH_4Cl \longrightarrow \underset{\mathbf{1}}{(NH_4)_2OsCl_6} + FeCl_3.6H_2O + 4H_2O + 2KCl + \text{other products} \quad (2)$$

This reaction gave compound **1** in quantitative yields of 98%, as red microcrystals. These were soluble in water, giving yellow solutions and were not soluble, or only very slightly soluble, in other inorganic or organic solvents. Solubility was later shown to be very critical in subsequent reactions that were attempted and some did not give the desired product due to solubility constraints of $(NH_4)_2[OsCl_6]$ **1**. This difficulty was overcome by adding water to the reactions to dissolve the salt so that it was in solution and could then easily react with appropriate ligands. The osmium is in an oxidation state of (VI) in the starting material and oxidation state (IV) in the product.

4.12.1 Synthesis of $Os_3(CO)_{12}$ [2] from $(NH_4)_2OsCl_6$ [1]

The carbonylation of $(NH_4)_2[OsCl_6]$ was attempted using dry methanol or ethanol as solvents. The carbonylation reactions described in the literature use OsO_4 as starting material as reported by Johnson and Lewis[3] and shown in eqn. (3).

$$3OsO_4 + 24CO \longrightarrow \underset{\mathbf{2}}{Os_3(CO)_{12}} + 12CO_2 \quad (3)$$

4.12.2 Reactions of $(NH_4)_2[OsCl_6]$ [1] with CO

Compound **2** has been known for over sixty five years [4] and was originally reported by Manchot *et al.*[5] They obtained it from the reaction of OsO_4 with CO in the gas phase but this synthetic route gave low yields of $[Os_3(CO)_{12}]$ (25%). The yellow crystals were first thought to be $Os_2(CO)_9$.

In 1967 Bradford and Nyholm[7] developed and reported better synthetic methods to this cluster in high yields of 70%. This resulted from a reaction of

OsO_4 with CO in xylene in a glass lined autoclave under conditions of moderate pressure and temperature, marking the beginning of the detailed study of the chemistry of $Os_3(CO)_{12}$.

Compound **2** is a yellow crystalline solid that shows only limited solubility in organic solvents and is also volatile. Infrared spectroscopy is a very useful tool for identification purposes and checking the purity of this cluster.

We have carried out the reactions of compound **1** in dry methanol or ethanol with carbon monoxide under a variety of conditions of pressure and temperature in order to optimize the yields of compound **2**. These high pressure reactions were carried out in the autoclave and a zinc granule was added into the reaction as a halogen acceptor, or as a possible reducing agent. When the zinc granule was not added, the yields were very low i.e 11 or 12% of compound **2** with ethanol as solvent and 35% with methanol as solvent.

The reactions with ethanol and methanol as solvents gave compound **2** but with after varying the CO pressure as shown in the eqns. (4) and (5).

$$3(NH_4)_2OsCl_6 \xrightarrow[125^0C,\ 24h]{CO(75atm),\ MeOH} \underset{\mathbf{2}}{Os_3(CO)_{12}} + 6NH_4Cl \qquad (4)$$

$$3(NH_4)_2OsCl_6 \xrightarrow[125^0C,\ 24h]{CO(50atm),\ EtOH} \underset{\mathbf{2}}{Os_3(CO)_{12}} + 6NH_4Cl \qquad (5)$$

Table 4.1 Conditions for the preparation of $Os_3(CO)_{12}$ **[2]** from $(NH_4)_2OsCl_6$ **[1]**

Pressure(atm)	Temp(^{0}C)	Solvent	Zinc added	% yield
50	125	MeOH	Yes	35
50	125	MeOH	No	12
50	125	EtOH	No	11
75	125	MeOH	Yes	64
75	140	MeOH	Yes	42

From the Table, it can be observed that to some extent better yields were obtained with methanol as solvent whether a zinc granule is added or not.

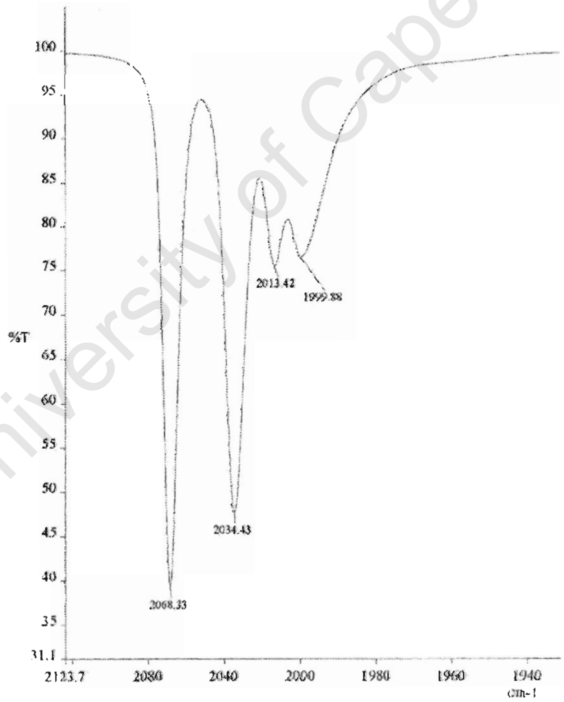


Figure 4.1 Infrared spectrum in dichloromethane of $Os_3(CO)_{12}$ **[2]** prepared from $(NH_4)_2[OsCl_6]$ **[1]**

The infrared spectra are useful for identification and for checking purity. The compound shows only limited solubility in most organic solvents.

An interesting observation was made when the reaction conditions were changed. When compound **1** was carbonylated in dry methanol for 22 h and at a higher CO pressure with no zinc granule added compound **3** was isolated in low yields (25%).

$$\underset{\textbf{1}}{2(NH_4)_2OsCl_6} \xrightarrow[175^0C,\ 22h]{CO(70atm),\ MeOH} \underset{\substack{\text{light yellow microcrystals}\\ \textbf{3}}}{[Os(CO)_3Cl_2]_2} + 4NH_4Cl + \text{other products} \qquad (6)$$

The infrared spectrum (in dichloromethane) of the crystals exhibited bands at 2136 (s) and 2061 (s) cm^{-1} which agreed very well with literature. (2134 (s) and 2059 (s) cm^{-1})[6] as shown in Figure 4.2. The other broad band at about 1990 cm^{-1} was due to either impurity or decomposition material and this could not be separated from the product.

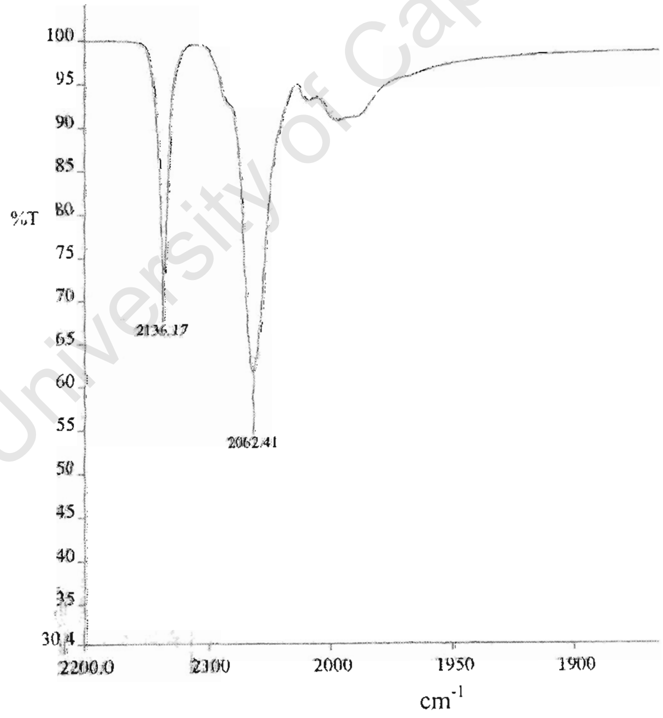


Figure 4.2 Infrared spectrum in dichloromethane of $[Os(CO)_3Cl_2]_2$ **[3]**

When ethanol was used instead, compound **3** was isolated in 12% yield. It was identified by infrared spectroscopy but the other broad peak was due to impurity which could not be separated from the product. At temperatures higher than 175°C only decomposition material was observed.

4.12.3 Alternative method for the synthesis of $[Os(CO)_3Cl_2]_2$ [3]

Compound **3** was also synthesised by heating $Os_3(CO)_{12}$ **[2]**, concentrated HCl and cyclohexane in a sealed tube at 170^0C in an oil bath as shown in eqn. (7).

$$2Os_3(CO)_{12} + HCl \xrightarrow[170^0C,\ 44\ h]{\text{cyclohexane}} \underset{\mathbf{3}}{3[Os(CO)_3Cl_2]_2} + \text{other products} \qquad (7)$$

This method gave compound **3** in good yields (87%) and it was shown to be pure by infrared spectroscopy and IR values agreed very well with literature values.[6] This also is a new procedure, as the one reported by Bruce *et al* used HCl as a gas.[9]

The synthesis of $Os_3(CO)_{12}$ **2** was also attempted from $K_2[OsO_2(OH)_4]$ as shown in eqn. (8).

$$3K_2OsO_2(OH)_4 \xrightarrow[125^0C,\ 22\ h]{\text{CO (65 atm), MeOH}} \underset{\mathbf{2}}{Os_3(CO)_{12}} + \text{other products} \qquad (8)$$

This reaction only gave compound **2** in yields ranging between 5-10%.The infrared spectrum (in dichloromethane) of the yellow crystals exhibited bands at 2068 (s), 2034 (s), 2013 (m) and 2000 (m) cm^{-1}. These IR values agree with values that were reported by Johnson and Lewis.[3] The other minor products that are formed from the reaction were identified by IR as the trinuclear derivatives $HOs_3(CO)_{10}(OMe)$ and $Os_3(CO)_{10}(OMe)_2$.[7]

According to our knowledge there has been no report of carbonylation reactions of refinery materials using high pressure autoclaves to produce $Os_3(CO)_{12}$ **[2]** and $[Os(CO)_3Cl_2]_2$ **[3]**. The only reports that we are aware of detail the synthesis of the $OsH_2(CO)(PPh_3)_3$ **[5]** and $Os(CO)_3(PPh_3)_2$ **[6]** complexes. In these reactions the source of carbon monoxide is usually a high boiling solvent such as 2-(2-methoxyethoxy)ethanol or 2-methoxyethanol and reactions are carried out in air. [35,36]

4.12.4 Attempted synthesis of $[CpOs(CO)_2]_2$

This reaction was attempted by heating an excess of dicyclopentadiene with $[Os(CO)_3Cl_2]_2$ **[3]** in a sealed tube as shown in eqn. (9).

$$\underset{\mathbf{3}}{[Os(CO)_3Cl_2]_2} + C_{10}H_{12} \xrightarrow{\text{EtOH, 140-160}^0\text{C}} 2[C_5H_5Os(CO)_2]_2 + \text{other products} \quad (9)$$

The initial yellow solution turned orange after 6 h of heating and was dark orange after 20 h. The reaction was allowed to cool to room temperature whilst stirring in the oil bath after which the solvent was removed *in vacuo* affording a light yellow oil which gave the IR spectrum shown below

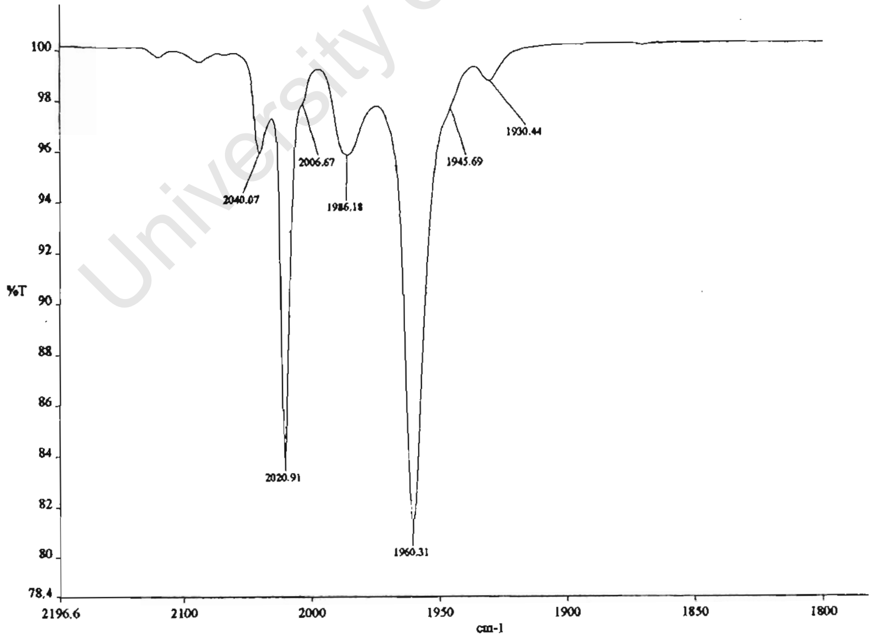
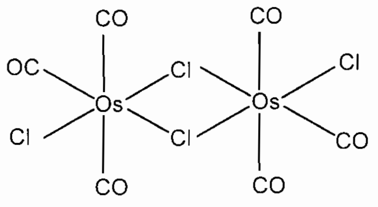
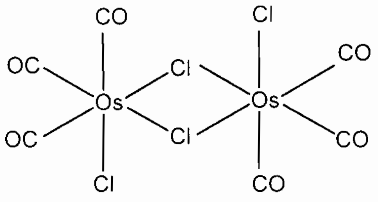


Figure 4.3 Infrared spectrum in dichloromethane of a mixture of the yellow oil from the reaction of $[Os(CO)_3Cl_2]_2$ **[3]** with $C_{10}H_{12}$

The peaks at 2040, 1986 and 1948 cm^{-1} correspond with those that were reported by Fischer *et al.*[41] for the dimer and this clearly shows that we do have some $[CpOs(CO)_2]_2$ in the intractable product mixture. The intensities of the other peaks at 2020 and 1960 cm^{-1} indicate an isomer of compound **3**. The isomers of compound **3** have been reported by Herrmann *et al.* and are shown below:[6]



mer



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^1H NMR in $CDCl_3$ of the product mixture exhibited a peak at 5.58 ppm.(lit.[45] 5.58 in $CDCl_3$ and 5.60 in acetone-d_6) indicating the presence of $[OsCl(CO)_2(Cp)]$. This product has been reported by Dev and Selegue as having been conveniently synthesised in 4 steps from OsO_4. The OsO_4 is converted to $(NH_4)_2[OsCl_6]$ which is then reduced to $OsCl_3$ and carbonylated to $[OsCl_2(CO)_3]_2$ and finally reacted with $[SiMe_3(C_5H_5)]$ to give $[OsCl(CO)_2(Cp)]$ in 26% yield.[45] Another NMR signal was observed at 5.25ppm and this signal was very small in intensity and is likely to be attributed to the presence of $[CpOs(CO)_2]_2$ in the product mixture.

Column chromatography was attempted to separate the components of the product mixture but was unsuccessful as the product mixture did not separate into different products.

4.12.5 Synthesis of $OsHCl(CO)(PPh_3)_3$ [4]

The divalent osmium complexes were synthesised from the hexahaloosmates(IV) $(NH_4)_2[OsX_6]$ (X = Cl, Br), $Na_2[OsCl_6]$, dihydrogen hexahaloosmates(IV), triphenylphosphine, and an alcohol as the reacting solvent.

$$\underset{\mathbf{1}}{(NH_4)_2OsCl_6} + 4PPh_3 \xrightarrow[H_2O,\ 190^0C,\ 4\ h]{\text{2-(2-Methoxy-ethoxy)-ethanol}} \underset{\substack{\text{white precipitate}\\ \mathbf{4}}}{OsHCl(CO)(PPh_3)_3} + 2NH_4Cl + 2PPh_3Cl_2 \qquad (10)$$

Compound **1** is virtually inert at 25°C in alcoholic solvents because of its very low solubility. This apparently suppresses the solubility of an intermediate complex so that no reaction is detected with alcohols within reasonable times and the compound is unchanged after 48 h reflux in pure alcohol.[23] Partial dissolution is effected by using water as a solvent component and thus water is not essential for the reaction to occur but to shorten the time of the experiment.[26]

The reduction of osmium(IV) halide to an osmium(II) complex may be effected by either the solvent alcohol or the neutral ligand used in excess[26] and in this case triphenylphosphine in a 7 : 1 molar ratio (to osmium(IV) halide).

A key feature is the low solubility of the compound **4** in the alcoholic solvents used, which results in the precipitation or crystallization of the product in good yield. During the preparation of compound **4** as in eqn. (10), the compound crystallises out as its concentration increases. This reaction was carried out in a vessel open to the atmosphere.

The preparation of compound **4** appeared to require that the temperature and the solvent composition be varied as the reaction proceeds. Mixtures of water (b.p.100°C) and 2-(2-methoxyethoxyethanol) (b.p.194°C) gave reasonable yields (54%) when used in a ratio of 1:2.5. The boiling temperature is raised gradually to 190°C (by allowing water to evaporate) at which point the high concentration of 2-(2-methoxyethoxyethanol) and of the Os complex causes the latter to precipitate. A further increase in temperature re-dissolves the product and initiates its decomposition.

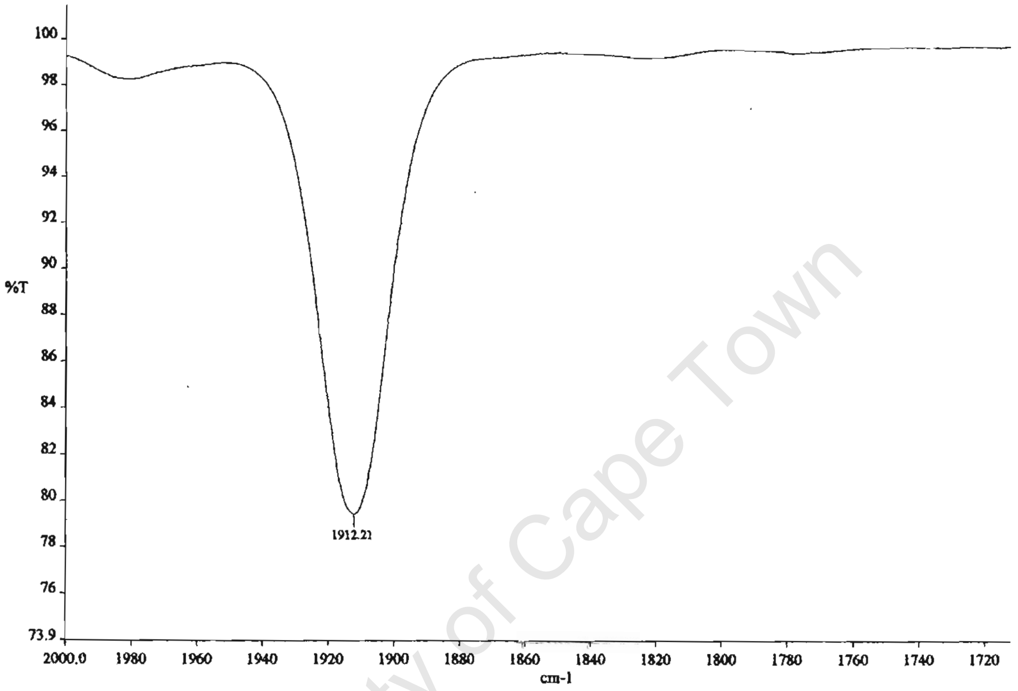


Figure 4.4 Infrared spectrum in dichloromethane of $OsHCl(CO)(PPh_3)_3$ **[4]**

For a monocarbonyl complex a single CO stretching band is expected and this was found for the compound **4** in solution as shown in the spectra above and agrees very well with what was reported by Vaska.[26]

4.12.6 Synthesis of $OsH_2(CO)(PPh_3)_3$ [5]

When the reaction conditions for the above reaction were changed by using a different solvent mixture of 2-methoxyethanol and water at a lower temperature of 120°C, and reduced reaction time of 1 h, compound **5** was isolated as white microcrystals in good yields (78%). The first report of this compound was by Vaska in 1966 where he reported that the dihydride was prepared by refluxing a suspension of $OsHCl(CO)(PPh_3)_3$ **4** in a solution of sodium hydroxide in 2-methoxyethanol.[35] It was later reported by Robinson *et al* to have been synthesised by refluxing solutions of $Na_2[OsCl_6]$ **[15]** in 2-methoxyethanol and potassium hydroxide in formaldehyde with triphenylphosphine in 2-methoxyethanol for 30 minutes.[36] We used $(NH_4)_2[OsCl_6]$ **[1]** for the same reaction as shown in eqn. (11).

$$\underset{\mathbf{1}}{(NH_4)_2OsCl_6} + 6PPh_3 \xrightarrow[H_2O,\ 120^0C,\ 1\ h]{\text{2-Methoxy-ethanol}} \underset{\mathbf{5}}{OsH_2(CO)(PPh_3)_3} + 2NH_4Cl + 3PPh_3Cl_2 + \text{other products} \qquad (11)$$

The solvent 2-methoxyethanol has a lower boiling point (124-125°C) than the 2-(2-methoxyethoxy)ethanol (194°C) and the reaction conditions are much milder. Hydride resonances are observed for compound **5** and these imply that there are no equivalent sites suggesting that compound **5** has three possible geometrical isomers.[36]

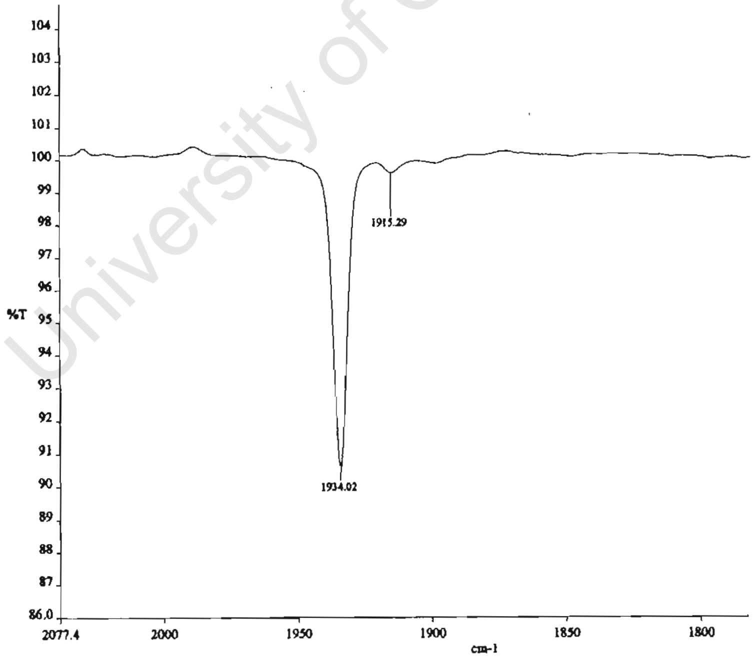


Figure 4.6 Infrared spectrum of $OsH_2(CO)(PPh_3)_3$ **[5]** in dichloromethane

The infrared spectrum of compound **5** shows bands at 1934(s) cm^{-1} attributed to *v*(CO) and 1915 (w) attributed to *v*(OsH). Similar infrared values were also obtained in chloroform solution. The v_{MH} of the tertiary phosphine-stabilized metal hydrides has been observed in the range 1600 to 2250 cm^{-1}.[26] Compound **5** is moderately soluble in benzene, chloroform and dichloromethane. The white microcrystals of compound 5 melt at 201-204°C

4.12.7 Attempted synthesis of $Os(CO)_3(PPh_3)_2$ [6]

Compound **6** was first reported by Collman and Roper in 1966.[28] They reported to have prepared it from the osmium(II) complexes $OsX_2(CO)_2(PPh_3)_2$ by zinc reduction in the presence of CO. However when we attempted to prepare the same compound using $Na_2[OsCl_6]$ **[15]** we obtained a mixture of products as shown in eqn. (12).

$$\underset{\mathbf{15}}{Na_2OsCl_6} + 4PPh_3 \xrightarrow{HCHO,\ 1\ h} \underset{\mathbf{6}}{Os(CO)_3(PPh_3)_2} + OsCl_2(CO)_2(PPh_3)_2 + 2NaCl + 2PPh_3Cl_2 + \text{other products} \quad (12)$$

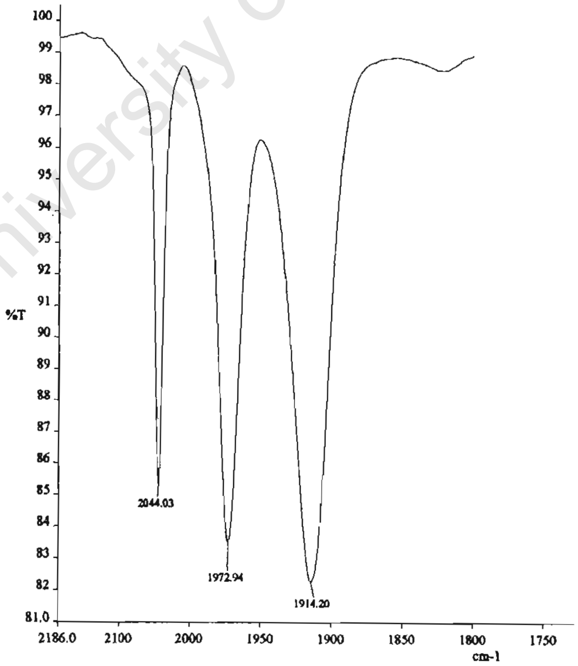
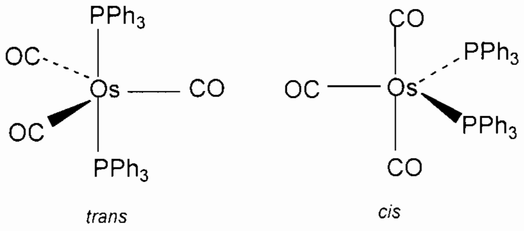


Figure 4.7 Infrared spectrum of the mixture of products from eqn. (12) in dichloromethane

The infrared spectrum of the product mixture exhibits bands at 2044 (s), 1973 (s) and 1914 (s) cm^{-1} attributed to ν(CO). The peaks at 2044 (s) and 1973 (s) are attributed to $OsCl_2(CO)_2(PPh_3)_2$.[51] The other peak at 1914 (s) cm^{-1} could be attributed to the *trans*-isomer of $Os(CO)_3(PPh_3)_2$ that was originally prepared by Collman and Roper.[28] They synthesised *trans*-$Os(CO)_3(PPh_3)_2$ and reported it to have a single peak at 1890 (s) cm^{-1}. The possible isomers are shown below:



Isomers of $Os(CO)_3(PPh_3)_2$

Compounds **4, 5 and 6** are insoluble in water, alcohols and aliphatic hydrocarbons and only slightly soluble in organic solvents such as chloroform, benzene and acetone. Because of their low solubility the compounds could not be conveniently recrystallised.

Compounds **4, 5 and 6** are found to be pure as prepared according to their melting points, visual appearance and infrared spectra. Decomposition on melting in air is probably due to a reaction with oxygen.[26]

4.13 Synthesis of $Ru_3(CO)_{12}$ [7]

$Ru_3(CO)_{12}$ **[7]** is a useful starting material for much ruthenium carbonyl chemistry. Compound **7** can be prepared by several methods using commercially available ruthenium trichloride hydrate. A disadvantage of some of the methods that have been used is that they require high pressures of CO and elevated temperatures.[2]

Johnson and Lewis treated ruthenium trichloride trihydrate, (2,4 pentanedionato) sodium with methanol in an autoclave with H_2 (40 atm), CO (120 atm) and these were heated at 165°C for 4 h and obtained yields of $Ru_3(CO)_{12}$ between 50-55%.[3] In 1980 C. R. Eady *et al.* improved the yields to between 85-95% by reacting the ruthenium trichloride trihydrate in dry methanol, pressurising with CO (50 atm) and heating at 125°C for 8 h.[11] Recently compound **7** has been obtained in higher yield but under 1 atm of carbon monoxide.[12] In this synthesis ruthenium trichloride trihydrate Ru(III) is reduced to Ru via Ru(II) intermediates in a reductive carbonylation process in ethylene glycol. Yields of up to 90% have been reported by this method but great care must be taken, for example a high flow rate of carbon monoxide might cause the sublimed product to escape through the carbon monoxide vent especially if the running water is not cold enough to allow sublimation on the walls of the condenser.[12] In our hands this significantly reduced the yield of the product.

In 2003 Lavigne *et al.* reported that addition of two equivalents of KOH per Ru under 1 atm CO at 75°C to a mixture of $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$, generated *in situ* by carbonylation of $RuCl_3.3H_2O$ in 2-ethoxyethanol, produces $Ru_3(CO)_{12}$ in yields exceeding 90%.[34]

$$RuCl_3.nH_2O \xrightarrow[\text{2-ethoxyethanol}]{CO} [Ru(CO)_2Cl_2]_n \overset{CO}{\rightleftharpoons} [Ru(CO)_3Cl_2]_2 \xrightarrow{+\,OH^-} 1/3\ Ru_3(CO)_{12} \qquad (13)$$

The formation of undesirable aqua monocarbonyl Ru species is avoided by performing the initial carbonylation step at 80°C for the first hour and then brought to reflux (135°C) within the next 45 minutes.[34]

Compound **7** was synthesised initially by us from ruthenium trichloride trihydrate following a reported procedure by Johnson *et al.*[11] Then in a new reaction compound **7** was obtained in good yields (75%) by the carbonylation reaction of refinery ammonium hexachlororuthenate with dry methanol as solvent in an autoclave. This reaction was done initially using the solid Anglo Platinum sample as received. This sample had 0.1% moisture which was removed by drying under vacuum for 3 h.

This moisture was later shown to be of critical importance as was seen in subsequent carbonylation reactions using the wet sample.

$$3(NH_4)_2RuCl_6 \xrightarrow[\text{MeOH, 125}^0\text{C, 8h}]{\text{CO (50atm)}} \underset{\mathbf{7}}{Ru_3(CO)_{12}} + \text{other products} \qquad (14)$$

The infrared spectrum (in *n*-hexane) of the orange red crystals of $Ru_3(CO)_{12}$ **[7]** exhibited sharp bands at 2060(s), 2030(s), and 2011(m) cm^{-1}. These IR values agree with values that were reported by Eady *et al.* and the values can be used in identifying and assessing the carbonyl purity of the compound.[11] The compound is soluble in most organic solvents but completely insoluble in water.

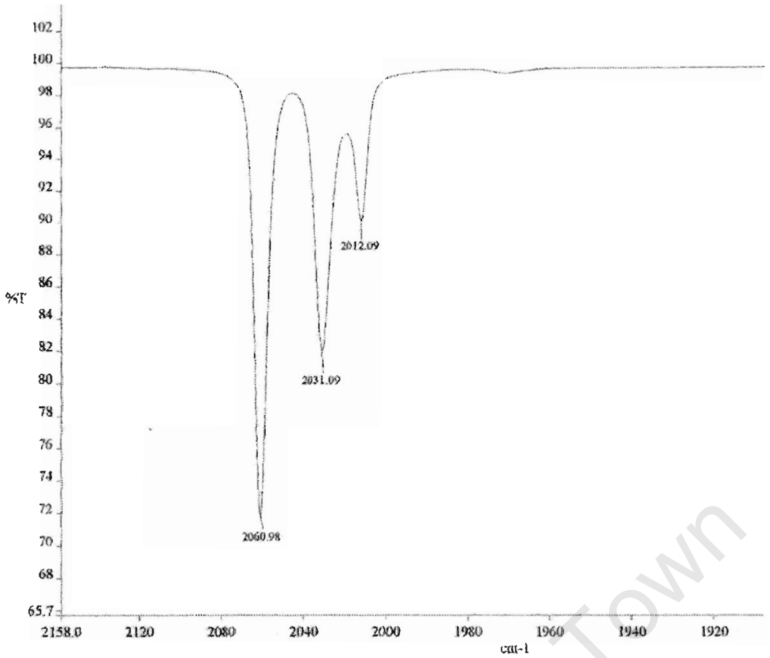


Figure 4.8 Infrared spectrum in (n-hexane) of $Ru_3(CO)_{12}$ **[7]** prepared from $(NH_4)_2RuCl_6$ as received.

Also of particular interest was the infrared spectrum that was obtained when the wet sample was carbonylated for 11 h with 60 atm of carbon monoxide and the time increased from 8 h to 11 h and with a zinc granule being added. The spectra in (n-hexane) exhibited bands at 2081(w), 2061(s), 2031(s) and 2012(m) cm^{-1} as shown in Figure 4.9.

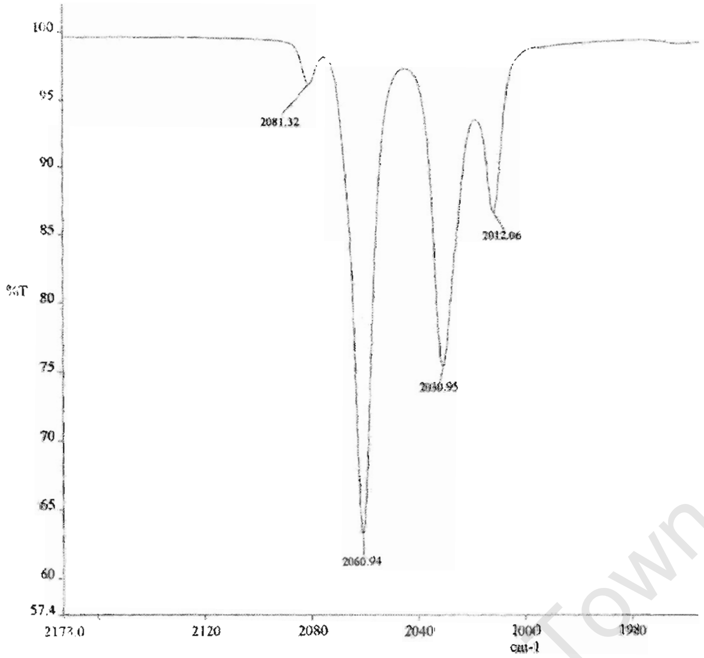


Figure 4.9 Infrared spectrum in hexane of a ruthenium carbonyl hydride from $(NH_4)_2[RuCl_6]$

The peak at 2081 cm^{-1} corresponds to a v(CO) peak of $H_4Ru_4(CO)_{12}$. The peaks at 2024 and 2029 cm^{-1} which occur in compound **8** are obscured by the peak at 2031 cm^{-1}. However TLC showed only one single spot confirming the presence of a single product. If there was maybe a mixture of products other shoulder peaks could have also been observed as in the case when we obtained a mixture of $Ru_3(CO)_{12}$ **[7]** and $H_4Ru_4(CO)_{12}$ **[8]**. The other possibility is that this is a mixture of $Ru_3(CO)_{12}$ **[7]** and $H_4Ru_4(CO)_{12}$ **[8]** but with compound **7** being present in a far larger percentage than compound **8**.

The ^1H NMR in $CDCl_3$ of the ruthenium carbonyl hydride exhibited a peak at -17.79 ppm confirming that the product was a ruthenium carbonyl hydride.

Formation of the species giving rise to the peak at 2081 cm^{-1} can also be ascribed to the reaction of $Ru_3(CO)_{12}$ **[7]** with trace amounts of water in the solvent. Eady *et al.* also mention a reaction of $Ru_3(CO)_{12}$ with small amounts of water leading to the formation of [α- $Ru_4H_4(CO)_{12}$] and [α-$Ru_4(CO)_{13}H_2$] complexes.[11]

4.13.1 Reaction of ammonium hexachlororuthenate with CO and H_2

By reacting $(NH_4)_2[RuCl_6]$ with a mixture of CO (50 atm) and H_2 (25 atm) we expected to obtain $H_4Ru_4(CO)_{12}$ **[8]** but only $Ru_3(CO)_{12}$ **[7]** was isolated in 75% yield. This can be ascribed to the fact that H_2 does not react with compound **[7]** in the presence of methanol. The hydride is known to be formed in hydrocarbon solvents like cyclohexane or octane.[10]

$$3(NH_4)_2RuCl_6 \xrightarrow[\text{MeOH, }125^0\text{C, 8h}]{\text{CO (50atm), }H_2\text{ (25atm)}} \underset{\mathbf{7}}{Ru_3(CO)_{12}} + \text{other products} \quad (15)$$

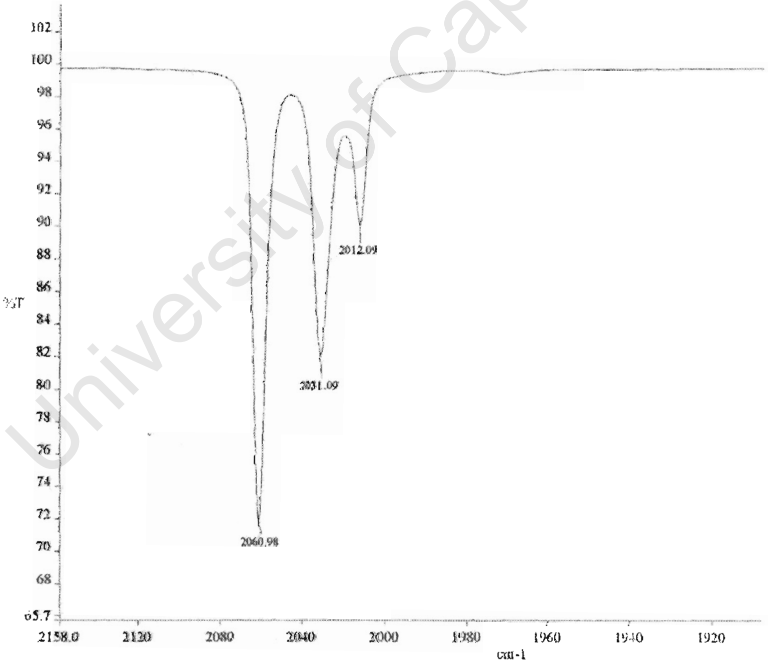


Figure 4.10 Infrared spectrum in (*n*-hexane) of $Ru_3(CO)_{12}$ **[7]** prepared from $(NH_4)_2[RuCl_6]$

The three bands are attributed to terminal CO ligands and no band assignable to a bridging carbonyl is observed.

Of particular interest was the reaction between $(NH_4)_2[RuCl_6]$ with 50 atm CO and 30 atm H_2. This reaction is known to us to produce $Ru_3(CO)_{12}$ **[7]** as the only product on carbonylation with CO in dry methanol as solvent. In this reaction when $(NH_4)_2[RuCl_6]$ was pressurised with CO and H_2 in a hydrocarbon solvent such as cyclohexane the products formed were a mixture of $Ru_3(CO)_{12}$ **[7]** and $H_4Ru_4(CO)_{12}$ **[8]** as orange-yellowish microcrystals.

$$7(NH_4)_2RuCl_6 \xrightarrow[\text{cyclohexane, } 125^0\text{C, 22h}]{\text{CO (50atm), } H_2 \text{ (30atm)}} \underset{\mathbf{7}}{Ru_3(CO)_{12}} + \underset{\mathbf{8}}{H_4Ru_4(CO)_{12}} + 7NH_4Cl + \text{other products} \qquad (16)$$

The mixture of products is easily observed in the IR spectrum below:

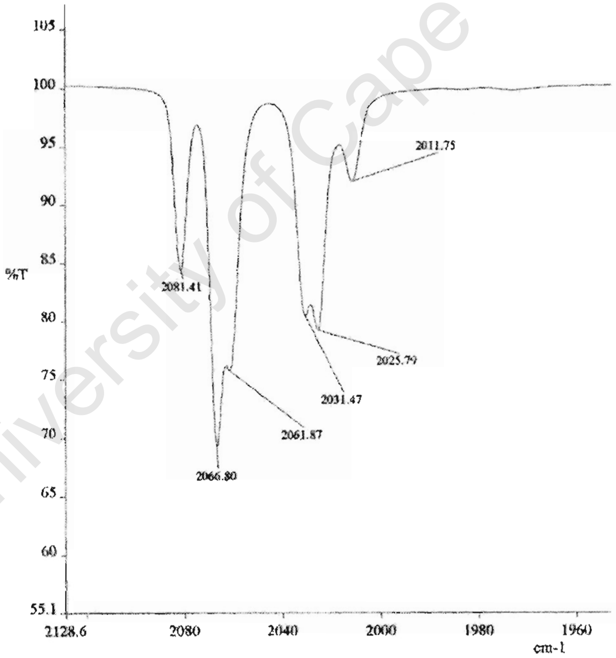


Figure 4.11 Infrared spectrum in hexane of a mixture of $Ru_3(CO)_{12}$ **[7]** and $H_4Ru_4(CO)_{12}$ **[8]** prepared from $(NH_4)_2[RuCl_6]$

The peaks 2062 (sh), 2031 (sh) and 2012 (m) are attributed to $Ru_3(CO)_{12}$ **[7]**[11] and the peaks at 2081 (s), 2067 (s) and 2026 (m) are due to $H_4Ru_4(CO)_{12}$ **[8]**.[14] The mixture of compounds **7** and **8** were separated by column chromatography using a solvent mixture of hexane and dichloromethane in a ratio of 1:1.

On altering the reaction conditions by pressurising $(NH_4)_2[RuCl_6]$ with 45 atm of CO and 35 atm of H_2, pure compound **8** was isolated as yellow microcrystals in 61% yield.

$$4(NH_4)_2RuCl_6 \xrightarrow[\text{cyclohexane, } 125^0\text{C, 8h}]{\text{CO (45atm), } H_2 \text{ (35atm)}} \underset{\mathbf{8}}{H_4Ru_4(CO)_{12}} + 8NH_4Cl + \text{other products} \qquad (17)$$

Compound **8** was easily identified by infrared spectroscopy and exhibited peaks at 2080 (s), 2066 (vs), 2029 (sh) and 2009 (w) cm^{-1} in cyclohexane which compared very well with literature values.[14]

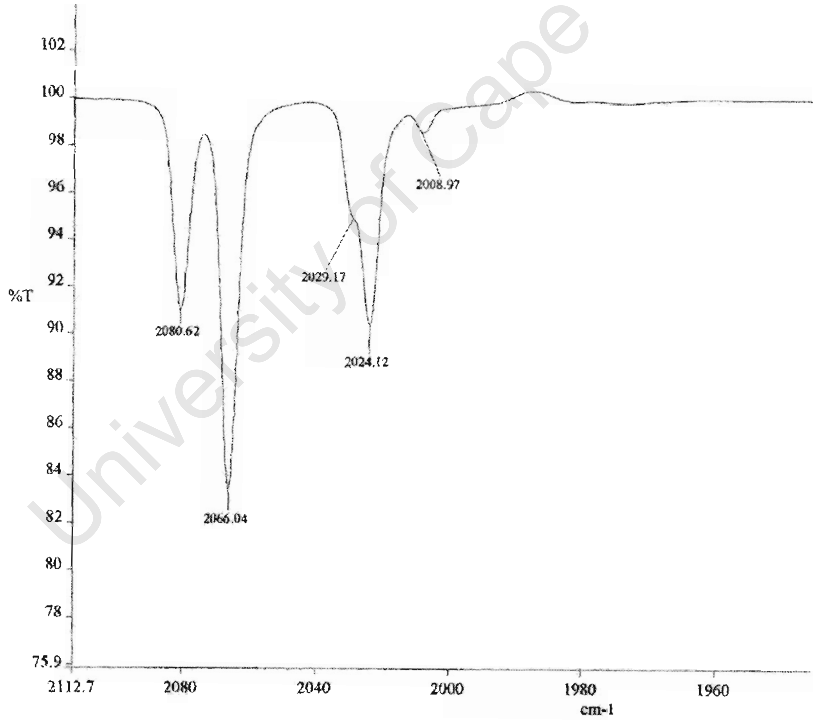


Figure 4.12 Infrared spectrum in cyclohexane of $H_4Ru_4(CO)_{12}$ **[8]** made from $(NH_4)_2[RuCl_6]$

Table 4.4 Infrared spectral data in cyclohexane of $Ru_3(CO)_{12}$ **[7]**, $H_4Ru_4(CO)_{12}$ **[8]** and a mixture of the two compounds.

Compound	**ν(CO) cm^{-1}**
$Ru_3(CO)_{12}$	2061 (s) 2031 (s) 2012 (m)
$H_4Ru_4(CO)_{12}$	2081 (s) 2066 (s) 2029 (sh) 2024 (s) 2009 (w)
mixture	2081 (s) 2067 (s) 2062 (sh) 2031 (sh) 2026 (s) 2011 (w)

4.13.2 Synthesis of $H_4Ru_4(CO)_{12}$ [8]

The preparation of compound **8** was first reported in 1966 by Lewis,[15] Wilkinson[16] and their co-workers and then followed by a joint publication thereafter.[17] In 1971 Piacenti and co-workers also reported that $Ru_3(CO)_{12}$ **[7]** reacts with CO at 150°C under a H_2 pressure of 150 atm with *n*-heptane as solvent.[13] They reported yields of up to 99%. In the same year Kaesz and co-workers reported a novel synthetic route to compound **8** by direct hydrogenation of compound **7** with H_2 at atmospheric pressure in hydrocarbon solvents and their technique also gave near quantitative yields.[18] In 1990 Bruce and Williams reported full preparation details for compound **8** from compound **7** by passing H_2 through a solution of compound **7** in refluxing octane.[14] They also reported that this hydrogenation could be carried out in an autoclave with cyclohexane as solvent.[14]

We find that treatment of $Ru_3(CO)_{12}$ **[7]**, obtained from $(NH_4)_2[RuCl_6]$, with H_2 (25 atm) in an autoclave affords $H_4Ru_4(CO)_{12}$ **[8]** in high purity and good yield (0.85 g, 73%). Excellent IR data were obtained for the product which displays the expected peaks in the carbonyl stretching region consistent with that obtained by Piacenti and coworkers.[13] The difference here is that Piacenti and coworkers used extreme pressures of 150 atm H_2 but we were able to obtain compound **8** using milder conditions of pressure.

4.14 Synthesis of $RuCl_2(PPh_3)_3$ [9]

The method reported by Hallman *et al.*[9] uses ruthenium trichloride trihydrate as the starting material for the synthesis of compound **9** as shown in eqn. (18).

$$RuCl_3.3H_2O + 6PPh_3 \xrightarrow[65^0C,\ 3\ h,\ N_2]{MeOH} \underset{\mathbf{9}}{RuCl_2(PPh_3)_3} + \text{other products} \quad (18)$$

The products from the reactions of PPh_3 with commercial ruthenium trichloride trihydrate are a function of reaction time and solvent. Thus reaction in methanol with a 6:1 PPh_3 : Ru ratio is known to produce different products at reflux temperature $RuCl_2(PPh_3)_3$ and room temperature $RuCl_2(PPh_3)_4$.[19] Solvents such as 2-methoxy and 2-ethoxyethanol also take part in the reaction and produce $[RuH(Cl)(CO)(PPh_3)_3]$ and $[RuCl_2(CO)(PPh_3)_2]$ respectively.[40]

We modified the above synthesis and carried out two separate reactions. Firstly we used the dihydrogen hexachlororuthenate solution and the reaction represented as shown in eqn. (19) was found to take place.

$$H_2RuCl_6 + 3PPh_3 \xrightarrow[65^0C,\ 3\ h,\ N_2]{MeOH} \underset{\mathbf{9}}{RuCl_2(PPh_3)_3} + HCl + \text{other products} \quad (19)$$

The reaction was allowed to stir overnight in an oil bath at 65°C before being filtered, washed thoroughly with diethyl ether to remove any free triphenylphosphine and dried under vacuum affording compound **9** as a brown solid in 75% yield. The product was characterised by analytical and spectroscopic methods (see later).

The second attempt was to prepare compound **9** using the $(NH_4)_2[RuCl_6]$ solid sample. Modification of the procedure shown in eqn. (19) by addition of water gave compound **9** as shown in eqn. (20) in yields of 78%.

$$(NH_4)_2RuCl_6 \ + \ 3PPh_3 \xrightarrow[65^0C,\ 3\ h,\ N_2]{MeOH} \underset{\textbf{9}}{RuCl_2(PPh_3)_3} \ + \ HCl \ + \ \text{other products} \qquad (20)$$

Water caused partial dissolution of the $(NH_4)_2[RuCl_6]$ when it was used as a solvent component with methanol. $(NH_4)_2[RuCl_6]$ dissolved in water and went into solution thereby allowing the triphenylphosphine ligand to coordinate to the ruthenium metal centre much more readily as $(NH_4)_2[RuCl_6]$ is not soluble in alcoholic solvents. Using water as a second solvent was very critical as only a 1:2 water:solvent system gave compound **9** in good yields (78%). A 1:1 ratio also gave compound **9** but the yields dropped to 20%.

Compound **9** was characterised by m.p, elemental analysis, infrared spectroscopy and the data were in agreement with literature values. [19]

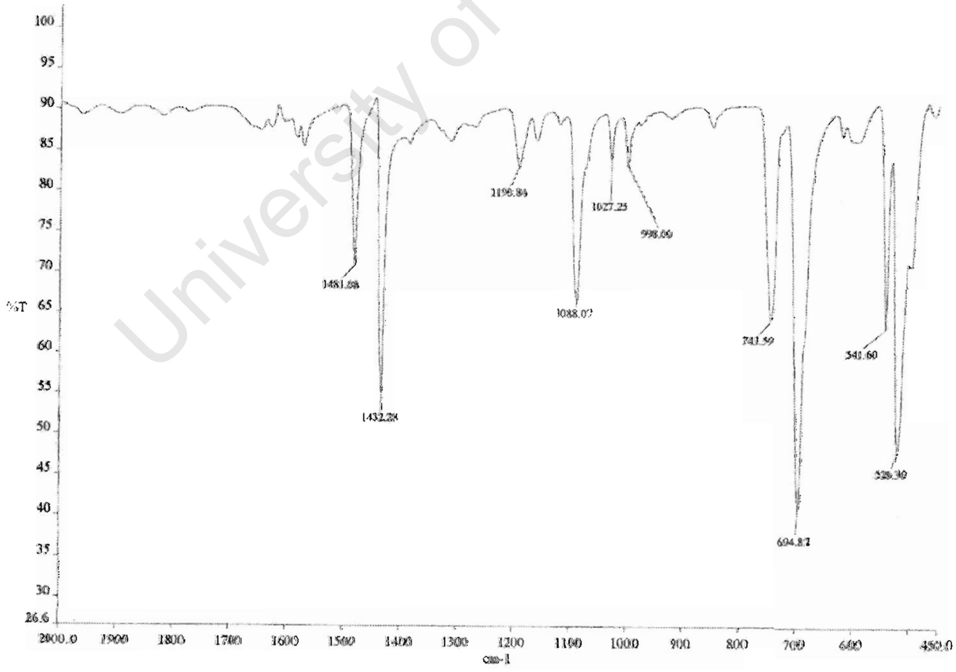


Figure 4.13 Infrared spectrum of $RuCl_2(PPh_3)_3$ **[9]** from H_2RuCl_6 as a KBr disc

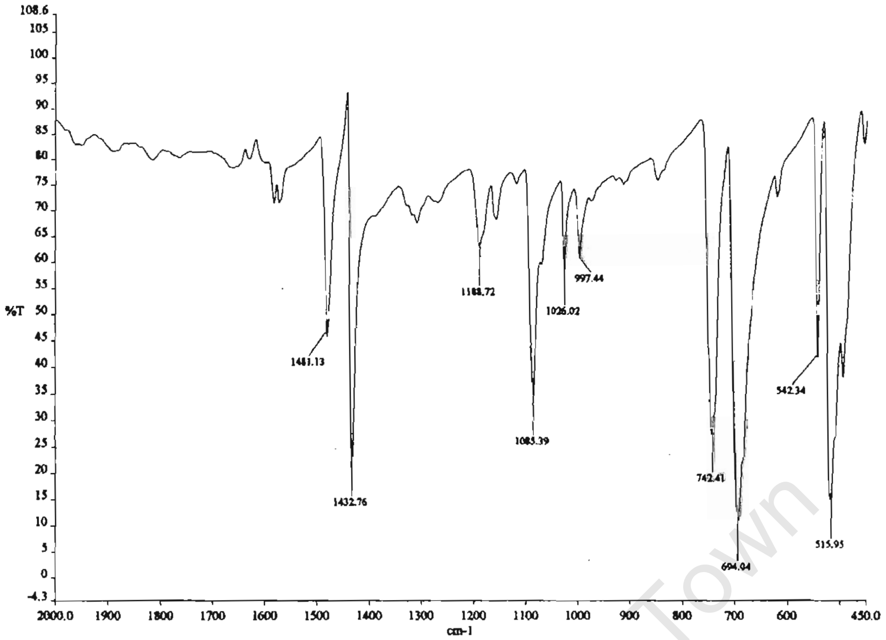


Figure 4.14 Infrared spectrum of $RuCl_2(PPh_3)_3$ **[9]** from $RuCl_3.3H_2O$ as a KBr disc

Solutions of compound **9** are extremely sensitive to oxygen as they rapidly changed colour from orange to green when left to stand in air. Cenini *et al.* postulated an intermediate oxygen complex $RuCl_2(PPh_3)_2O_2$,[38] James and Markham observed the uptake of oxygen to be consistent with the overall stoichiometry of the equation with no direct evidence of formation a molecular oxygen complex.[39]

$$RuCl_2(PPh_3)_3 + 1.5O_2 \longrightarrow 3Ph_3PO + \text{"}RuCl_2\text{"} \quad (21)$$

The $^{31}P\{^1H\}$ NMR spectrum of compound **9** in $CDCl_3$ exhibits a sharp singlet at 29.3 ppm indicating that the PPh_3 ligands are all in the same environment. During the reaction a small singlet at -8.7 ppm was observed but this disappeared when the reaction had gone to completion. This peak is due to a free PPh_3.

4.14.1 Synthesis of $[RuCl_2(C_8H_{12})]_x$ [10]

Singleton *et al.* used ruthenium trichloride trihydrate as the starting material for the synthesis of compound **10** as shown in eqn. (22).[20]

$$RuCl_3.3H_2O + 2C_8H_{12} \xrightarrow{EtOH} \underset{\mathbf{10}}{[RuCl_2(C_8H_{12})]_x} + CH_3CHO + 2HCl \quad (22)$$

A modified procedure of Singleton *et al.* was used to obtain compound **10** but starting from $(NH_4)_2[RuCl_6]$ as shown in eqn. (23).

$$(NH_4)_2RuCl_6 + 2C_8H_{12} \xrightarrow{EtOH/H_2O} \underset{\mathbf{10}}{[RuCl_2(C_8H_{12})]_x} + CH_3CHO + 2NH_4Cl \quad (23)$$

Water dissolved $(NH_4)_2[RuCl_6]$ and it went into solution and the 1,5-cyclooctadiene ligand coordinated to the ruthenium centre. When water was not added compound **10** could not be isolated and this is ascribed to dissolution effects.

The reaction with the $H_2[RuCl_6]$ did not need water because the ruthenium was already in solution and readily coordinated with the COD ligand.

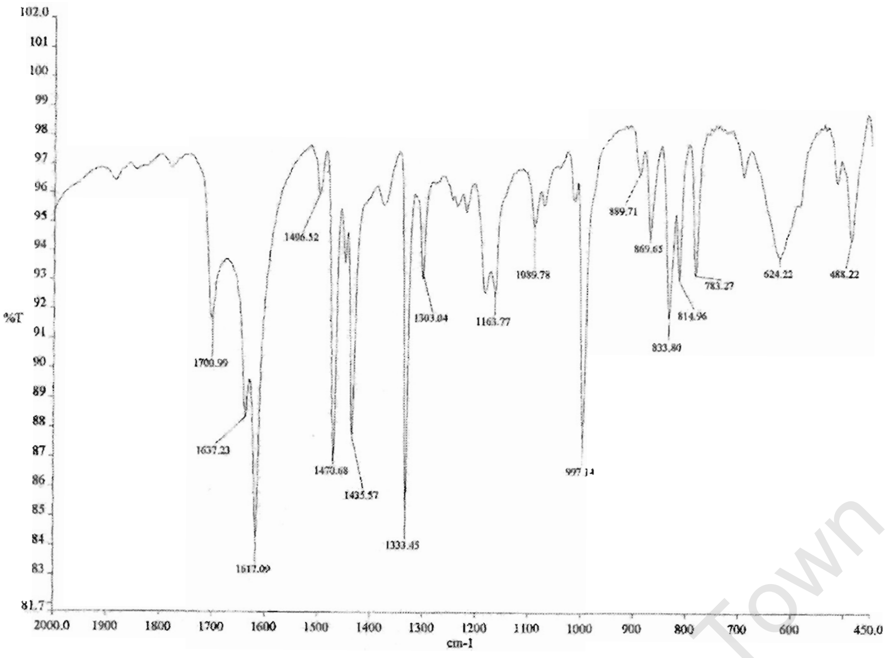


Figure 4.15 Infrared spectrum of $[RuCl_2(C_8H_{12})]_x$ **[10]** prepared from $(NH_4)_2[RuCl_6]$ as a KBr disc

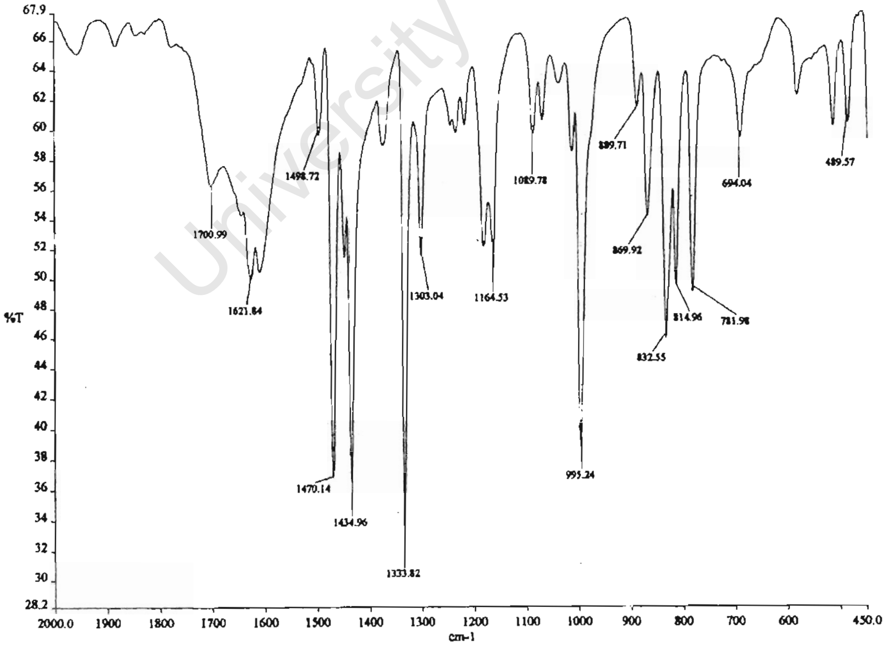


Figure 4.16 Infrared spectrum of $[RuCl_2(C_8H_{12})]_x$ **[10]** prepared from $RuCl_3.3H_2O$ as a KBr disc

The COD ligand in compound **10** is labile due to the high trans-influence of the Cl group and the greater electronegativity of Cl, which contracts the ruthenium-5d orbitals and synergistically weakens the ruthenium-COD bond. Therefore a variety of ligands readily displace COD from compound **10** forming complexes of the general formular RuL_3Cl_2. Herein we describe the displacement of COD from compound **10** by the PPh_3 ligand to give compound **9** in reasonable yields (67%) as shown in eqn. (24).

$$\underset{\textbf{10}}{[RuCl_2(C_8H_{12})]_x} + 3PPh_3 \xrightarrow[65^0C,\ 3\ h,\ N_2]{MeOH} \underset{\textbf{9}}{RuCl_2(PPh_3)_3} + C_8H_{12} \quad (24)$$

Compound **10** and PPh_3 in a ratio of 1:6 were refluxed in methanol under nitrogen for 3 h after which a precipitate was collected on a glass filter and dried *in vacuo* affording the product as a brown solid which was identified by infrared spectroscopy, melting point and elemental analysis to be pure compound **9**.[20]

Compound **10** is highly insoluble in most organic solvents and thus NMR studies where not performed for this compound. It is thought to have a polymeric chloride-bridge structure.[22] Compound **10** reacts via halogen bridge cleavage and is a useful synthetic precursor to a variety of ruthenium complexes owing to the ease with which the halogen bridges are cleaved.[22]

4.14.2 Synthesis of $(NH_4)_2[RuCl_6]$ [11]

Compound **11** can readily be prepared from a reaction of ruthenium trichloride trihydrate with ammonium chloride and concentrated HCl on a steam bath as shown in the eqn. (25) and this is a new reaction which has not been reported as far as we are aware.

$$RuCl_3.3H_2O + 2NH_4Cl + HCl \longrightarrow \underset{\textbf{11}}{(NH_4)_2RuCl_6} + \text{other products} \quad (25)$$

Herein we also describe a new method of obtaining compound **11** in good yields (78%) from the $H_2[RuCl_6]$ solution which contains about 38 g/l of ruthenium metal.

$$H_2RuCl_6 + 2NH_4Cl \longrightarrow \underset{\mathbf{11}}{(NH_4)_2RuCl_6} + 2HCl \quad (26)$$

The reaction was performed on a steam bath for 2.5 h with a 12-fold excess of NH_4Cl which precipitates the product out of solution as reddish brown microcrystals in good yields (78%). For the reaction with ruthenium trichloride trihydrate the NH_4Cl is in 6-fold excess and the reaction time is 4 h.

The reddish brown microcrystals do not melt below $350^{\circ}C$ and were characterised by elemental analysis. They dissolve in cold water affording dark orange solutions and are only very slightly soluble in hot and cold organic solvents giving purple solutions. Compound **11** is very useful as it has been converted to the useful precursor compounds **7**, **8**, **9** and **10**

4.14.3 Synthesis of $Cp^*{}_2Ru_2Cl_4$ [12]

The synthesis of compound **12** was first reported by 1984 by Grubbs *et al.* and this made the $(C_5Me_5)Ru$ fragment easily accessible.[29,30] It was synthesised using ruthenium trichloride trihydrate as the starting material as shown in eqn. (27).

$$RuCl_3.3H_2O + C_5Me_5H \xrightarrow[\text{- HCl}]{\text{ROH reflux, 6 h}} \frac{1}{2}\underset{\mathbf{12}}{[Cp^*RuCl_2]_2} + RuCp^*_2 \quad (27)$$

We have been able to prepare compound **12** from the acidic $H_2[RuCl_6]$ as shown in eqn. (28).

$$2H_2RuCl_6 + 2C_{10}H_{16} \xrightarrow[\text{reflux, } N_2\text{, 4 h}]{\text{EtOH}} \underset{\textbf{12}}{2[Cp^*RuCl_2]_2} + 6HCl \quad (28)$$

The brown solid product that was obtained was washed with pentane in order to remove decamethylruthenocene. Compound **12** is soluble in dichloromethane and chloroform and slightly soluble in methanol. As a solid it is stable in air for short periods of time and it is recommended that it be stored at 4°C as samples left at ambient temperatures for several weeks show diminished solubilities.[31]

However we have not been successful in our attempts to prepare the compound **12** from compound **11**.

$$\underset{\textbf{11}}{2(NH_4)_2RuCl_6} + 2C_{10}H_{16} \not\longrightarrow \underset{\textbf{12}}{C_{20}H_{30}Ru_2Cl_4} + 6HCl + 2NH_4Cl \quad (29)$$

The product that we obtained still contained nitrogen as seen in the elemental analysis, even after several attempts of using water as a second solvent for causing the partial dissolution of the ammonium hexachlororuthenate.

4.15 Attempted synthesis of $[OsCl_2(COD)]_n$

This compound is a useful starting material for a range of osmium compounds. It was first reported by Schrock *et al.*[33] and was synthesised using OsO_4 as the starting material as shown in eqn. (30).

$$OsO_4 + 2HCl + C_5H_{12}O + C_8H_{12} \longrightarrow [OsCl_2(C_8H_{12})]_n + \text{other products} \quad (30)$$

Our attempts to prepare the compound using $(NH_4)_2[OsCl_6]$ **[1]** did not give the required product.

$$\underset{\textbf{1}}{(NH_4)_2OsCl_6} + 2HCl + C_5H_{12}O + C_8H_{12} \not\longrightarrow [OsCl_2(C_8H_{12})]_n + \text{other products} \qquad (31)$$

Compound **1** was dissolved in water and heated with concentrated HCl and isoamyl alcohol as the reacting solvent on a steam bath for 1 h after which COD was added and the mixture distilled at 1 atm until the temperature above the solution reached *ca* 120°C. The mixture was then allowed to cool to room temperature and the product was filtered and dried *in vacuo* affording a light brown product which was characterised by elemental analysis and melting point and did not correlate with literature values reported by Schrock *et al.*[33] The elemental analysis still showed that nitrogen was still in the product (5.62%). The nitrogen is from the starting material. When the reaction was done without adding water, nitrogen did not appear in the elemental analysis, the hydrogen agreed with literature but there was just a slight percentage of carbon in the product (0.16%) instead of 26%. This indicated that the COD had not coordinated with the osmium metal centre. Longer reaction times also proved equally ineffective giving unidentified decomposition material.

4.16 Synthesis of H_2OsCl_6 [13] and H_2OsBr_6 [14] from $K_2OsO_2(OH)_4$

Compound **13** was synthesised by refluxing $K_2[OsO_2(OH)_4]$ with concentrated HCl (37%) in air as shown in eqn. (32).

$$K_2OsO_2(OH)_4 + 10HCl \xrightarrow{93\%} \underset{\substack{\text{purple microcrystals} \\ \textbf{13}}}{H_2OsCl_6} + Cl_2 + 6H_2O + 2KCl \qquad (32)$$

The analogous H_2OsBr_6 **[14]** was synthesised by refluxing $K_2[OsO_2(OH)_4]$ with concentrated HBr (48%) in air as shown in eqn. (33).

$$K_2OsO_2(OH)_4 + 10HBr \xrightarrow{85\%} \underset{\substack{\text{black microcrystals} \\ \mathbf{14}}}{H_2OsBr_6} + Br_2 + 6H_2O + 2KBr \quad (33)$$

Compounds **13** and **14** were obtained in good yields (93 and 85%). Both compounds are very soluble in water, compound **13** giving yellow solutions and compound **14** giving blood-red solutions.

Characterisation of compounds **13** and **14** proved difficult as there was no literature data obtained relating to melting points on these salts, except for their preparation method and respective colours.[1] Both compounds did not melt below 350°C.

$Na_2[OsCl_6]$ **[15]** was synthesised using a modified literature procedure[1] according to eqn. (34).

$$K_2OsO_2(OH)_4 + 7HCl + FeCl_2.4H_2O + 2NaCl \longrightarrow \underset{\substack{\text{red microcrystals} \\ \mathbf{15}}}{Na_2OsCl_6} + FeCl_3.6H_2O + 4H_2O + 2KCl \quad (34)$$

Compounds **13** and **14** could have been analysed by halogen analysis, but this was not readily available so we decided to prepare their derivatives

4.17 Characterisation of $H_2[OsCl_6]$ [13] and $H_2[OsBr_6]$ [14]

Compounds **13** and **14** were used to prepare known compounds which were then characterised by their melting points, elemental analysis, ^{31}P NMR and infrared spectroscopy which were found to be in agreement with reported values.[23]

$$H_2OsCl_6 + 3PPh_3 \xrightarrow[\text{reflux, } N_2\text{, 12hr}]{\text{t-butyl alcohol/ } H_2O} \underset{\substack{\text{64\% green solid} \\ \mathbf{16}}}{OsCl_2(PPh_3)_3} + \text{other products} \quad (35)$$

$$H_2OsBr_6 + 3PPh_3 \xrightarrow[\text{reflux, } N_2\text{, 12hr}]{\text{t-butyl alcohol/ } H_2O} \underset{\substack{\text{59\% dark green solid} \\ \mathbf{17}}}{OsBr_2(PPh_3)_3} + \text{other products} \quad (36)$$

The synthesis $OsCl_2(PPh_3)_3$ **[16]** and $OsBr_2(PPh_3)_3$ **[17]** was first reported in 1975 by Hoffman and Caulton[23] and later the yields were improved by Elliot *et al.* in 1989.[24] In both reactions these compounds were synthesised from hexahaloosmate(IV) compounds, $(NH_4)_2[OsX_6]$ (X = Cl, Br) as the starting materials and carefully chosing the solvent. *tert-* Butyl alcohol is employed as the solvent in order to avoid carbonyl extraction from the solvent.

$$\underset{\mathbf{1}}{(NH_4)_2OsCl_6} + 3\,PPh_3 \xrightarrow[\text{reflux } N_2 \text{ 122hr}]{\text{t-butyl alcohol/ } H_2O} \underset{\substack{\text{70\% green solid} \\ \mathbf{16}}}{OsCl_2(PPh_3)_3} + \text{other products} \quad (37)$$

The reaction time used was much longer from $(NH_4)_2[OsCl_6]$ **[1]** than when $H_2[OsCl_6]$ **[13]** and $H_2[OsBr_6]$ **[14]** were used. This can be attributed to the fact that compounds **13** and **14** are much more soluble in water than $(NH_4)_2[OsCl_6]$ **[1]** and $(NH_4)_2[OsBr_6]$ **[18]**. Compound **1** remained unchanged after 122 h reflux in pure alcohol. This was due to the lack of solubility of compound **1** in the alcohol and this necessitates the addition of water to the reaction mixture.

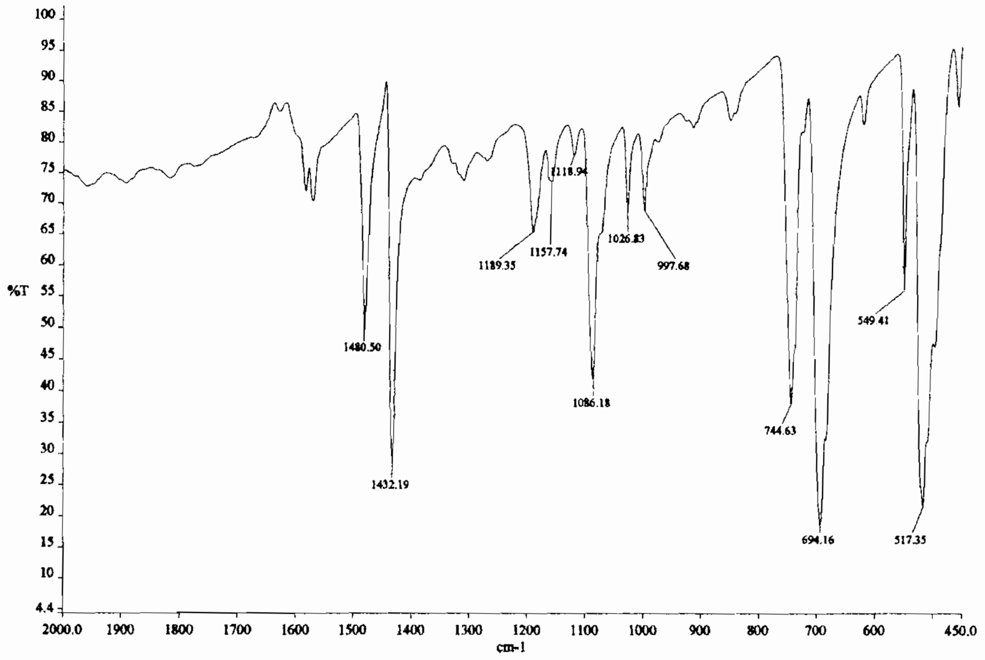


Figure 4.17 Infrared spectrum of $OsCl_2(PPh_3)_3$ **[16]** as a KBr disc

In the infrared spectrum of $OsCl_2(PPh_3)_3$ **[16]** the bands at 517, 694, 744 and 1086 cm^{-1} are due to coordinated PPh_3 ligands.[27]

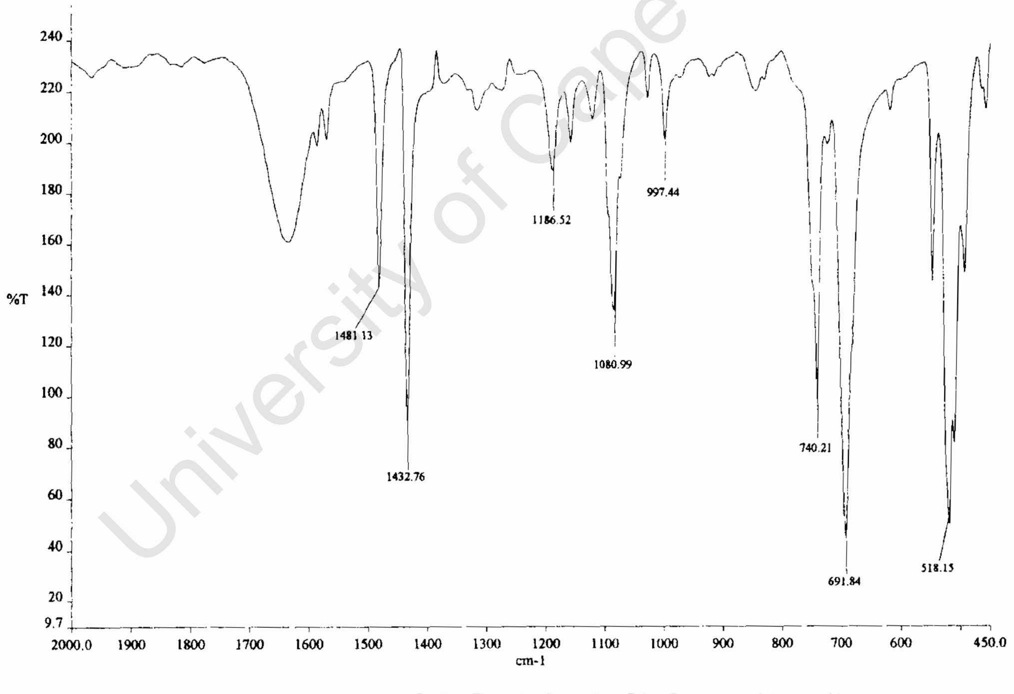


Figure 4.18 Infrared spectrum of $OsBr_2(PPh_3)_3$ **[17]** as a KBr disc

Similarly for the analogous $OsBr_2(PPh_3)_3$ **[17]** peaks occur at 518, 692, 740 and 1081 cm^{-1} as shown in the spectra in Figure 4.18.

The infrared spectrum of free triphenylphosphine (450-2500 cm^{-1}) is identical to the spectrum of this ligand coordinated to the osmium metal, except in the 500 cm^{-1} region where P-C (phenyl) absorptions occur.[37]

The $^{31}P\{^1H\}$ NMR spectrum of $OsCl_2(PPh_3)_3$ **[16]** shows a singlet at 29.2 ppm and that of $OsBr_2(PPh_3)_3$ **[17]** exhibits a singlet at 26.5ppm suggesting that in both cases three phosphorus nuclei are equivalent on the NMR time scale.

The synthesis of $(NH_4)_2[OsBr_6]$ **[18]** was also useful in the characterisation of $H_2[OsBr_6]$ **[14]**. Compound **18** has been prepared by refluxing $K_2[OsO_2(OH)_4]$ with concentrated HBr and precipitating the product out of solution with NH_4Br as shown in eqn. (38).

$$K_2OsO_2(OH)_4 + 6HBr + 2NH_4Br \longrightarrow \underset{\substack{\text{black microcrystals}\\ \mathbf{18}}}{(NH_4)_2OsBr_6} + 2KBr + 6H_2O \quad (38)$$

$H_2[OsBr_6]$ **[14]** was dissolved in water and then reacted with NH_4Br with ethanol as the reacting solvent. No evidence of decomposition was observed below 170°C for both $H_2[OsCl_6]$ **[13]** and $H_2[OsBr_6]$ **[14]**.

$$\underset{\mathbf{14}}{H_2OsBr_6} + 2NH_4Br \longrightarrow \underset{\substack{\text{black microcrystals}\\ \mathbf{18}}}{(NH_4)_2OsBr_6} + 2HBr \quad (39)$$

Compound **18** crystallises as black microcrystals in good yields (80%) and is insoluble in methanol, ethanol or acetone. It is very soluble in cold water giving dark orange solutions. Compound **18** was characterised by elemental analysis.

$Cp^*{}_2Os_2Br_4$ **[19]** is reported in the literature[25] as having been synthesised from compound $H_2[OsBr_6]$ **[14]** and is an ideal compound to synthesise as this would prove that the compound that we had prepared was indeed compound **14**.

$$\underset{\mathbf{14}}{2H_2OsBr_6} + 2Cp^*H \xrightarrow[\text{reflux, } N_2\text{, 2 h}]{\text{EtOH}} \underset{\mathbf{19}}{Cp^*_2Os_2Br_4} + 6HBr \quad (40)$$

Refluxing a mixture of compound **14** with 1.5 equiv. of C_5Me_5H in ethanol afforded compound **19** as a brown black precipitate in good yields and compound **19** was characterised by elemental analysis infrared spectroscopy as KBr disks and ^1H NMR. Compound **19** exhibits a singlet at 2.54 ppm in CD_2Cl_2 attributed to the methyl protons of the cyclopentadienyl ring. This value agrees very well with that reported by Gross *et al.*[25]

4.17.1 Attempted synthesis of $Cp^*_2Os_2Cl_4$

After a careful review of the literature it was noted that this complex has not been reported before. A similar procedure as used in the preparation of the the analogous $Cp^*_2Os_2Br_4$ **[19]** was attempted as shown in eqn. (41).

$$2H_2OsCl_6 + 2Cp^*H \not\longrightarrow Cp^*_2Os_2Cl_4 + 6HCl \quad (41)$$

$H_2[OsCl_6]$ **[13]**, water and Cp*H were refluxed in EtOH under N_2 for 18 h. The yellow precipitate was filtered on a glass filter affording white microcrystals which were identified by elemental analysis to be $[Os(C_5Me_5)_2]_2$ in 10% yield but this product was contaminated with $[OsCl(\eta^5\text{-}C_5Me_5)_2]Cl$. The direct reaction of $Na_2[OsCl_6]$ **[15]** with Cp*H in refluxing EtOH has been reported to give $[Os(\eta^5\text{-}C_5Me_5)_2]_2$ as the product.[48]

The reaction was also done using $(NH_4)_2[OsCl_6]$ **[1]** and similarly gave $[Os(C_5Me_5)_2]_2$ in 8% yield but this was also contaminated with $[OsCl(\eta^5\text{-}C_5Me_5)_2]Cl$.

4.17.2 Electronic spectroscopic studies of H_2OsCl_6 [13] and H_2OsBr_6 [14]

Electronic spectroscopic studies were carried out in order to characterise compounds **13** and **14**. The salts have absorptions in the visible region and therefore appear coloured.

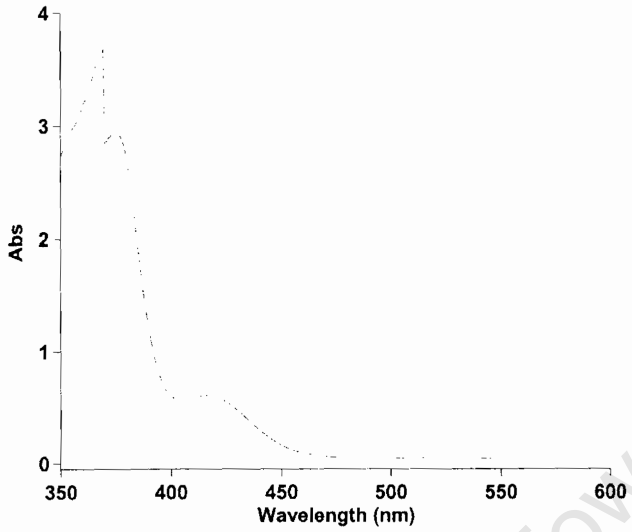


Figure 4.19 Absorption spectrum of an $H_2[OsCl_6]$ **[13]** solution in water

$H_2[OsCl_6]$ **[13]** and $H_2[OsBr_6]$ **[14]** were studied as solutions in water as they are not very soluble in other solvents. The absorption spectrum of $H_2[OsCl_6]$ **[13]** exhibits a very sharp band at about 375 nm possibly due to the transition between t_{2g} and e_g orbitals and this corresponds to the energy difference between the levels, and a shoulder peak at about 390 nm. A very weak broad peak is observed at about 420 nm. Broadening is due to the accompanying vibrational excitations, occurance of the Jahn-Teller effect, and spin-orbit coupling effects.[32] In the Os(IV) chloro-complex the charge-transfer (L→M) is not very strong and hence the weaker colour of the complex.[46]

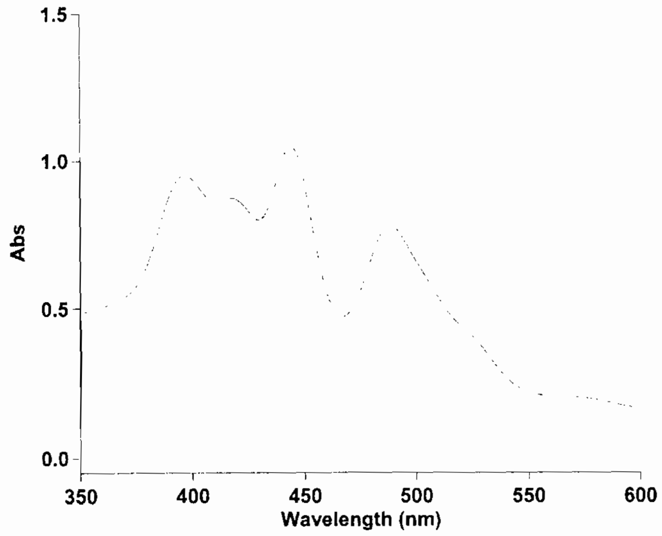


Figure 4.20 Absorption spectrum of an $H_2[OsBr_6]$ **[14]** solution in water

The electronic absorption spectrum of the compound **14** in aqueous solution in the range of 350 to 600 nm has weak bands at about 395 and 420 nm and these are due to 'spin-forbidden' transitions. There are also two bands with intermediate transitions and these might be due to *d-d* transitions derived from the metal *d* orbitals and their energies might also differ on account of interelectronic repulsions. The dark colour of a solution containing $[OsBr_6]^{-2}$ is attributed to strong charge-transfer (L→M) absorption in an Os(IV) bromo-complex.[46,47] It has also been shown that the positions of the bands in the hexahalide solutions can be correlated with the dielectric constant of the solvent.[47] The literature data for other hexahalide solutions compares very well with the data that we obtained.[46,47,50]

4.18 Synthesis of $[Cp^*Ru(CO)_2]_2$ [20]

Compound **20** was synthesised by refluxing a mixture of $Ru_3(CO)_{12}$ **[7]** (synthesised from $(NH_4)_2[RuCl_6]$ and Cp*H in decane as shown in eqn. (42).[49]

$$2Ru_3(CO)_{12} + 3Cp^*H \xrightarrow[175^0C,\ 4\ h]{decane,\ N_2} \underset{\text{orange crystals}}{3[Cp^*Ru(CO)_2]_2} \quad (42)$$

Compound **20** was obtained in good yields (83%) and identified by IR spectroscopy, melting point and elemental analysis to be pure.

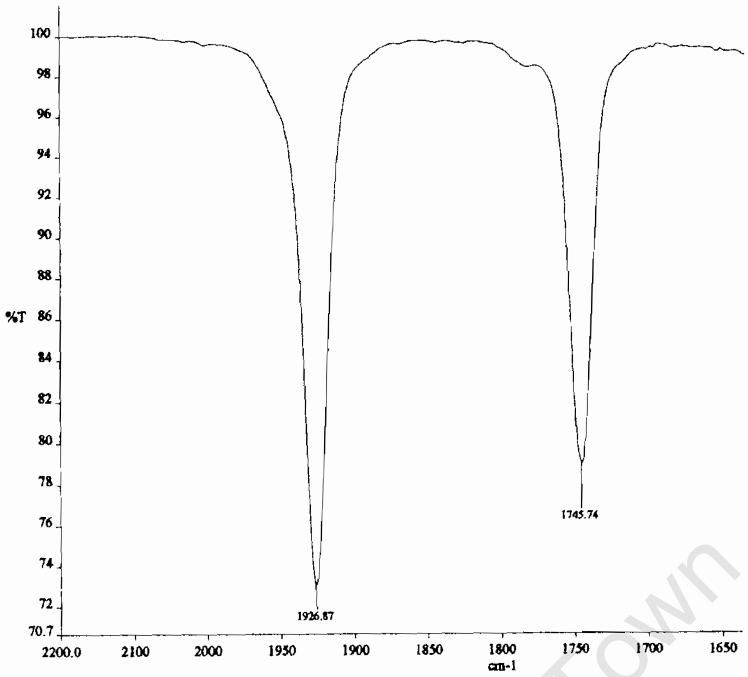


Figure 4.21 Infrared spectrum in dichloromethane of $[Cp^*Ru(CO)_2]_2$ **[20]**

The infrared spectrum of compound **20** in dichloromethane exhibits a very strong band at 1927 cm^{-1} attributed to a terminal carbonyl. The band at 1746 cm^{-1} is attributed to a bridging carbonyl. [49]

4.18.1 Attempted synthesis of $Cp^*_3Ru_3H_5$

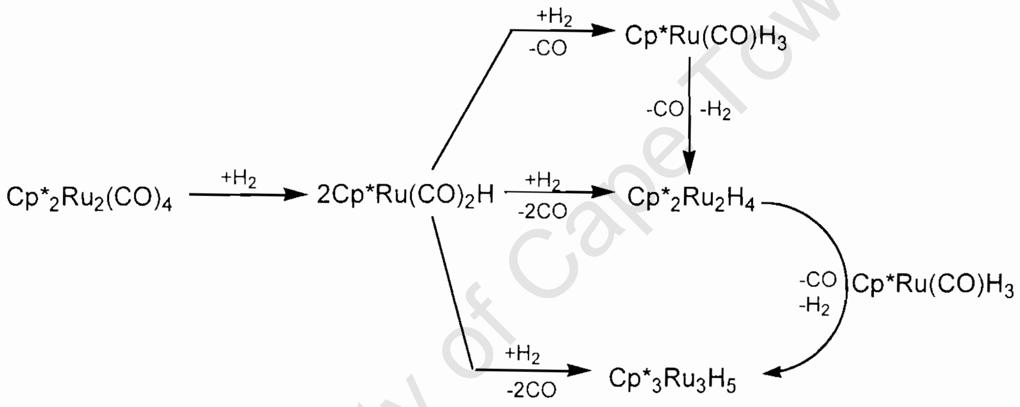
This trinuclear polyhydride cluster of ruthenium has been reported by Suzuki *et al* and was synthesised in a multistep procedure as shown in the reaction scheme below.[42]

$$Cp^*_2Ru_2Cl_4 \xrightarrow[\text{2) EtOH}]{\text{1) LiAlH}_4} Cp^*_2Ru_2H_4 \xrightarrow{H^+X^-} [Cp^*_3Ru_3H_6]^+X^- \xrightarrow{\text{base}} Cp^*_3Ru_3H_5 \quad (43)$$

Scheme 4.1

The dinuclear tetrahydride-bridge complex of ruthenium was synthesised by treatment of $(C_5Me_5)_2Ru_2Cl_4$ with $LiAlH_4$ followed by workup with ethanol. When $(C_5Me_5)_2Ru_2H_4$ is reacted with an acid a cationic triruthenium hexahydride cluster $(C_5Me_5)_3Ru_3H_6^+$ is obtained and treatment of this cationic cluster with a base such as sodium methoxide affords the neutral pentahydride cluster $(C_5Me_5)_3Ru_3H_5$.[43]

We attempted to synthesise this complex by hydrogenating $[Cp^*Ru(CO)_2]_2$ **[20]**. The reaction was attempted in an autoclave which was pressurised with H_2 (80 atm) and heated at 250°C for 4 h. At the end of this period the product was identified by infrared spectroscopy and ^1H NMR to be starting material i.e no reaction had occured. We had expected the hydrogen to be able to replace the CO ligands at this temperature as shown in the scheme 4.2.



Scheme 4.2

$Cp^*_3Ru_3H_5$ is reported to be very thermally stable in solution at very high temperatures in sterically bulky solvents such as 1,3,5 trimethylcyclohexane and does not decompose into mono- or bimetallic fragments.[44]

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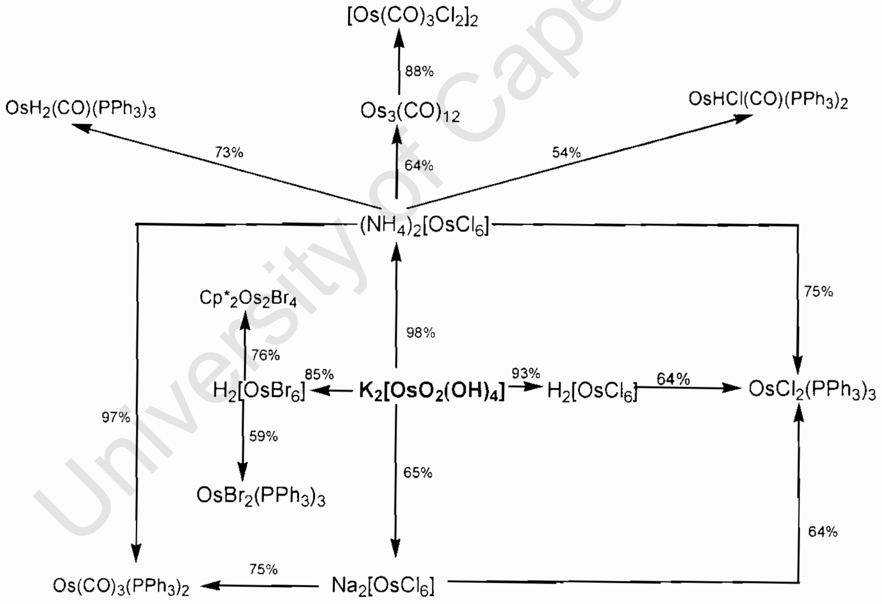
Chapter 5

Conclusions and future work

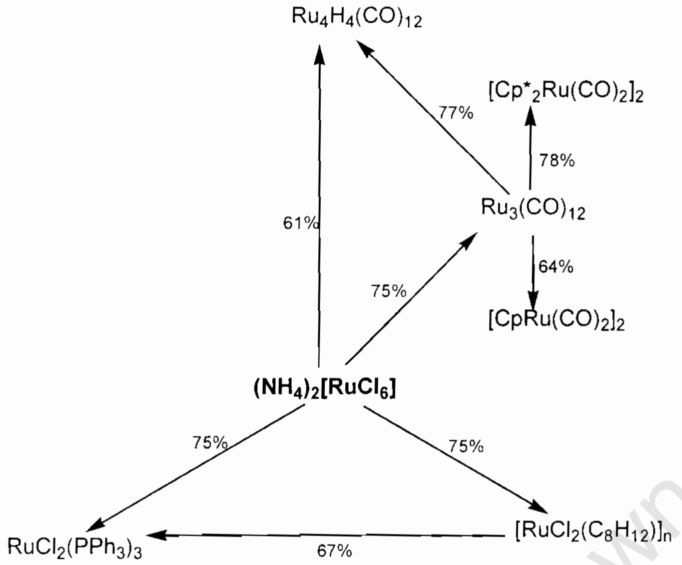
5.1 Brief summary of thesis results

By modifying the conventional literature procedures we have been able to demonstrate that locally available refinery materials can be converted into useful known inorganic and organometallic precursors. Conventional methods were modified by either using different solvent mixtures or using water as a second solvent, which caused dissolution of the osmium salts which are otherwise known to be very insoluble in most solvents. Some useful osmium complexes that have been synthesised from $K_2[OsO_2(OH)_4]$ and described in this thesis are shown in the scheme below:

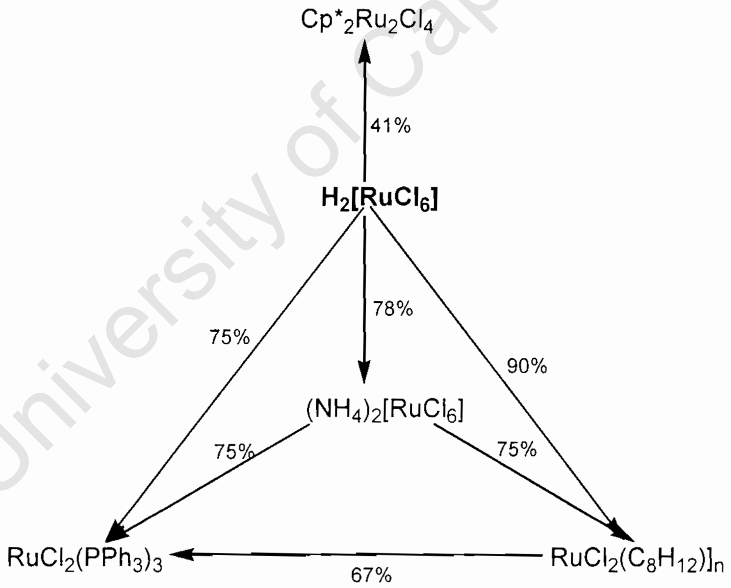


Scheme 5.1.1 Reactions that have been carried out using $K_2OsO_2(OH)_4$, from the refinery

Useful ruthenium compounds have also been prepared in good yields, from either solid $(NH_4)_2[RuCl_6]$ or the acidic $H_2[RuCl_6]$ solution as shown in the schemes below:



Scheme 5.1.2 Reactions that have been carried out using solid $(NH_4)_2RuCl_6$, from the refinery



Scheme 5.1.3 Reactions using that have been carried out using the H_2RuCl_6 solution, from the refinery

The chemistry of $Cp_2Fe_2(CO)_4$, $Cp^*{}_2Fe_2(CO)_4$, Cp_2Fe and $Cp^*{}_2Fe$ is well established, but the chemistry of the analogous ruthenium and osmium complexes is not well reported.[1] This can not only be ascribed to the relatively high cost of osmium and ruthenium starting materials, but also unavailability of these starting materials. The natural abundance of iron is also much higher than that for osmium and ruthenium.

In this project we have been able to synthesise various useful osmium and ruthenium starting materials from Anglo Platinum refinery materials. The hexahaloosmium complex $(NH_4)_2[OsCl_6]$ which has been prepared from potassium osmate $K_2[OsO_2(OH)_4]$, is an important precursor in the synthesis of a variety of osmium(II) and osmium(0) complexes which are very useful in homogeneous catalysis. Ruthenium(IV) complexes were also successfully prepared from hexachlororuthenate $(NH_4)_2[RuCl_6]$ and dihydrogen hexachlororuthenate $H_2[RuCl_6]$ in good yields.

5.2 Future work

Although this project focused on the synthesis of known complexes, more work can be done in the future to prepare new osmium and ruthenium complexes from the Anglo Platinum refinery materials. The new complexes would then be tested for potential applications as catalysts, materials and medicines.

Sanchez-Delgado envisaged that homogenous catalysis by osmium complexes is more promising than hitherto realised due to more enhanced oxidative and thermal stabilities that these complexes have, as compared to other analogous complexes from other transition metals.[2]

New complexes with a broad range of phosphines, could also be synthesised in a similar manner as for the analogous $Os(CO)_3(PPh_3)_2$ complex, which we have prepared in quantitative yields from sodium hexachloroosmate Na_2OsCl_6. It is hoped that some of these complexes will show catalytic activity, specifically towards the activation of C-H, C-S, C-N, N-H and O-H bonds.

We have reported in this project that locally available $K_2OsO_2(OH)_4$ has been investigated as a precursor in the synthesis of the osmium cluster $Os_3(CO)_{12}$. Conversion of this cluster to $CpOs(CO)_2H$ and $Cp^*Os(CO)_2H$ is another area which needs to be explored further, and direct routes of synthesis of $[CpOs(CO)_2]_2$ and $[CpOs(CO)_2X]$ also need to be investigated as the route from $(NH_4)_2OsCl_6$ suffers from poor yields and is less convenient because it is a multistep procedure. When a search was done on Sci-Finder Scholar it was noted that there were only 4 hits on the complex $Cp^*{}_2Os_2(CO)_4$ and this could be another possible compound to try and prepare.

In conclusion, it is hoped that, due to the relative ease with which we can obtain useful osmium and ruthenium starting materials from refinery materials, novel synthetic methods can also be developed and these may pave way to variations in the design of new osmium and ruthenium complexes with sophisticated ligands and their application to a number of useful catalytic reactions. We are currently furthering our studies in this regard.

5.3 References

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