

The Preparation and Characterisation of Osmium (IV), Osmium (II) and Osmium (0) Complexes from Refinery Materials

Haleden Chiririwa, and Edison Muzenda

Abstract—By modifying the conventional literature procedures we have been able to demonstrate that locally available refinery materials can be converted into useful 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. The hexahaloosmium complex $(\text{NH}_4)_2\text{OsCl}_6$ which has been prepared from potassium osmate $\text{K}_2\text{OsO}_2(\text{OH})_4$, is an important precursor in the synthesis of a variety of osmium (II) and osmium (0) complexes which are very useful in homogeneous catalysis. The complexes were characterized by elemental analysis and infrared spectroscopy.

Keywords— Osmium complexes, Potassium osmate, Refinery materials

I. 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].

This paper presents an overview of the work done using refinery materials in the synthesis of osmium complexes. Synthesis and characterisation of the various osmium

complexes is reported and most of the synthesis have been modified as the literature procedures mainly use the commercially available very toxic starting material osmium tetroxide (OsO_4) whereas all the complexes discussed in this paper have been prepared from refinery materials obtained from Anglo Platinum.

II. EXPERIMENTAL

A. Synthesis of ammonium hexachloroosmate (IV) [1]

A modified literature procedure by Dwyer and Hogarth was followed [4]. 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 $169-170^\circ\text{C}$ subl. (lit.¹ m.p 170°C subl). Anal. Calc for $\text{N}_2\text{H}_8\text{OsCl}_6$: H, 1.86%; N, 6.38%. Found: H, 1.67%; N, 6.36%.

B. Synthesis of ammonium hexabromoosmate [2]

A modified literature procedure was followed [4]. 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: $\text{N}_2\text{H}_8\text{OsBr}_6$: H, 1.13%; N 3.96% Found: H, 1.25 % N, 3.89%.

H. Chiririwa was with the University of Cape Town and is now a Lecturer in the Department of Applied Chemistry, National University of Science & Technology, P.O Box AC939 Ascot Bulawayo, Zimbabwe (phone: +263-9-2828442 ext 2445; fax: +263-9-286803; e-mail: (harrychiririwa@yahoo.com))

Edison Muzenda is a Full Professor in the Department of Chemical Engineering Technology at the University of Johannesburg, Doornfontein, South Africa e-mail: emuzenda@uj.ac.za

C. Synthesis of carbonylchlorohydrotris (triphenylphosphine) osmium (II) [3]

A modified literature procedure by Robinson *et al* was followed [5]. 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 C₅₅H₄₆ClOsP₃: C, 63.40%; H, 4.40%; Found: C, 62.95%; H, 3.99%. IR ν_{co} (in CH₂Cl₂) 1912 (s) cm⁻¹. M.p. 180-181 °C (lit² 179-183 °C)

D. Synthesis of carbonyldihydrotris (triphenylphosphine) osmium (II) [4]

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 C₅₅H₄₇OOsP₃: C, 63.60%; H, 4.70%; Found: C, 63.95%; H, 4.99%. IR ν_{co} (in CH₂Cl₂) 1934 (s) and ν_{osH} (in CH₂Cl₂) 1915 (w) cm⁻¹. M.p. 201-204 °C (lit.² 202-204 °C).

E. Synthesis of tricarbonylbis (triphenylphosphine) osmium (0) [5]

Modified literature procedures were used [6-7]. 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 as pure product in quantitative yields (0.46 g, 97%). Anal. Calc. for C₃₉H₃₀O₃OsP₂: C, 58.54%; H, 3.85%; Found: C, 58.47%; H, 3.46%. m.p. 190 °C dec. IR ν_{co} (in CH₂Cl₂): 2044 (vs) 1973 (s) and 1914 (s).

F. Synthesis dichlorotris (triphenylphosphine) osmium (II) [6]

A literature procedure by Hoffman and Caulton was used [8]. Ammonium hexachloroosmate (IV) (137 mg, 0.31 mmol), 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 C₅₄H₄₅Cl₂OsP₃: 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 (CDCl₃) 29.24 (s).

G. Synthesis of sodium hexachloroosmate (IV) Na₂OsCl₆ [7]

A modified literature procedure by Dwyer and Hogarth was followed [4]. 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 4h 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%) [7] was characterised by its colour [9] and synthesis of the known Os(CO)₃(PPh₃)₂ also assisted in characterising it.

H. Synthesis of dihydrogen hexabromoosmate H₂OsBr₆ [8]

Potassium osmate (1.06 g, 2.88 mmol) and hydrobromic acid (40 ml, 48%) were refluxed in air in a round bottomed flask for 5 h and mixture 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.

I. Synthesis of dihydrogen hexachloroosmate [9]

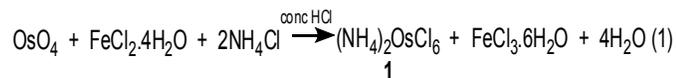
A similar methodology used to prepare dihydrogen hexabromoosmate was used here replacing hydrobromic acid with concentrated hydrochloric acid (40 ml, 37%). Filtration afforded purple reddish microcrystals in quantitative yield. (1.02 g, 93%). The microcrystals are soluble in cold water

giving yellowish green solutions and are insoluble in other inorganic and organic solvents.

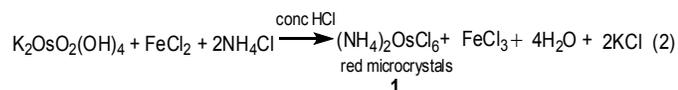
III. RESULTS AND DISCUSSIONS

A. Synthesis of $(\text{NH}_4)_2\text{OsCl}_6$ and $(\text{NH}_4)_2\text{OsBr}_6$ [1-2]

The literature method that was reported by Dwyer and Hogarth¹ 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%.



We used instead potassium osmate $\text{K}_2\text{OsO}_2(\text{OH})_4$ 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.



This reaction gave compound 1 in quantitative yields of 98%, as red microcrystals. These were only 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 $(\text{NH}_4)_2\text{OsCl}_6$ [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.

B. Synthesis of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ [3]

The divalent osmium complexes were synthesised from the hexahaloosmates(IV) $(\text{NH}_4)_2\text{OsX}_6$ ($\text{X} = \text{Cl}, \text{Br}$), Na_2OsCl_6 , dihydrogen hexahaloosmates(IV), triphenylphosphine, and an alcohol as the reacting solvent as shown in eqn (3).



Compound 1 is virtually inert at 25°C in alcoholic solvents because of its very low solubility. 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 [10] but this apparently suppresses the solubility of an intermediate complex so that no reaction is detected with alcohols within reasonable times and compound is unchanged after 48 h reflux in pure alcohol [8].

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 [10] and in this case triphenylphosphine in a 7 : 1 molar ratio (to osmium(IV) halide).

A key feature is the low solubility of the complex 3 in the alcoholic solvents used, which results in the precipitation or crystallization of the product in good yield. During the preparation of compound 3 as in eqn. (3), 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 redissolves the product and initiates its decomposition.

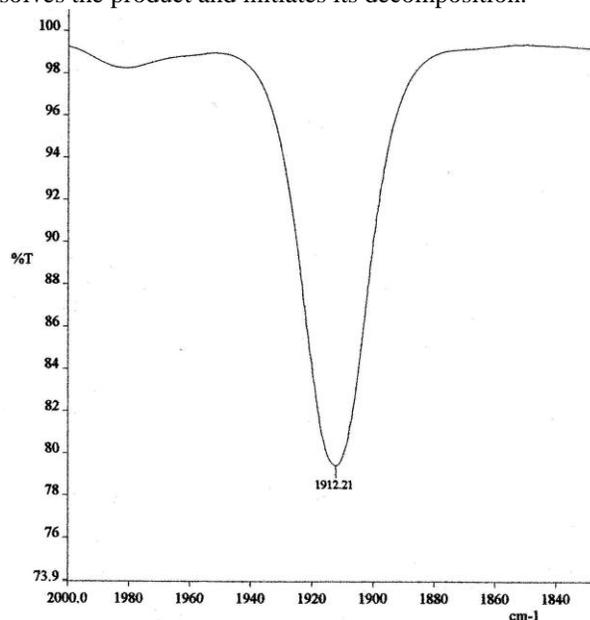


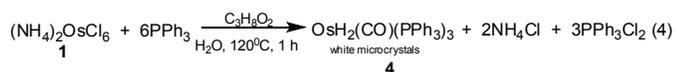
Fig 1 IR spectrum of $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ [3] in dichloromethane

For a monocarbonyl complex a single CO stretching band is expected and this was found for the compound 3 in solution as shown in the spectra above and agrees very well with what was reported by Vaska [10].

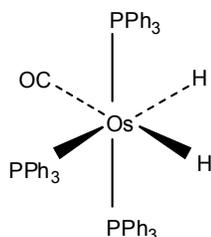
C. Synthesis of $\text{OsH}_2(\text{CO})(\text{PPh}_3)_3$ [4]

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 [4] 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 $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ [3] in a solution of sodium hydroxide in 2-methoxyethanol [11]. It was later reported by Robinson *et al* to have been synthesised by refluxing solutions of Na_2OsCl_6 [7] in 2-methoxyethanol and potassium hydroxide in formaldehyde with triphenylphosphine in 2-methoxyethanol

for 30 minutes [5]. We used $(\text{NH}_4)_2\text{OsCl}_6$ [1] for the same reaction as shown in eqn. (4).



The solvent 2-methoxyethanol has a lower boiling point (124-125 °C) than the 2-(2-methoxy-ethoxy) ethanol (194 °C) and the reaction conditions are much milder. There are three possible geometrical isomers for the complex but the resonance is only expected in the one with the structure shown below:



Compound 4

The resonance interactions occur when the hydrogen and carbonyl ligands are *trans* to one another. In the other two isomers the hydrogens are *trans* to one another or both hydrogens are *trans* to the PPh_3 ligands [5].

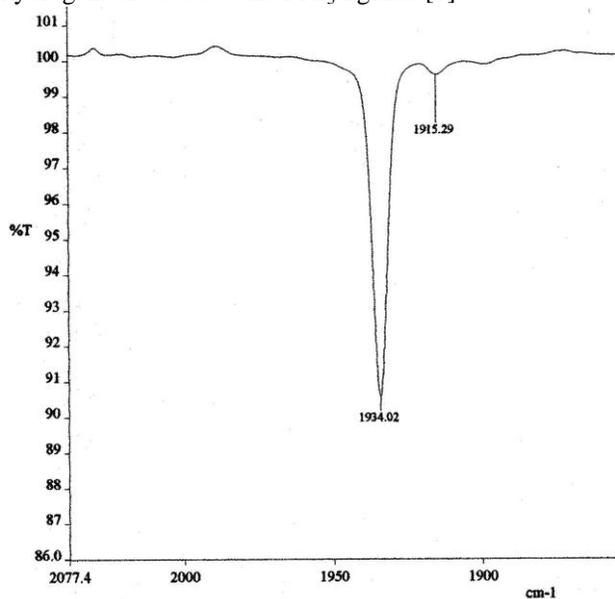


Fig 2 IR spectrum of $\text{OsH}_2(\text{CO})(\text{PPh}_3)_3$ [4] in dichloromethane

The infrared spectrum of compound 4 shows bands at $1934(\text{s})\text{ cm}^{-1}$ attributed to $\nu(\text{CO})$ and $1915(\text{w})$ attributed to $\nu(\text{OsH})$. Similar infrared values were also obtained in chloroform solution. The ν_{MH} of the tertiary phosphine-stabilized metal hydrides has been observed in the range 1600 to 2250 cm^{-1} [10]. Compound 5 is moderately soluble in benzene, chloroform and dichloromethane. The white microcrystals of compound 5 melt at 201 - $204\text{ }^\circ\text{C}$.

D. Synthesis of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ [5]

Compound 5 was first reported by Collman and Roper in 1966 [7]. They reported to have prepared it from the

osmium(II) complexes $\text{OsX}_2(\text{CO})_2(\text{PPh}_3)_2$ by zinc reduction in the presence of CO. However we have been able to prepare compound 6 in quantitative yields (97%) using Na_2OsCl_6 [7] as shown in eqn. (5).

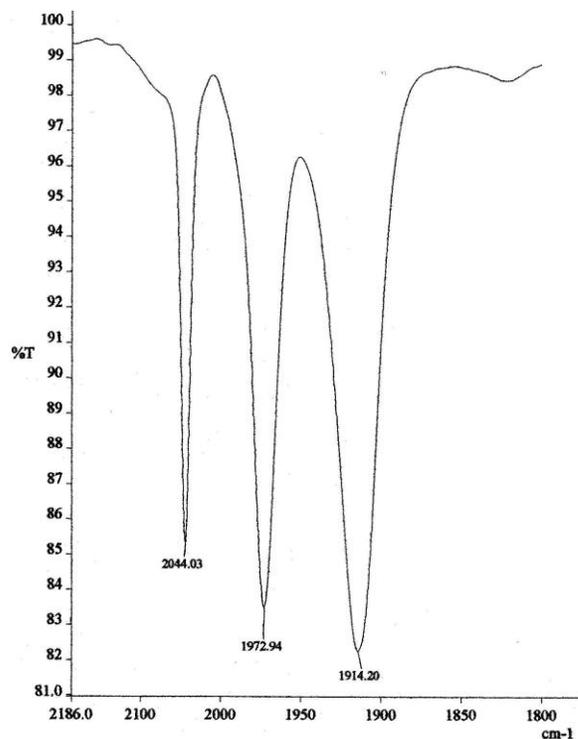
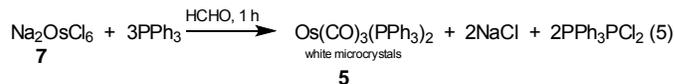


Fig 3 IR spectrum of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ [5] in dichloromethane

The infrared spectrum of compound 5 exhibits bands at $2044(\text{s})$, $1973(\text{s})$ and $1914(\text{s})\text{ cm}^{-1}$ attributed to $\nu(\text{CO})$. The peaks at $2044(\text{s})$ and $1973(\text{s})$ could also have been attributed to $\text{OsCl}_2(\text{CO})_2[\text{P}(\text{PPh}_3)_2]$ [7, 12] implying that this was a mixture of products but this was not the case as tlc only showed a single spot proving that this was a single product. This product is therefore an isomer of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ originally prepared by Collman and Roper [7].

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ [6] in CDCl_3 showed a single peak at 29.3 ppm with ^{187}Os satellites. The measured coupling constant $^1J_{\text{Os-P}}$ was 4341 Hz . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra obtained for $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ [5] might also demonstrate the presence of two isomers, which are in rapid exchange in solution at room temperature. The fluxional process involves a concerted rotational movement of the two triphenylphosphine ligands and pivoting of the carbonyls along the osmium metal centre. Phosphine substituted compounds of osmium complexes often show fluxional behaviour often observed on reaction of osmium compounds with triphenylphosphine.

