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New Routes to The Preparation of $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(COD)]_n$ From Anglo Platinum Refinery Materials

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Abstract

New and improved routes for the preparation of ruthenium complexes are described. $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(COD)]_n$ have been prepared from $[(NH_4)_2RuCl_6]$ and $[H_2RuCl_6]$. Traditionally these ruthenium complexes have been prepared from commercially available $RuCl_3.3H_2O$, but here we describe their preparation from refinery materials.

Keywords: Ruthenium complexes; Ruthenium trichloride trihydrate; Refinery materials; Ammonium hexachlororuthenate: Dihydrogen hexachlororuthenate.

1. INTRODUCTION

Here we describe the conversion of refinery materials to several known ruthenium complexes. Most of the syntheses have been modified, and thus they vary from the literature procedures, which mainly use commercially $(RuCl_3.3H_2O)$ as the starting material, whereas the complexes discussed herein have been prepared from raw refinery materials. From the literature survey it appears that no work has been reported about the direct preparation of ruthenium complexes using refinery materials.

$[Ru_3(CO)_{12}]$ is a useful starting material for much of ruthenium carbonyl chemistry. It can be prepared by several methods using commercially available ruthenium trichloride trihydrate $(RuCl_3.3H_2O)$. A disadvantage of some of the methods that have been used is that they require high pressures of CO and elevated temperatures.[1] Johnson and Lewis reacted ruthenium trichloride trihydrate with (2,4-pentanedionato)sodium in methanol in an autoclave, with H_2 (40 atm) and CO (120 atm).[2] The mixture was heated at 165 °C for 4 h to give $[Ru_3(CO)_{12}]$ in yields of 50 - 55%. In 1980 C. R. Eady *et al.* improved the yields to 85 – 95% by reacting ruthenium trichloride trihydrate in dry methanol, under a pressure of 50 atm CO and heating at 125 °C for 8 h.[3] More recently, $[Ru_3(CO)_{12}]$ has been obtained in higher yield but under 1 atm of carbon monoxide.[4] In this synthesis ruthenium trichloride hydrate (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 condenser water is not cold enough to allow sublimation on the walls of the condenser.[4] In our hands this reduced the yield of the product significantly. In 2003 Lavigne *et al.* reported that addition of two equivalents of KOH per $RuCl_3$ 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%.[5]

2. RESULTS AND DISCUSSION

$[Ru_3(CO)_{12}]$ was initially synthesized from ruthenium trichloride trihydrate according to the procedure by Johnson *et al*.[3] Then, in a new reaction, $[Ru_3(CO)_{12}]$ was obtained in high yields (96%) by the carbonylation reaction of refinery ammonium hexachlororuthenate in dry methanol in an autoclave. The latter reaction was performed using the solid refinery sample as received. This sample contained about 0.1% moisture, which was removed by drying *in vacuo* for 3 h. This moisture was later shown to be of critical importance as was seen in subsequent carbonylation reactions using the wet sample.

The infrared spectrum (in *n*-hexane) of the orange red crystals of $[Ru_3(CO)_{12}]$ (**1**) exhibited sharp absorptions at 2060(s), 2030(s) and 2011(m) cm^{-1}. These absorptions agree with the reported values by Eady *et al.;* the values can be used in identifying and assessing the carbonyl purity of the compound.[3] The complex is soluble in most organic solvents, but it is completely insoluble in water. Also of particular interest was the infrared spectrum that was obtained when the wet sample was carbonylated for 11 h under 60 atm of carbon monoxide and the time increased from 8 h to 11 h. To this reaction, a zinc granule was added as a reducing agent. The IR spectra in (*n*-hexane) exhibited absorptions at 2081(w), 2061(s), 2031(s) and 2012(m) cm^{-1}. The absorption at 2081 cm^{-1} corresponds to a v(CO) of $[H_4Ru_4(CO)_{12}]$ (**2**). The absorptions at 2024 and 2029 cm^{-1}, which occur in compound **2**, are obscured by the sharp absorption at 2031 cm^{-1}. However TLC showed only one single spot, confirming the presence of a single product. If there was a mixture of products present, other shoulders should be observed - as in the case when we obtained a mixture of $[Ru_3(CO)_{12}]$ (**1**) and $[H_4Ru_4(CO)_{12}]$ (**2**). The ^1H NMR spectrum in $CDCl_3$ of the ruthenium carbonyl hydride exhibited a peak at δ -17.79 ppm, confirming the ruthenium carbonyl hydride.

Formation of the species giving rise to the absorption at 2081 cm^{-1} in the IR spectrum can also be ascribed to the reaction of $[Ru_3(CO)_{12}]$ (**1**) with trace amounts of water from the solvent. Eady *et al.* also mentioned a reaction of $[Ru_3(CO)_{12}]$ with small amounts of water, leading to the formation of $[\alpha\text{-}Ru_4H_4(CO)_{12}]$ and $[\alpha\text{-}Ru_4(CO)_{13}H_2]$ complexes.[3]

2.1. Reaction of ammonium hexachlororuthenate with CO and H_2

By reacting crude $[(NH_4)_2RuCl_6]$ with a mixture of CO (50 atm) and H_2 (25 atm) we expected to obtain $[H_4Ru_4(CO)_{12}]$ (**2**), however, only $[Ru_3(CO)_{12}]$ (**1**) was isolated in 95% yield. This can be ascribed to the fact that H_2 does not react with compound **1** in the presence of methanol. The hydride **2** is known to be formed in hydrocarbon solvents like cyclohexane or octane.[6] Three absorptions attributed to terminal CO ligands in the IR spectrum and no band assignable to a bridging carbonyl is observed.

Of particular interest was the reaction between [$(NH_4)_2RuCl_6$], 50 atm CO and 30 atm H_2. This reaction is known to produce [$Ru_3(CO)_{12}$] (**1**) as the only product on carbonylation with CO in dry methanol as solvent. In this instance we attempted the reaction of [$(NH_4)_2RuCl_6$] with CO and H_2 in a hydrocarbon such as cyclohexane. Initially this reaction formed a mixture of [$Ru_3(CO)_{12}$] (**1**) and [$H_4Ru_4(CO)_{12}$] (**2**) as a orange-yellow microcrystalline powder. The absorptions at 2062(sh), 2031(sh) and 2012(m) cm^{-1} in the IR spectrum are attributed to [$Ru_3(CO)_{12}$] (**1**)[3] and the absorptions at 2081(s), 2067(s) and 2026(m) are due to [$H_4Ru_4(CO)_{12}$] (**2**).[7] The mixture of compounds **1** and **2** were separated by conventional chromatography using a solvent mixture of hexane and dichloromethane in a ratio of 1:1. On altering the reaction conditions by pressurizing [$(NH_4)_2RuCl_6$] with 45 atm of CO and 35 atm of H_2, pure compound **2** was isolated as a yellow microcrystalline powder in 91% yield. Compound **2** was easily identified by infrared spectroscopy in cyclohexane which compared very well with literature values.[7]

Table 1.1 Infrared spectral data of [$Ru_3(CO)_{12}$] mixture of [$Ru_3(CO)_{12}$] (1), [$H_4Ru_4(CO)_{12}$] (2) and a mixture of the two compounds.

Compound	**v(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)

2.2 Synthesis of [$H_4Ru_4(CO)_{12}$] (2)

The preparation of compound **2** was first reported in 1966 by Lewis,[8] Wilkinson[9] and their co-workers and then followed by a joint publication thereafter.[10] In 1971 Piacenti and co-workers also reported that [$Ru_3(CO)_{12}$] (**1**) reacts with CO at 150°C in the presence of H_2 (150 atm) in *n*-heptane.[11] They reported yields of up to 99%. In the same year Kaesz and co-workers reported a novel synthetic route to compound **2** by direct hydrogenation of compound **1** with H_2 at atmospheric pressure in hydrocarbon solvents and their technique also gave near quantitative yields.[12] In 1990 Bruce and Williams reported full preparation details for compound **2** from compound **1** by passing H_2 through a solution of compound **1** in octane heated under reflux.[7] They also reported that this hydrogenation could be carried out in an autoclave with cyclohexane as solvent.[7]

We find that treatment of [$Ru_3(CO)_{12}$] (**1**), obtained from crude [$(NH_4)_2RuCl_6$] as above, with H_2 (25 atm) in an autoclave affords [$H_4Ru_4(CO)_{12}$] (**2**) in high purity and yields up to 95%. Excellent IR data were obtained for the product which displays the expected absorptions in the carbonyl region consistent with those reported by Piacenti and coworkers.[11] The main difference is that Piacenti and coworkers reported pressures as high as 150 atm of H_2. Here we report the synthesis of compound (**2**) using mild conditions of H_2 (50 atm) and good yields (95%).

2.3 Synthesis of $[RuCl_2(PPh_3)_3]$ (3)

The method reported by Hallman *et al.* uses ruthenium trichloride trihydrate as the starting material for the synthesis of compound **3**.[14] The products from the reactions of PPh_3 with commercial ruthenium trichloride trihydrate are a function of reaction time and solvent. Thus, the reaction of PPh_3 with $RuCl_3$ in a 6:1 ratio in methanol is known to produce different products. When the mixture is heated under reflux, $[RuCl_2(PPh_3)_3]$ is formed, and at room temperature, $[RuCl_2(PPh_3)_4]$ forms.[14] Solvents such as 2-methoxy- and 2-ethoxy-ethanol also take part in the reaction and produce $[RuH(Cl)(CO)(PPh_3)_3]$ and $[RuCl_2(CO)(PPh_3)_2]$ respectively.[15]

We modified the above synthesis and carried out two separate reactions. Firstly, a mixture of co-solvent was critical since only a 1:2 water : solvent system gave compound **3** in good yields (88%). Different ratios gave compound **3**, however the yields were significantly reduced (down to 60%). Compound **3** was characterized by melting point, elemental analysis, infrared spectroscopy and the data were in agreement with literature values.[14] Solutions of compound **3** are extremely

The $^{31}P\{^1H\}$ NMR spectrum of compound **3** in $CDCl_3$ exhibits a sharp singlet at δ 29.3 ppm, indicating that the PPh_3 ligands are all in the same environment. During the reaction a small singlet at δ -8.7 ppm was observed but this disappeared when the reaction had gone to completion. This peak is due to a free PPh_3.

2.4 Synthesis of $[RuCl_2(C_8H_{12})]_x$ [4]

dihydrogen hexachlororuthenate and triphenylphosphine in methanol was reacted at 65°C for 16 hours and the precipitate filtered, washed with diethyl ether (to remove any free triphenylphosphine) and dried *in vacuo* to give compound **3** as a brown solid in 95% yield. The product was characterized by analytical and spectroscopic methods.

The second attempt was to prepare compound **3** using the crude $[(NH_4)_2RuCl_6]$ sample. Modification of the procedure by addition of water gave compound **3** in yields of 88%. Water caused partial dissolution of $[(NH_4)_2RuCl_6]$ when it was used as a co-solvent with methanol. The dissolution of $[(NH_4)_2RuCl_6]$ allowed the triphenylphosphine ligand to coordinate to the ruthenium metal centre much more readily – $[(NH_4)_2RuCl_6]$ is not soluble in dry alcoholic solvents. Using water as a

sensitive to oxygen as they rapidly changed colour from orange to green when left to stand in air. Cenini *et al.* postulated an intermediate oxo complex $[RuCl_2(PPh_3)_2O_2]$,[15] whereas James and Markham observed the uptake of oxygen to be consistent with the overall stoichiometry of the equation with no direct evidence of formation of a molecular oxygen complex.[16]

Singleton *et al.* [17] reported the use of ruthenium trichloride trihydrate as the starting material in the synthesis of compound **4**. A modified procedure of Singleton *et al* was used to obtain compound **4** but starting from $[(NH_4)_2RuCl_6]$. A solution of $[(NH_4)_2RuCl_6]$ in water reacted with the 1,5-cyclooctadiene ligand to give compound **4** in 90% yield. When water was not added, compound **4** could not be isolated. We ascribe this to dissolution effects. The reaction of 1,5-cyclooctadiene with [H_2RuCl_6] did not need water to proceed, because the ruthenium was already in solution and readily coordinated with the COD ligand. The COD ligand in compound **4** is labile due to the high *trans*-influence of the chlorine. The greater electronegativity of Cl, which contracts the ruthenium-*5d* orbitals, synergistically weakens the ruthenium-COD bond. Therefore a variety of ligands readily displace COD from compound **4** forming complexes of the general formula [RuL_3Cl_2]. Herein we describe the displacement of COD from compound **4** by the PPh_3 ligand to give compound **3** in very good yields (87%).

Compound **4** and PPh_3, in a ratio of 1: 6 were heated under reflux in methanol for 3 h, after which a precipitate was collected on a glass filter and dried *in vacuo*. The product was isolated as a brown solid, which was identified by infrared spectroscopy, melting point and elemental analysis to be pure compound **3**.[17] Compound **4** is insoluble in organic solvents and thus NMR studies where not performed for this compound. It is thought to have a polymeric chloride-bridge structure.[18] Compound **4** 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.[18]

3. EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques unless otherwise stated. All solvents were purified prior to use by standard literature procedures and were stored under nitrogen in Teflon sealed storage bottles. The starting materials ammonium hexachlororuthenate [$(NH_4)_2RuCl_6$] and an acidic ruthenium solution of dihydrogen hexachlororuthenate [H_2RuCl_6] containing about 38g/l of ruthenium metal were all obtained from Anglo Platinum Corporation and used as received. Triphenylphosphine was purchased from Lancaster and used as received. Cycloocta-1,5-diene was purchased from Aldrich. 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 in solution cells with NaCl windows in hexane or dichloromethane or as KBr discs for solids. Carbonylation reactions were carried out in a 200 cm^3 Parr autoclave.

3.1 Compounds prepared using ammonium hexachlororuthenate

3.1.1 Preparation of compound 1

The procedure in the literature by Hallman *et al.* using $RuCl_3.3H_2O$ was modified.[13] 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 purple. The autoclave was sealed and purged three times with carbon monoxide (30 atm) before being finally pressurized with carbon monoxide (50 atm) and heated at 125 °C for 8 h. Following cooling (~2 h) and depressurization, the product was filtered using a Buchner funnel, recrystallized from hot toluene and dried *in vacuo* for 2 h. Compound **1** was isolated as orange-red crystals. Yield 95%. m.p. 132-133°C. Anal. Calc. for $C_{12}O_{12}Ru_3$: C, 22.54%. Found: C, 22.65%; IR v_{co} (in C_6H_{14}) 2060 (s), 2030 (s) and 2011 (m) cm^{-1}. Data was in accordance with literature.[13]

3.1.2 Preparation of compound 2

Ammonium hexachlororuthenate (1.50 g, 4.29 mmol) was combined with cyclohexane (50 cm^3) in a 200 cm^3 Parr autoclave and the mixture was observed to turn purple. The autoclave was sealed and purged three times with carbon monoxide (20 atm) before being pressurized with carbon monoxide (45 atm) and hydrogen (25 atm) (total pressure of 70 atm) and heated at 125 °C for 8 h after which it was allowed to stir overnight. Following depressurization, the crystals were filtered using a Hirsch funnel and washed with methanol (3 x 10 cm^3) and dried *in vacuo* for 2 h affording yellow crystals of the title compound. Yield 95%. m.p. 132-133°C. Anal. Calc. for $C_{12}O_{12}H_4Ru_4$: C, 19.35%; H, 0.54%. Found: C, 19.65%; H, 0.50%. $v_{co}(C_6H_{12})$: 2080 (s), 2066 (vs), 2029 (sh), 2024 (s) and 2009 (w) cm^{-1}. All data were in accordance with literature.[7]

3.1.3 Preparation of compound 3

The procedure in the literature by Hallman *et al* was modified.[13] Ammonium hexachlororuthenate (2.00 g, 5.72 mmol), water (20 cm^3) and methanol (40 cm^3) were placed in a Schlenk-tube and heated under reflux for 40 min. After cooling, an excess of triphenylphosphine (12.00 g, 45.75 mmol) was added and the mixture was heated under reflux for another 3 h. The reaction was allowed to cool to room temperature whilst stirring. The formed precipitate was filtered using a Buchner funnel and washed with diethylether (5 x 10 cm^3) and dried *in vacuo* for 2 h to give compound **3** as a brown solid. Yield 88%. m.p. 132-133°C. (lit.[13] 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%. v(KBr): 1481 (s), 1432 (s), 1191 (m), 1088 (s),1027 (m), 998 (m), 744 (s), 695 (vs), 542 (s), 520 (s).

3.2 Compounds prepared using dihydogen hexachlororuthenate

3.2.1 Preparation of compound 4

A modified literature procedure by Singleton *et al* was used.[17] Dihydrogen hexachlororuthenate solution (20 cm^3, 0.76 g Ru), cycloocta-1,5-diene (1 cm^3, 8 mmol) and ethanol (10 ml) were added to a two-necked round bottomed flask under nitrogen and the mixture was heated under reflux for *ca* 26 h. On cooling to room temperature, the solid was filtered using a Buchner funnel and washed with diethylether (5 x 10 cm^3) and dried *in vacuo* for 2 h to give compound **4** as a brown solid. Yield: 90%. m.p. 132-133°C. Anal. Calcd. for $C_8H_{12}Cl_2Ru$: C, 34.30%; H, 4.29%. Found: C, 34.64%; H, 3.86%.

3.2.2 Preparation of compound 3

The procedure in the literature by Hallman *et al* was modified.[14] Dihydogen hexachlororuthenate (10 cm^3, 0.38 g Ru) and methanol (35 cm^3) were charged into a Schlenk-tube, and the mixture was heated under reflux 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 heated under reflux for another 3 h and subsequently left stirring overnight. The product was filtered using a Buchner funnel and washed with diethylether (5 x 10 cm^3) and dried *in vacuo* for 2 h to give compound **3** as a brown solid. Yield: 87%. m.p. 131-133 $^{\circ}$C. (lit.[14] 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%. v(KBr): 1481 (s), 1432 (s), 1191 (m), 1088 (s), 1027 (m), 998 (m), 744 (s), 695 (vs), 542 (s), 520 (s).

3.3.3 Alternative synthesis of compound 3

$[RuCl_2(COD)]_n$ (0.25 g, 0.89 mmol), triphenylphosphine (1.40 g, 5.34 mmol) and methanol (45 ml) were heated under reflux for 3 h and allowed to cool to room temperature. The product that had precipitated out was filtered on a sintered glass filter, washed with diethylether (5 x 10 cm^3) and dried *in vacuo* for 2 h to give compound **3** as a brown solid. Yield: 87%. m.p.131-132°C. (lit.[8] 132-134°C). v(KBr): 1480 (s), 1433 (s), 1191 (m), 1086 (s), 1024 (m), 996 (m), 743 (s), 692 (vs), 540 (s) and 519 (s).

4. CONCLUSION

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. The relative ease with which we can obtain useful ruthenium starting materials from refinery materials serves to demonstrate that novel synthetic methods can also be developed and these may pave way to variations in the design of new ruthenium complexes with sophisticated ligands which can be applied to a number of useful catalytic reactions. We are currently conducting further investigations in this direction.

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