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Oxidation of olefins catalyzed by half-sandwich osmium(II) arene complexes

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Abstract

Ten complexes $[(\eta^6-(\text{arene})\text{OsCl}(\text{C}_5\text{H}_4\text{N}-2-\text{CH}=\text{N}-\text{C}_6\text{H}_5\text{X})]\text{PF}_6$ (with arene = *p*-cymene (1) or benzene (2); X = 4-F (a), 4-Cl (b), 4-Br (c), 4-I(d) and 4-methyl (e)) were synthesized by reacting the corresponding N,N'-bidentate ligands with the osmium arene dimers $[(\eta^6$ arene)Os(μ -Cl)Cl]₂ in a 2:1 ratio. Complexes **1a-e** and **2c-d** are new. The compounds were fully characterized via ¹H and ¹³C NMR, IR and UV-Vis spectroscopy, and elemental analyses. The xray crystal structure of compound **2e** is also reported. The Os(II) complex shows the expected " piano stool" type geometry. These Os(II) compounds were investigated in the catalytic oxidation of olefins to carbonyl compounds with NaIO₄ as terminal oxidant in a H₂O/t-BuOH biphasic system. All of the compounds were very effective catalysts for this reaction and gave the corresponding aldehyde in high yields.

Key words: Osmium; N,N-bidentate ligands; arene; styrene oxidation; olefin oxidation; x-ray structure

1. Introduction

The oxidative cleavage of alkenes to give the corresponding aldehydes, ketones or acids is a very important transformation in organic synthesis [1]. There are two main oxidative pathways discussed in literature for this oxidative cleavage [2]; the first pathway involves the oxidation of the alkenes into 1,2-diols which is followed by cleavage with NaIO₄ or other oxidants. The second route involves ozonolysis where the alkene is cleaved into a number of possible functionalized products, which depend on the workup conditions [2]. Ozonolysis is the standard method; however, it needs to be very carefully controlled due to the risk of explosion. Therefore, alternate reactions for the direct cleavage of alkenes, some without 1,2-diol intermediates, are

being developed by researchers [3]. This reaction can be performed by the use of transition metal complexes. The use of transition metal complexes of iron, ruthenium, manganese and copper have been widely reported [4]. However, few publications have been devoted to osmium as catalysts [5,6]. Osmium compounds have been used in the oxidative cleavage of alkyl and aryl alkenes to their corresponding aldehydes, employing various oxidants [7]. Osmium is also known to catalyze various organic reactions such as dihydroxylation, oxidation of alkanes with various oxidants and oxygenation of alkanes [4,8-10]. Since osmium is in the same group as iron, some osmium catalysts have been viewed as models of iron-containing enzymes and as biomimetic systems [5].

The continued interest in complexes of osmium has led us to investigate some reactions of $[(\eta^6-arene)Os(\mu-Cl)Cl]_2$ with pyridine-imines and the properties of the products. We report the preparation and characterization of the new compounds $[(\eta^6-(arene)OsCl(C_5H_4N-2-CH=N-C_6H_5X)].PF_6$ (with arene = *p*-cymene (1) or benzene (2); X = 4-Br (c), 4-I (d), as well as arene = benzene (2); and X = 4-F (a), 4-Cl (b), and 4-methyl (e)). These complexes were then employed in the oxidation of olefins using NaIO₄ as the terminal oxidant in a H₂O/tert-butanol biphasic system.

2. Experimental

The reported reactions were carried out using dry, distilled solvents under nitrogen making use of standard Schlenk techniques. α -Phellandrene, 1,4-cyclohexadiene, 2-pyridinecarboxaldehyde, 4-flouroaniline, 4-chloroaniline, 4-bromoaniline and 4-methylaniline (all Sigma-Aldrich) were used as supplied. A Thermal-Scientific Flash 2000 analyzer was used for the elemental analyses. Solid-state IR spectra were determined with a Perkin Elmer Spectrum 100 ATR spectrometer. Mass spectra were obtained using a Waters Micromass LCT Premier TOF-MS. Details were as previously reported [11]. UV-visible spectra were obtained using a Perkin-Elmer LAMBDA 35 spectrometer. The ¹H and ¹³C NMR spectra were obtained from a Bruker Top Spin 400 MHz spectrometer using DMSO- d_6 (Merck). Melting points were determined using an Ernest Leitz Wetzlar hot stage microscope. The dimers [(η^6 -arene)Os(μ -Cl)Cl]₂, arene = benzene or *p*cymene, were synthesized via reported procedures [12], as were the pyridine-imine ligands [13,14]. The complexes [(η^6 -(arene)OsCl(C₅H₄N-2-CH=N-C₆H₅X)]PF₆ (with arene = benzene (**2**); X = 4-F (**a**), 4-Cl (**b**), and 4-methyl (**e**)) were synthesized as reported [15].

1.0 General method for the preparation of the Os(II) iminopyridyl complexes

The pyridine-imine ligand (0.32 mmol) in methanol (10 ml) was added dropwise to a methanol (30 ml) solution of $[(\eta^6\text{-arene})Os(\mu\text{-Cl})Cl]_2$ (0.15 mmol) at 40 °C. The solution's colour changed from yellow to red immediately. The solution was stirred at 40 °C for 3 h, after which the volume was reduced to *ca*. 10 ml using a rotary evaporator. This was followed by addition of NH₄PF₆ (0.33 mmol) and allowing the solution to stand overnight at 0 °C. The precipitate was filtered off, followed by washing with cold ethanol, then diethyl ether and finally drying under vacuum.

1a

Red solid, yield 85%, m.p. 161 °C (dec.). ¹H NMR: δ 9.52 (d, J_{HH} = 5.5 Hz, 1H, Py); 9.30 (s, 1H, CH=N); 8.39 (m, 1H, Py); 8.26 (m, 1H, Py); 7.86 (m, 3H, Ar); 7.79 (m, 2H, Ar); 6.38 (d, J_{HH} = 5.8 Hz, 1H, *p*-cymene); 6.00 (d, J_{HH} = 5.8 Hz, 1H, *p*-cymene); 5.90 (d, J_{HH} = 5.8 Hz, 1H, Ar, *p*-cymene); 5.8 (d, J_{HH} = 5.75 Hz, 1H, Ar, *p*-cymene); 2.40 (m, 1H, C*H*(CH₃)₃); 2.24 (s, 3H, CH₃); 0. 93 (m, 6H, Me₂, cymene). ¹³C NMR: 168.99 (CH=N); 155.84 (Py); 155.67 (Py); 140.10 (Py); 129.97 (Py); 129.80 (Py); 125.20 (Py); 125.11 (Ar); 116.51 (Ar); 116.29 (Ar); 97.64 (Ar); 96.82 (Ar); 78.83 (Ar, *p*-cymene); 78.80 (Ar, *p*-cymene); 75.47 (Ar, *p*-cymene); 75.35 (Ar, *p*-cymene); 30.67 (CH₃, *p*-cymene); 21.91 (CH₃, *p*-cymene); 18.25 (CH₃, *p*-cymene). IR (solid state): v(C=N) 1610.0 cm⁻¹, v(P-F) 830.5 cm⁻¹. Anal. Calculated for C₂₂H₂₃ClF₇N₂OsP: C, 37.48; H, 3.29; N, 3.97. Found: C, 37.68; H, 3.35 H; N 4.37. MS (ESI, m/z): 561.0 [C₂₂H₂₃ClFN₂Os]⁺

1b

Red solid, yield 80%, m.p. 171 °C (dec.). ¹H NMR: δ 9.53 (d, J_{HH} = 5.4 Hz, 1H, Py); 9.36 (s, 1H, CH=N); 8.40 (d, J_{HH} = 7.6 Hz, 1H, Py); 8.30 (d, J_{HH} = 7.6 Hz, 1H, Ar); 7.86 (m, 1H, Ar); 7.76 (m, 4H, Ar); 6.42 (m, 1H, Ar, *p*-cymene); 6.05 (m, 1H, Ar, *p*-cymene); 5.99 (m, 1H, Ar, *p*-cymene); 5.77 (m, 1H, Ar, *p*-cymene); 2.42 (d, J_{HH} = 6.9 Hz, 1H, C*H*(CH₃)₃); 2.24 (s, 3H, CH₃); 0. 92 (m, 6H, Me₂, cymene). ¹³C NMR: δ 169.37 (CH=N); 155.77 (Py); 150.48 (Py); 140.11 (Py); 134.24 (Py); 130.18 (Py); 129.93 (Ar); 129.55 (Ar); 124.76 (Ar); 97.82 (Ar); 96.89 (Ar); 78.94 (Ar, *p*-cymene); 78.16 (Ar, *p*-cymene); 75.39 (Ar, *p*-cymene); 75.34 (Ar, *p*-cymene)); 30.68 (CH₃, *p*-cymene); 21.92 (CH₃, *p*-cymene); 18.27 (CH₃, *p*-cymene). IR (solid state):

v(C=N) 1615.4 cm⁻¹, v(P-F) 825.2 cm⁻¹. Anal. Calculated for C₂₂H₂₃ClF₇N₂OsP: C, 36.62; H, 3.21; N, 3.88. Found: C, 36.89; H, 3.12; N 4.05. MS (ESI, m/z): 577.0 [C₂₂H₂₃ClFN₂Os]⁺

1c

Red solid, yield 80%, m.p. 191 °C (dec.). ¹H NMR: δ 9.52 (d, J_{HH} = 5.3 Hz, 1H, Py); 9.32 (s, 1H, CH=N); 8.40 (d, J_{HH} = 7.6 Hz, 1H, Py); 8.30 (d, J_{HH} = 7.6 Hz, 1H, Py); 7.84 (d, J_{HH} = 8.4 Hz, 3H, Ar); 7.69 (d, J_{HH} = 8.4 Hz, 2H, Ar); 6.39 (d, J_{HH} = 5.6 Hz, 1H, *p*-cymene); 6.00 (d, J_{HH} = 5.6 Hz, 1H, Ar, *p*-cymene); 5.92 (d, J_{HH} = 5.6 Hz, 1H, Ar, *p*-cymene); 5.74 (d, J_{HH} = 5.6 Hz, 1H, Ar, *p*-cymene); 2.24 (m, 1H, CH(CH₃)₃); 2.30 (s, 3H, CH₃); 0. 92 (m, 6H, Me₂, cymene). ¹³C NMR: δ 169.35 (CH=N); 155.77 (Py); 155.71 (Py); 150.88 (Py); 140.10 (Py); 132.47 (Py); 130.17 (Py); 129.92 (Ar); 124.98 (Ar); 122.87 (Ar); 97.86 (Ar); 96.91 (Ar); 78.96 (Ar, *p*-cymene); 78.14 (Ar, *p*-cymene). IR (solid state): v(C=N) 1613.9 cm⁻¹, v(P-F) 825.8 cm⁻¹. Anal. Calculated for C₂₂H₂₃ClBrF₆N₂OsP : C, 34.50; H, 3.03; N, 3.66 Found: C, 34.39; H, 2.98; N 3.33. MS (ESI, m/z): 621[C₂₂H₂₃BrClN₂Os]⁺

1d

Red solid, yield 82%, m.p. 201 °C (dec.). ¹H NMR: δ 9.52 (d, J_{HH} = 5.4 Hz, 1H, Py); 9.31 (s, 1H, CH=N); 8.40 (d, J_{HH} = 7.6 Hz, 1H, Py); 8.29 (d, J_{HH} = 7.6 Hz, 1H, Py); 7.85 (m, 1H, Ar); 7.53 (d, J_{HH} = 8.4 Hz, 2H, Ar); 6.39 (d, J_{HH} = 5.8 Hz, 1H, *p*-cymene); 5.99 (d, J_{HH} = 5.7 Hz, 1H, Ar, *p*-cymene); 5.90 (d, J_{HH} = 5.6 Hz, 1H, Ar, *p*-cymene), 5.73 (d, J_{HH} = 5.7 Hz, 1H, Ar, *p*-cymene); 2.41 (m, 1H, CH(CH₃)₃); 2.23 (s, 3H, CH₃); 0.92 (m, 6H, Me₂, cymene). ¹³C NMR: δ 169.11 (CH=N); 155.79 (Py); 155.73 (Py); 151.32 (Py); 140.10 (Py); 138.29 (Py); 130.16 (Py); 129.91 (Ar); 124.96 (Ar); 97.93 (Ar); 96.83 (Ar); 96.43 (Ar); 78.98 (Ar, *p*-cymene); 78.18 (Ar, *p*-cymene); 75.34 (Ar, *p*-cymene). IR (solid state): v(C=N) 1615.7 cm⁻¹, v(P-F) 815.8 cm⁻¹. Anal. Calculated for C₂₂H₂₃ClIF₆N₂OsP: C, 32.50; H, 2.85; N, 3.45 Found: C, 31.86; H, 2.75; N 3.29. MS (ESI, m/z): 669 [C₂₂H₂₃IClN₂Os]⁺

1e

Red solid, yield 80%, m.p. 189 °C (dec.). ¹H NMR: δ 9.51 (d, J_{HH} = 5.5 Hz, 1H, Py); 9.28 (s, 1H, CH=N); 8.38 (d, J_{HH} = 7.6 Hz, 1H, Py); 8.28 (t, J_{HHH} = 7.6 Hz, 1H, Py); 7.84 (t, J_{HHH} = 6.2 Hz,

4

1H, Ar); 7.62 (d, $J_{HH} = 8.2$ Hz, 2H, Ar); 7.43 (d, $J_{HH} = 8.1$ Hz, 2H, Ar); 6.37 (d, $J_{HH} = 5.7$ Hz, 1H, *p*-cymene); 5.97 (d, $J_{HH} = 5.8$ Hz, 1H, Ar, *p*-cymene); 5.82 (d, $J_{HH} = 5.8$ Hz, 1H, Ar, *p*cymene); 5.73 (d, $J_{HH} = 5.7$ Hz, 1H, Ar, *p*-cymene); 2.45 (s, CH₃); 2.20 (s, 3H, C*H*(CH₃)₃); 0. 92 (m, 6H, Me₂, cymene). ¹³C NMR: δ 167.96 (CH=N); 155.95 (Py); 155.64 (Py); 149.47 (Py); 140.05 (Py); 139.83 (Py); 129.88 (Ar); 129.76 (Ar); 129.64 (Ar); 122.80 (Ar); 97.52 (Ar); 96.59 (Ar); 78.66 (Ar, *p*-cymene); 78.37 (Ar, *p*-cymene); 75.60 (Ar, *p*-cymene), 75.26 (Ar, *p*-cymene); 30.68 (CH₃, *p*-cymene); 21.89 (CH₃, *p*-cymene); 21.89 (CH₃); 18.25 (CH₃, *p*-cymene). IR (solid state): v(C=N) 1615.9 cm⁻¹, v(P-F) 824.6 cm⁻¹. Anal. Calculated for C₂₃H₂₆ClF₆N₂OsP: C, 39.40; H, 3.74; N, 4.00 Found: C, 38.80; H, 3.81 H; N 3.66. MS (ESI, m/z): 557 [C₂₃H₂₆ClN₂Os]⁺

2c

Red solid. Yield 82%. m.p. 210 °C (dec.). ¹H NMR: δ 9.62 (d, J_{HH} = 5.4 Hz, 1H, Py); 9.31 (s, 1H, CH=N); 8.40 (m, 1H, Py); 8.28 (m, 1H, Py); 7.84 (m, 3H, Ar); 7.69 (d, J_{HH} = 8.8 Hz, 2H, Ar); 6.11 (s, 6H, C₆H₆). ¹³C NMR: δ 169.34 (CH=N); 155.82 (Py); 155.76 (Py); 150.73 (Py); 140.23 (Py); 132.37 (Py); 129.99 (Py); 129.18 (Ar); 124.89 (Ar); 122.76 (Ar); 78.78 (C₆H₆). IR (KBr, cm⁻¹): ν (C=N) 1613.2, ν (P-F) 822.2. Anal. Calculated for C₁₈H₁₅ClBrF₆N₂OsP: C, 30.45; H, 2.13; N, 3.95. Found C, 30.68; H, 2.00; N, 3.47. MS (ESI, m/z): 564.97 [C₁₈H₁₅ClBrN₂Os]⁺

2d

Red solid. Yield 82%. m.p. 205 °C (dec.). ¹H NMR: δ 9.61 (d, J_{HH} = 8.8 Hz, 1H, Py); 9.29 (s, 1H, CH=N); 8.37 (m,1H, Py); 8.26 (m, 1H, Py); 7.99 (m, 2H, Ar); 7.85 (m, 1H, Ar); 7.53 (d, J_{HH} = 8.5 Hz, 2H, Ar); 6.11 (s, 6H, C₆H₆). ¹³C NMR: δ 169.13 (CH=N); 155.79 (Py); 151.17 (Py); 140.22 (Py); 138.19 (Py); 129.96 (Py); 129.76 (Ar); 124.86 (Ar); 98.30 (Ar); 78.77 (C₆H₆). IR (KBr, cm⁻¹): ν (C=N) 1613.9, ν (P-F) 822.9 . Anal. Calculated for C₁₈H₁₅ClIF₆N₂OsP: C, 28.56; H, 2.00; N, 3.70. Found C, 29.06; H, 1.92; N, 3.28. MS (ESI, m/z): 610.0 [C₁₈H₁₅ClIN₂Os]⁺

Suitable crystals for X-ray diffraction were obtained by layering a fourfold volume of hexane on a dry acetone solution of compound 2e, then leaving the mixture at RT in the dark for 2 days. Data collection was carried out using a Bruker Smart *APEXII* diffractometer, while the reduction was done with the program *SAINT*+ [14]. The structure was solved by direct methods via *SHELXS* [16] and refined with *SHELXL* [14]. The details are as previously reported [16]. Structure refinement and crystal data information for compound 2e are given in Table 1.

| Empirical formula | C ₂₂ H ₂₄ ClF ₆ N ₂ OOsP |
|------------------------------------------|----------------------------------------------------------------------|
| Formula weight | 703.05 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | a = 27.7514(10) Å |
| | <i>b</i> = 8.4921(3) Å |
| | c = 21.7276(8) Å |
| | $\beta = 112.055(2)^{\circ}$ |
| V | 4745.8(3) Å ³ |
| Ζ | 8 |
| Density _{calc} | 1.968 mg/m ³ |
| Absorption coefficient | 5.620 mm ⁻¹ |
| F(000) | 2720 |
| Crystal size | 0.58 x 0.53 x 0.37 mm ³ |
| Theta range for data collection | 2.023 to 27.999° |
| Index ranges | -36≤h≤36, -11≤k≤11, -8≤l≤29 |
| Collected reflections | 55233 |
| Independent reflections | 5728 [R(int) = 0.0493] |
| Completeness to theta = 25.242° | 100% |
| Max. and min. transmission | 0.2283 and 0.1396 |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.175 and 0.089 |
| Refinement method | Full-matrix least-squares on \vec{F}^2 |
| Data / restraints / parameters | 5959 / 0 / 305 |
| Final <i>R</i> indices [I>2sigma(I)] | $R_1 = 0.0232, wR_2 = 0.0533$ |
| R indices (all data) | $R_1 = 0.0306, wR_2 = 0.0569$ |
| Largest diff. peak and hole | 1.402 and -1.217 e.Å ³ |

Table 1. Summary of the crystal data of 2e

2.5 Alkene oxidation reactions

All catalytic reactions were carried out in Schlenk tubes heated at 60 °C. The products were identified and quantified by GC (Perkin Elmer Auto system) equipped with a capillary column (Varian wax, 25 m x 0.15 mm x 2 μ m) and a flame ionization detector. The injector temperature was 250 °C. The ratio of catalyst to substrate was 1:100. The products were confirmed by comparison of their retention times with those of standards obtained commercially (Sigma Aldrich), as well as GC-MS analyses. The alkene (0.5 mmol), internal standard (biphenyl, 0.5 mmol) and catalyst (0.5 mol %) were dissolved in a water (3 ml) and *tert*-butanol (3 ml) mixture. Three equivalents of oxidant, NaIO₄, were subsequently added in one batch and the immiscible mixture stirred vigorously, at 60 °C. The reactions were monitored by removing aliquots hourly and injecting 1 μ L into the GC each time. Furthermore, control experiments were done under the same conditions, where the reactions were carried out without either the catalyst or NaIO₄.

3.0 Results and Discussion

3.1 The preparation and characterization of the osmium compounds

Reacting the N,N-bidentate ligands with the osmium dimers $[(\eta^6\text{-arene})Os(\mu\text{-Cl})Cl]_2$ in methanol at 40 °C gave the mononuclear compounds $[(\eta^6\text{-arene})OsCl(C_5H_4N-2\text{-}CH=N-C_6H_5X)]PF_6$ (with arene = *p*-cymene (1) or benzene (2); X = 4-F (a), 4-Cl (b), 4-Br (c), 4-I(d) and 4-methyl (e)). They were crystalised as hexafluorophosphate salts as shown in Scheme 1. These air-stable complexes are not hygroscopic and dissolve in polar solvents including acetonitrile, acetone, DMF and DMSO, but do not dissolve in non-polar solvents like diethyl ether, dichloromethane and hexane.



 $X = F(a); Cl(b); Br(c); I(d); CH_3(e).$

Scheme 1: Preparation of $[(\eta^6\text{-arene})OsCl(C_5H_4N-2-CH=N-C_6H_4-X)]PF_6$ (arene = *p*-cymene (1a-1e) or C₆H₆ (2a-2e))

Confirmation of formation of complexes **1a-1e** and **2c** and **2d** is found by comparing the ¹H and ¹³C NMR spectra by monitoring the proton and carbon signal of the imine (CH=N) group of the ligands and the complexes. On complexation the imine proton peaks shift downfield to $\delta = 9.25$ - 9.36 ppm from $\delta = 8.49$ - 8.58 ppm of the uncoordinated ligands (Table 2), because the imine proton is deshielded since the nitrogen donates a lone pair of electrons to the osmium [15]. In addition, the ¹³C NMR spectra showed that the imine carbon peak shifted from $\delta = 160.1$ - 163.2 for the free ligands to $\delta = 167.9$ - 170.3 for the complexes. This observation agrees well with those on related compounds [17]. Also, the bonding of the bidentate ligands to the Os *para*-cymene moiety is further confirmed because the proton resonances of the phenyl ring of the *p*-cymene group resolve into separate peaks because the arene ring loses symmetry once of the bidentate ligand coordinated to the osmium centre, which also has been observed for related compounds [18].

Furthermore, comparison of the IR spectra supported complex formation. Thus, a strong absorption band is seen for all the complexes between 1610 - 1616 cm⁻¹, due to the symmetrical v(C=N) vibration. This peak was at lower wavenumbers than those of the corresponding band of the free pyridine-imine ligands at 1623 - 1626 cm⁻¹. This shift indicates that the bidentate ligands

have bonded to the osmium (**Table 2**). A distinctive peak is seen for the complexes between 816 and 830 cm⁻¹ and is assigned to the PF_6^- counter ion [19,20].

High-resolution mass spectra of **1a-2e** further confirm the proposed formulation of the mononuclear complexes. All complexes give the base peak $[(\eta^6\text{-arene})OsCl(C_5H_4N-2-CH=N-C_6H_5X)]^+$. Furthermore, each fragment shows the expected characteristic multiple peaks that are due to the isotopes of osmium.

| Complex | ¹ H NMR (ppm) | | ¹³ C NMR (ppm) | | IR (CH=N) _{imine} (cm ⁻¹) | |
|---------|--------------------------|---------|---------------------------|---------|------------------------------------------------|---------|
| | Ligand | Complex | Ligand | Complex | Ligand | Complex |
| 1a | 8.57 | 9.30 | 161.4 | 168.9 | 1624.5 | 1610.0 |
| 1b | 8.58 | 9.36 | 160.6 | 169.4 | 1623.3 | 1615.4 |
| 1c | 8.59 | 9.32 | 160.1 | 169.3 | 1622.7 | 1613.9 |
| 1d | 8.56 | 9.31 | 162.1 | 155.8 | 1627.1 | 1615.7 |
| 1e | 8.49 | 9.28 | 163.2 | 169.1 | 1625.6 | 1615.9 |
| 2c | 8.59 | 9.31 | 160.1 | 169.3 | 1622.7 | 1613.2 |
| 2d | 8.56 | 9.29 | 162.2 | 169.1 | 1627.1 | 1613.9 |

Table 2. The ¹H NMR, ¹³C NMR and IR shifts observed for the imine functionality of the free ligands and the complexes **1a-e** and **2c-d**

The UV-vis spectra of the ligands and their complexes (**Figure 1**) were obtained in CH₃CN. For the ligands, absorption bands occur between 230 nm - 249 nm and 282 nm - 327 nm. These are assigned to $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively. A bathochromic shift of these bands to 255 nm - 273 nm and 311 nm - 316 nm, respectively, is seen on complexation. The complexes further showed bands in the region 410 nm - 423 nm, due to metal to ligand ($d\pi-\pi^*$) charge transfer transitions from the filled 5d orbitals to the empty π^* orbitals [11,17]. The UV-vis spectra of the ligands do not show these bands, which confirms also that the proposed complexes formed.



Figure 1: The UV-Vis spectra of complexes 1a - 1e and 2c-2d

3.2 Molecular structure of 2e

Compound **2e** crystallizes in red block-like crystals with single molecules of the cation, $[(\eta^6 - benzene)Os(C_5H_4N-2-CH=N(4-Me-Ph))]^+$, acetone and the counter ion in the asymmetric unit. The molecular structure is given in **Figure 2**, while **Table 3** gives selected bond angles and distances. In the structure, osmium is bonded to the bidentate ligand via the N atoms of the imine and pyridine groups, which together with the chloride make up three legs of a "piano stool", while the disordered arene group forms the apex of the three-legged piano stool". This leads to a "pseudo-octahedral geometry around the Os(II) center.. The Os—Cl distance in the complex is 2.3920(8) Å and this is comparable to reported values for similar compounds [21-23]. The lengths of the Os—N bonds are 2.057(3) Å and 2.091(3) Å, which are also similar to those of comparable compounds with values of between 2.074(4) Å and 2.08(5) Å [23]. The N—Os—N bond angle was found to be 75.70(10)° and the N—Os—Cl angles were found to be 84.07(7)° to 86.57(7)°, which again are comparable to those of similar compounds [21,23].



Figure 2: A diagram showing the molecular structure of **2e**, which also shows the atom numbering and the displacement ellipsoids at a 50% probability level. Hydrogen atoms and the disordered component of the complex have been omitted from the diagram for clarity purposes, as have the counter anion and the acetone molecule.

| 2e | | | | | |
|------------------|-----------|-------------------|-----------|--|--|
| Bond Lengths (Å) | | Bond angles (°) | | | |
| Os(1)—N(1) | 2.057(3) | N(1)—Os(1) —N(2) | 75.70(10) | | |
| Os (1) —N(2) | 2.091(3) | N(1)—Os(1) —Cl(1) | 86.570(7) | | |
| Os (1) —Cl(1) | 2.3920(8) | N(2)—Os(1) —Cl(1) | 84.070(7) | | |
| | | | | | |

Table 3: Selected bond distances (Å) and angles (deg)

3.3 The oxidation of styrene

3.3.1 Optimization

From a previous study on the oxidation of olefins using ruthenium arene complexes, the following reaction conditions were chosen [17]: a 1:1 *tert*-butanol: water ratio, 60 °C reaction temperature and a co-oxidant to oxidant ratio of 3:1. However, for the osmium compounds, the optimum catalytic loading was found to be 0.5 mol %. At lower loadings, the reaction was very slow and at higher loadings, there was no improvement in reaction time or yield. Blank experiments, which were done under the same conditions, revealed that the osmium(II) complexes gave only very low conversions without NaIO₄ present. Furthermore, the oxidant, NaIO₄, without catalyst present, gave low conversion also.

3.3.2 Catalytic results discussion

Complexes **1a-e** and **2a-e** were investigated for catalytic activity in the oxidation of styrene (Table 4). The main oxidation product obtained from this reaction was benzaldehyde, which is either due to direct oxidative cleavage of the C=C bond of styrene or the rapid further reaction of the intermediate styrene oxide to give benzaldehyde [24]. In this work, the second route seems most likely because the reaction of styrene oxide under identical catalytic conditions gave benzaldehyde quantitatively. The highest conversion was reached after one hour with all the catalysts, with TOF values ranging from 175 to 195.

Once the optimum conditions for the reaction were established, to establish the scope and limitations of the reaction, the oxidation of a number of other olefins was examined. For this extended study, catalyst **1d** was chosen, since it showed the highest TOF of the complexes investigated. Complex **1d** gave high conversions for all of the styrene derivatives studied (Table 5). These contained electron donating (entries 1 and 2) and withdrawing (entry 6) groups, and gave the expected aldehydes in high yields. The catalyst further cleaved the double bond in transstilbene to give benzaldehyde and reacted with a linear alkene, where 1-octene gave 1-heptanal (Table 5).

| Catalyst | Conversion (%) | Yield (%) | TON ^a | TOF (h ⁻¹) ^b |
|----------|----------------|-----------|------------------|----------------------------------------------------|
| 1a | 98 | 91 | 181 | 181 |
| 1b | 100 | 91 | 183 | 183 |
| 1c | 100 | 92 | 183 | 183 |
| 1d | 100 | 97 | 195 | 195 |
| 1e | 100 | 93 | 186 | 186 |
| 2a | 100 | 91 | 183 | 183 |
| 2b | 99 | 95 | 191 | 191 |
| 2c | 100 | 95 | 190 | 190 |
| 2d | 100 | 97 | 195 | 195 |
| 2e | 99 | 90 | 181 | 181 |

Table 4: Oxidation of styrene catalyzed by catalysts 1a-d and 2a-d.

^a: Turnover number = mol product/mol catalyst,

^b: Turnover frequency = mol product/mol catalyst/hour (determined once the reaction was complete)

When the osmium complex precursor $[(\eta^6-p\text{-}cymene)Os(\mu\text{-}Cl)Cl]_2$ (0.5 mol%) was employed as a catalyst for styrene oxidation, the reaction took three hours with a benzaldehyde yield of 86 %. Thus, the precursor required a longer reaction time than the complex although it has double the concentration of the osmium. Furthermore, when the osmium precursor was mixed with the ligand **d** in a 1:2 ratio and used for the styrene oxidation reaction, the reaction took two hours with an 82% yield to benzaldehyde, suggesting that the formation of the complex is important in the oxidation reaction.

Investigations were made towards determining the mechanism of the osmium(II) arene catalysed oxidation of olefins. The UV-Vis spectrum obtained for the yellow compound recovered at the end of the reaction with catalyst **1d** showed a peak at ca. 250 nm. A similar peak was observed by Sugimoto and coworkers [25] who assigned the band at around 250-300 nm to Os=O species. In addition, the solid-state IR spectrum obtained for the recovered catalyst, from complex **1d**, showed a peak at 881cm⁻¹ which could be assigned to the symmetric stretches v(Os=O) for an osmium-dioxo species [25-27]. The proton NMR of the recovered catalyst shows that the arene ring remains attached. This has been observed for a similar compound of ruthenium in oxidation reactions [17]. Also, the ESI-MS spectrum of the catalyst residue after the oxidation reaction

showed an Os fragment peak at 539, which was the maximum of the isotopic cluster. This peak might be assigned to $[(benzene)OsClO_2]^+.(MeCN)(H_2O)_9$. Thus, this peak may suggest the presence in solution of an osmium species which contains a coordinated benzene group, and it implies also that the N, N-bidentate ligand cleaves.

| | Substrate | Product | Conversion % | Yield % | Time h | TON | TOF h ⁻¹ |
|---|-----------|------------------------|-----------------|------------|-----------|-----|------------------------|
| 1 | | 4-methyl benzaldehyde | 100 | 90 | 0.5 | 181 | 362 |
| 2 | | 4-methoxy benzaldehyde | 99 | 89 | 1 | 163 | 163 |
| 3 | | benzaldehyde | 100 | 91 | 1 | 183 | 183 |
| 4 | | 4-chloro benzaldehyde | 100 | 99 | 1 | 196 | 196 |
| 5 | | 1-heptanal | 99 | 85 | 1 | 170 | 170 |

Table 5: Data for the oxidative cleavage of selected olefins by 1d with the co-oxidant NaIO₄

From the observations mentioned and literature reports, a mechanism involving an Os(VI) oxo species is suggested. Thus, the complex reacts with the oxidant $NaIO_4$ to give an Os(VI)-cis dioxo intermediate. Electrophilic attack of this high-valent dioxo-intermediate on the C=C bond of the olefin via a concerted [3+2] cycloaddition reaction gives an Os(IV) cyclo adduct.



Scheme 2: The mechanistic scheme proposed for the oxidation of styrene using complexes 1a-2e.

Conclusion

The mononuclear complexes **1a-1e** and **2a-2e** were synthesized, isolated and characterized. The molecular structure of compound **2e** reveals the expected pseudo octahedral three legged piano stool geometry. These compounds oxidized styrene very effectively and showed very good selectivity to benzaldehyde, with the yield to benzaldehyde being 91-97%. Furthermore, the reactions of 1-octene, stilbene, 4-methoxy styrene, 4-methyl styrene and 4-chloro styrene over

compound **1d** gave the corresponding aldehydes via oxidative cleavage in equally good yield. The mechanism is believed to involve an Os(VI) oxo species, which is indicated by the UV, IR, ¹H NMR and ESI spectral data.

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Supplementary material

CCDC 1571550 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

References

- [1] K.N. Parida, J.N. Moorthy, Tetrahedron 70 (2014) 2280.
- [2] B.R. Travis, R.S. Narayan, B. Borhan, J. Am. Chem. Soc. 124 (2002) 3824.
- [3] D. Naicker, H.B. Friedrich, P.B. Pansuriya, RSC Adv. 6 (2016) 31005.
- [4] M.M. Vinogradov, Y.N. Kozlov, D.S. Nesterov, L.S. Shul'pina, A.J.L. Pombeiro, G.B. Shul'pin, Catal. Sci. Technol., 4 (2014) 3214.
- [5] M.M. Vinogradov, L.S. Shul'pina, Y.N. Kozlov, A.R. Kudinov, N.S. Ikonnikov, G.B. Shul'pin, J. Organomet. Chem. 784 (2015) 52.
- [6] P.P. Pescarmona, A.F. Masters, J.C. van der Waal, T. Maschmeyer, J. Mol. Cat. A: Chem. 220 (2004) 37.
- [7] S.R. Hart, D.C. Whitehead, B.R. Travis, B. Borhan, Org. Biomol. Chem., 9 (2011) 4741.
- [8] M.A. Esteruelas, T. García-Obregón, J. Herrero, M. Oliván, Organometallics 30 (2011) 6402.
- [9] R. Castarlenas, M.A. Esteruelas, E. Oñate, Organometallics 24 (2005) 4343.
- [10] M.L. Buil, M.A. Esteruelas, J. Herrero, S. Izquierdo, I.M. Pastor, M. Yus, ACS Catalysis 3 (2013) 2072.
- [11] J.M. Gichumbi, H.B. Friedrich, B. Omondi, J. Mol. Catal. A: Chem. 416 (2016) 29.
- [12] A.F.A. Peacock, A. Habtemariam, S.A. Moggach, A. Prescimone, S. Parsons, P.J. Sadler, Inorganic Chemistry 46 (2007) 4049.
- [13] S. Dehghanpour, N. Bouslimani, R. Welter, F. Mojahed, Polyhedron 26 (2007) 154.
- [14] S. Dehghanpour, A. Mahmoudi, Main Group Chem. 6 (2007) 121.
- [15] J.M. Gichumbi, H.B. Friedrich, B. Omondi, J. Coord.Chem. Submitted.
- [16] J.M. Gichumbi, H.B. Friedrich, B. Omondi, J. Mol. Struct. 1113 (2016) 55.
- [17] J.M. Gichumbi, H.B. Friedrich, B. Omondi, J. Organomet. Chem. 808 (2016) 87.
- [18] M.J. Chow, C. Licona, D. Yuan, G. Pastorin, C. Gaiddon, W.H. Ang, J. Med. Chem. 57 (2014) 6043.

- [19] F. Marchetti, C. Pettinari, A. Cerquetella, A. Cingolani, R. Pettinari, M. Monari, R. Wanke, M.L. Kuznetsov, A.J.L. Pombeiro, Inorg. Chem. 48 (2009) 6096.
- [20] S. Orbisaglia, C. Di Nicola, F. Marchetti, C. Pettinari, R. Pettinari, L.M.D.R.S. Martins, E.C.B.A. Alegria, M.F.C. Guedes da Silva, B.G.M. Rocha, M.L. Kuznetsov, A.J.L. Pombeiro, B.W. Skelton, A.N. Sobolev, A.H. White, Chem. Eur. J. 20 (2014) 3689.
- [21] A.F.A. Peacock, A. Habtemariam, R. Fernández, V. Walland, F.P.A. Fabbiani, S. Parsons, R.E. Aird, D.I. Jodrell, P.J. Sadler, J. Am. Chem. Soc. 128 (2006) 1739.
- [22] D.F. Schreiber, C. O'Connor, C. Grave, H. Müller-Bunz, R. Scopelliti, P.J. Dyson, A.D. Phillips, Organometallics 32 (2013) 7345.
- [23] Y. Fu, M.J. Romero, A. Habtemariam, M.E. Snowden, L. Song, G.J. Clarkson, B. Qamar, A.M. Pizarro, P.R. Unwin, P.J. Sadler, Chem. Sci. 3 (2012) 2485.
- [24] J. Valand, H. Parekh, H.B. Friedrich, Catal. Commun. 40 (2013) 149.
- [25] H. Sugimoto, K. Kitayama, S. Mori, S. Itoh, J. Am. Chem. Soc. 134 (2012) 19270.
- [26] W.P. Griffith, J. Chem. Soc. (1964) 245.
- [27] W.A. Herrmann, R.M. Kratzer, J. Blümel, H.B. Friedrich, R.W. Fischer, D.C. Apperley, J. Mink, O. Berkesi, J. Mol. Catal. A: Chem. 120 (1997) 197.

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Research Highlights

- New half-sandwich Osmium(II) pyridine-imine complexes prepared and characterized
- They show good catalytic activity in the oxidation of olefins to aldehydes
- They work best in a biphasic medium (H₂O/*t*-butanol)
- The crystal structure of $[(\eta^6$ -benzene)Os(C₅H₄N-2-CH=N(4-Me-Ph))]^+ is reported