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Synthesis, structure, and reactivity of osmium π-thiophene complexes

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Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday

Abstract

$[\{(\eta^6\text{-}p\text{-cymene})OsCl(\mu\text{-Cl})\}_2]$ reacts with silver triflate and thiophenes to give the sandwich compounds $[Os(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-thio})](OTf)_2$ (thio = thiophene, 2,5-dimethylthiophene (DMT), 2,3,4,5-tetramethylthiophene (TMT)). While these compounds do not react cleanly with nucleophiles to form thiopheneyl derivatives, they do react via base hydrolysis to give new acyl thiolate complexes, $[Os(\eta^6\text{-}p\text{-cymene})(SC_3R_3C(O)R)]$, which have closely related ruthenium analogues. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The hydrodesulfurisation of crude oil is one of the key industrial processes of the late twentieth century. The reaction involves the removal of sulfur contaminants from the oil in the form of H_2S, and is catalysed by metal sulfides deposited on a support. Commonly Mo and W are the essential components of the catalyst; however, doping of the catalyst with late transition metals, particularly those of Group 8, can increase the catalytic efficiency by creation of new sites with enhanced activity [1–4]. Since thiophenes and benzothiophenes are usually the contaminants that are the most difficult to remove, much of the work on modelling the industrial process has been done with molecular, thiophene coordinated, late transition metals [5–9].

Of particular relevance to this work are the papers of Rauchfuss and co-workers on the 'Ru(η^5-thiophene)' moiety [10–15]. Complexes of the type [Ru(η^5-thiophene)(η^6-arene)]$^{2+}$ undergo two-electron reduction to the corresponding Ru(0) derivatives [Ru(η^4-thiophene)(η^6-arene)] [10] and are susceptible to base hydrolysis and amminolysis, leading ultimately to C–S bond cleavage [11,12]. However, we have shown that the attack of nucleophiles, Y (Y = H$^-$, CN$^-$, OR$^-$, SR$^-$), on [Ru(η^5-TMT)(L$_3$)]$^{2+}$ complexes (L$_3$ = [2.2]-paracyclophane, *tris*(pyrazolyl)methane, [9]aneS$_3$) involves retention of the heterocyclic ligand in the form of the η^4-C$_4$Me$_4$S-2-Y moiety [16,17].

In contrast to the chemistry of ruthenium, the π-thiophene chemistry of osmium, excluding that of cluster compounds, remains largely unexplored. There are several reports of η^2-thiophene derivatives of pentamine-osmium(II) [18,19], a brief mention of an unsuccessful attempt to carry out an optical resolution of the [Os(η^6-p-cymene)(η^5-2-MeC$_4$H$_3$S)]$^{2+}$ cation [15], and a report of electrochemical investigations on a series of [Os(η^5-C$_5$H$_5$)(η^5-oligothiophene)][PF$_6$] compounds [20]. As a first step to deepening our knowledge in this area, we have prepared several sandwich compounds of the type [Os(η^6-p-cymene)(η^5-thio)](OTf)$_2$ (thio = thiophene, 2,5-dimethylthiophene (DMT), 2,3,4,5-tetramethylthiophene (TMT)), one of which has been crystallographically characterised, and examined their reactions with nucleophiles, and under base hydrolysis conditions.

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2. Experimental

2.1. Materials

All manipulations were carried out under anaerobic conditions in a dry nitrogen atmosphere using conventional Schlenk-line techniques. Dichloromethane and acetonitrile were pre-dried, by standing over 4 Å molecular sieves, and distilled from CaH_2 under a nitrogen atmosphere; methanol was distilled from CaH_2. All solvents were de-gassed by three repetitions of pump–freeze–thaw cycles prior to use. The compounds [{(p-cymene)OsCl(μ-Cl)}$_2$] [21] and tetramethylthiophene (TMT) [22] were prepared according to literature methods. Thiophene and 2,5-dimethylthiophene (DMT) were obtained commercially and dried and distilled prior to use. All other reagents were used as received.

2.2. Instrumentation

Infrared spectra were recorded on a Nicolet-205 spectrometer between 4000 and 400 cm^{-1} in the solid state, as KBr discs, or in solution (CH$_2$Cl$_2$). The ^{1}H- and ^{13}C-NMR spectra were recorded using Bruker spectrometers (AMX 300, AMX 400 or Avance 500) referenced internally against the respective deuterated solvents (CDCl$_3$, δ 7.27; (CD$_3$)$_2$CO, δ 2.04 ppm). Elemental analyses were carried out by the departmental service at University College London. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded by the University of London Intercollegiate Research Service (ULIRS) at the London School of Pharmacy (assignments based on the ^{192}Os isotope). Electrochemical measurements were made utilising a PAR 174A polarographic analyser and a PAR 175 waveform generator in conjunction with a Bryans Instruments 60000 series $X–Y/t$ chart recorder. Platinum wires were used as the working, counter and reference electrodes. Cyclic voltammograms were recorded in the temperature range -40 to 30°C at scan rates in the range 10–200 mV s^{-1} in acetonitrile solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. Potentials are referenced against the ferrocene/ferrocenium couple ($+$0.55 V).

2.3. Synthesis

2.3.1. [Os(η^5-thiophene)(η^6-p-cymene)][PF$_6$]$_2$

A dichloromethane (20 cm^3) solution of [{(p-cymene)OsCl(μ-Cl)}$_2$] (0.131 g; 0.17 mmol) was stirred with silver trifluoromethanesulfonate (0.171 g; 0.67 mmol) in the dark for 2 h. The yellow suspension was filtered to remove the precipitated silver chloride. The yellow filtrate was stirred with an excess of thiophene (1 cm^3) for 16 h. Removal of the solvent and residual

thiophene by vacuum distillation left a brown oil which was extracted with ethanol. The ethanolic solution was filtered through Celite and the filtrate treated with an excess of ethanolic NH$_4$[PF$_6$]. After storing at -20°C for 4 h a light-chestnut solid was collected by filtration, washed with dichloromethane (10 cm^3) and diethyl ether (10 cm^3), and dried in vacuo. Yield 0.154 g, 67%. Mass spectrum (FAB): m/z 410 [M $-$ 2PF$_6$]. Anal. Found C 24.18, H 2.52%. Calc. for C$_{14}$H$_{18}$F$_{12}$OsP$_2$S: C 24.07, H 2.60%. Infrared (KBr): ν(PF$_6$) 834 cm^{-1}. ^{1}H-NMR (300 MHz, acetone-d_6, 22°C); p-cymene resonances, δ 1.40 (d, $^3J = 6.9$ Hz, 6H, CH(CH$_3$)$_2$), δ 2.74 (s, 3H, CH$_3$), δ 3.07 (sp, $^3J = 7.0$ Hz, 1H, CH(CH$_3$)$_2$), δ 7.31 (AA′BB′, 4H); thiophene resonances, δ 7.75 ppm (m, 4H,). Cyclic voltammetry (25°C, $v = 100$ mV s^{-1}) $E_{1/2} = -0.20$ V (irreversible).

2.3.2. [Os(η^5-DMT)(η^6-p-cymene)](OTf)$_2$

In a similar manner to that described above [{(p-cymene)OsCl(μ-Cl)}$_2$] (0.098 g; 0.12 mmol) was reacted with first 4 equivalents of silver trifluoromethanesulfonate (0.129 g; 0.50 mmol) and then an excess of 2,5-dimethylthiophene (0.5 cm^3). After stirring for 16 h the solution was concentrated to ca. 10 cm^3 and cooled to 0°C. The pale cream precipitate that formed was collected by filtration, washed with cold dichloromethane (10 cm^3) and diethyl ether (10 cm^3), and subsequently dried in vacuo. Yield 0.157 g, 86%. Mass spectrum (FAB): m/z 587 [M $-$ CF$_3$SO$_3$], 438 [M $-$ 2CF$_3$SO$_3$]. Anal. Found C 29.27, H 2.90%. Calc. for C$_{18}$H$_{22}$F$_6$O$_6$OsS$_3$: C 29.42, H 3.02%. Infrared (KBr): ν(SO) 1270 cm^{-1}. ^{1}H-NMR (300 MHz, acetone-d_6, 22°C); p-cymene resonances, δ 1.42 (d, $^3J = 6.9$ Hz, 6H, CH(CH$_3$)$_2$), δ 2.69 (s, 3H, CH$_3$), δ 3.09 (sp, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), δ 7.30 (AA′BB′, 4H); DMT resonances, δ 2.74 (s, 6H, CH$_3$), δ 7.61 ppm (s, 2H,). Cyclic voltammetry (25°C, $v = 100$ mV s^{-1}) $E_f = -0.31$ V (irreversible).

2.3.3. [Os(η^5-TMT)(η^6-p-cymene)](OTf)$_2$

This complex was prepared by an analogous method to that described above. Yield 78%. Mass spectrum (FAB): m/z 466 [M $-$ 2CF$_3$SO$_3$]. Anal. Found C 31.26, H 3.16%. Calc. for C$_{20}$H$_{26}$F$_6$O$_6$OsS$_3$: C 31.49 H 3.44%. Infrared (KBr): ν(SO) 1273 cm^{-1}. ^{1}H-NMR (300 MHz, acetone-d_6, 22°C); p-cymene resonances, δ 1.42 (d, $^3J = 7.0$ Hz, 6H, CH(CH$_3$)$_2$), δ 2.59 (s, 3H, CH$_3$), δ 3.09 (sept, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), δ 7.17 ppm (AA′BB′, 4H); TMT resonances, δ 2.62 (s, 6H, CH$_3$), δ 2.69 (s, 6H, CH$_3$). Cyclic voltammetry (25°C, $v = 100$ mV s^{-1}) $E_{1/2} = -0.37$ V (quasi-reversible).

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

An excess of KOH (0.031 g, 0.55 mmol) was added to a solution of [Os(η^5-thiophene)(η^6-p-cymene)][PF$_6$]$_2$ (0.101 g, 0.16 mmol) in methanol (15 cm^3) and the

mixture stirred for 4 h. After this time the methanol was removed under reduced pressure and the yellow oily residue was extracted into dichloromethane (3×15 cm^3), filtered through Celite, and washed through with fresh dichloromethane (10 cm^3). The volume was reduced to ca. 5 cm^3 and the solution was loaded onto a short silica column. Eluting with dichloromethane–methanol (100:1) led to the recovery of a yellow band. Evaporation of the solvent gave an air-sensitive yellow–tan viscous oil which was dried in vacuo. Yield 0.042 g, 64%. Mass spectrum (EI): m/z 426 [M], 398 [M − CO], 358 [M − C$_4$H$_4$O]. Anal. Found C 40.04, H 4.73%. Calc. for C$_{14}$H$_{18}$OOsS: C 39.60, H 4.27%. Infrared (CH$_2$Cl$_2$): ν(CO) 1667 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$, 22°C); p-cymene resonances, δ 1.25 and δ 1.26 (d,d, 3H + 3H, CH(CH_3)$_2$), δ 2.34 (s, 3H, CH$_3$), δ 2.59 (sp, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), δ 5.37 (d, $^2J = 5.4$ Hz, 1H), δ 5.49 (d, $^2J = 5.4$ Hz, 1H), δ 5.53 (d, $^2J = 5.4$ Hz, 1H), δ 5.60 (d, $^2J = 5.4$ Hz, 1H); SC$_3$H$_3$C(O)H resonances, δ 2.37 (m, 1H), δ 6.07 (d, $^2J = 3.5$ Hz, 1H), δ 6.26 (dd, 1H), δ 9.54 ppm (d, $^2J = 4.2$ Hz, 1H).

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

An analogous procedure to that described above was used for the preparation of [Os(η^6-p-cymene)(SCMeC$_2$H$_2$C(O)Me)]. However, to obtain a sample of the highest purity the silica column must first be eluted with dichloromethane, prior to eluting with the dichloromethane–methanol mixture. Yield 61%. Mass spectrum (EI): m/z 454 [M], 438 [M − O], 426 [M − CO], 411 [M − C$_2$H$_3$O], 358 [M − C$_6$H$_8$O]. Anal. Found C 42.76, H 4.73%. Calc. for C$_{16}$H$_{22}$OOsS: C 42.46, H 4.90%. Infrared (KBr): ν(CO) 1654 cm^{-1}. ^{1}H-NMR (500 MHz, CDCl$_3$, 22°C): p-cymene resonances, δ 1.29 and 1.30 (d,d, $^3J = 6.9$ Hz, 3H + 3H, CH(CH_3)$_2$), δ 2.46 (s, 3H, CH$_3$), δ 2.57 (sp, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), δ 5.10 (d, $^2J = 5.4$ Hz, 1H), δ 5.20 (d, $^2J = 5.4$ Hz, 1H), δ 5.35 (d, $^2J = 5.4$ Hz, 1H) δ 5.45 (d, $^2J = 5.4$ Hz, 1H); SCMeC$_2$H$_2$C(O)Me resonances, δ 2.09 (s, 3H, CH$_3$), δ 2.22 (d, $^3J = 6.1$ Hz, 1H), δ 2.23 (s, 3H, CH$_3$), δ 6.09 ppm (d, $^2J = 6.1$ Hz, 1H). ^{13}C-{^{1}H}-NMR (126 MHz, CDCl$_3$, internal ref. δ 77.0 ppm, 22°C): δ 19.1, 23.5, 24.2, 26.8, 30.7, 31.6 ppm (aliphatic). δ 55.3, 73.5, 73.6, 75.4, 75.8, 79.6 ppm (unsaturated). δ 89.3, 90.7, 100.8 ppm (quaternary). δ 206.8 ppm (carbonyl).

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

An analogous procedure to that described above was used for the preparation of [Os(η^6-p-cymene)(SC$_3$Me$_3$C(O)Me)]. Yield 76%. Mass spectrum (EI): m/z 482 [M], 439 [M − C$_2$H$_3$O], 358 [M − C$_8$H$_{12}$O]. Anal. Found C 44.56, H 6.13%. Calc. for C$_{18}$H$_{26}$OOsS · MeOH: C 44.51, H 5.90%. Infrared (CH$_2$Cl$_2$): ν(CO) 1652 cm^{-1}. ^{1}H-NMR (400 MHz,

CDCl$_3$, − 20°C): p-cymene resonances, δ 1.24 and 1.27 (d, d 3H + 3H, CH(CH_3)$_2$), δ 2.49 (s, 3H, CH$_3$), δ 2.59 (sp, $^3J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), δ 4.98 (d, $^2J = 5.4$ Hz, 1H), δ 5.25 (d, $^2J = 5.4$ Hz, 1H), δ 5.36 (d, $^2J = 5.4$ Hz, 1H), δ 5.47 (d, $^2J = 5.4$ Hz, 1H); SC$_3$Me$_3$C(O)Me resonances, δ 1.63 (s, 3H, CH$_3$), δ 2.01 (s, 3H, CH$_3$), δ 2.07 (s, 3H, CH$_3$), δ 2.23 ppm (s, 3H, CH$_3$).

2.4. Crystallography

Crystal data for [Ru(η^6-p-cymene)(η^5-TMT)][CF$_3$SO$_3$]$_2$ C$_{20}$H$_{26}$F$_6$O$_6$OsS$_3$, M = 762.8 g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 8.370(2)$, $b = 26.414(5)$, $c = 12.256(3)$ Å, $\beta = 109.38(3)$°, $U = 2556.1(9)$ Å^3, $\lambda = 0.71073$ Å, $Z = 4$, $F(000) = 1488$, $D_{calc} = 1.98$ g cm^{-3}, μ(Mo–K$_\alpha$) = 5.312 mm^{-1}, 4826 unique data, 326 parameters, $R_1 = 0.0547$ [$F^2 = 2\sigma(F)^2$], wR_2 (all data) = 0.1565.

A crystal of dimensions $0.22 \times 0.04 \times 0.02$ mm^3 was mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. A total of 90 oscillation frames each of width 2° in ϕ, respectively, and of 45 s exposure time were recorded using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 25 mm. Crystals were indexed from the first ten frames using the DENZO package and positional data were refined along with diffractometer constants to give unit cell parameters suitable for integration. Integration and scaling (DENZO, Scalepack [23]) of a total of 11 403 data resulted in 4826 unique data corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction based on average signal intensity on each frame. The final unit cell parameters were refined using the entire data set by the program Scalepack [23]. Structures were solved using SHELXS-97 [24] and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97 [24]). In general, all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom and allowed to ride. All calculations were carried out with either a Silicon Graphics Indy R5000 workstation or an IBM-compatible PC.

3. Results and discussion

The reaction of [{(η^6-p-cymene)OsCl(μ-Cl)}$_2$] with silver triflate in dichloromethane proceeds smoothly to give a yellow solution of [(η^6-p-cymene)Os(OTf)$_2$]. Addition of a thiophene (thiophene, 2,5-dimethylthiophene, 2,3,4,5-tetramethylthiophene) followed by stirring for ca. 16 h gives, after work-up, a good yield

(65–85%) of the cationic complexes [Os(η^6-p-cymene)(η^5-thio)](OTf)$_2$. Some of the triflate salts are somewhat hydroscopic and it is often useful to carry out a metathesis of the triflate counterion for hexafluorophosphate. The three complexes are unremarkable each showing two sets of ^{1}H-NMR ligand resonances which integrate in a 1:1 ratio. Microanalytical data confirm the dicationic nature of the complexes and the counterions show characteristic infrared bands (see Section 2). The compound [Os(η^6-p-cymene)(η^5-

Fig. 1. The structure of the cation in [Os(η^6-p-cymene)(η^5-TMT)][CF$_3$SO$_3$]$_2$ showing the atom labelling scheme.

Table 1
Selected bond lengths and angles for [Os(η^6-p-cymene)(η^5-TMT)][CF$_3$SO$_3$]$_2$

Bond lengths (Å)

Os(1)–S(3)	2.347(2)	Os(1)–C(2)	2.290(8)
Os(1)–C(11)	2.224(8)	Os(1)–C(3)	2.220(8)
Os(1)–C(12)	2.271(8)	Os(1)–C(4)	2.253(9)
Os(1)–C(13)	2.272(8)	Os(1)–C(5)	2.213(8)
Os(1)–C(14)	2.232(8)	Os(1)–C(6)	2.224(7)
S(3)–C(11)	1.769(9)	Os(1)–C(7)	2.277(8)
S(3)–C(14)	1.755(8)	C(2)–C(3)	1.436(11)
C(11)–C(12)	1.437(11)	C(3)–C(4)	1.397(13)
C(12)–C(13)	1.443(11)	C(4)–C(7)	1.453(11)
C(13)–C(14)	1.420(11)	C(6)–C(7)	1.424(11)
C(5)–C(6)	1.426(11)	C(2)–C(5)	1.419(11)

Angles (°)

C(11)–S(3)–C(14)	92.3(4)	C(2)–C(3)–C(4)	121.2(7)
S(3)–C(11)–C(12)	110.3(6)	C(3)–C(4)–C(7)	121.5(8)
C(11)–C(12)–C(13)	113.2(7)	C(4)–C(7)–C(6)	117.3(7)
C(12)–C(13)–C(14)	112.0(7)	C(5)–C(6)–C(7)	120.1(7)
S(3)–C(14)–C(13)	112.1(6)	C(2)–C(5)–C(6)	122.5(7)
C(3)–C(2)–C(5)	116.9(7)		

TMT)](OTf)$_2$ crystallises readily and was conclusively identified by a single-crystal structure determination (Fig. 1 and Table 1). The sandwich structure is confirmed by the X-ray diffraction study and the two aromatic rings are essentially parrallel and planar, with the angle formed at the metal by the centroids of the two rings being 176.9°. Interestingly the deviation of the sulfur atom from the C(11)–C(12)–C(13)–C(14) plane is only 0.07 Å, which is much less than we have observed previously in a number of Ru(II) π-thiophene complexes [26]. Subtituents on both the arene and thiophene ligand are displaced somewhat from the metal, with deviations in the range 0.9–5.6°. The aromatic C–C bond lengths in the thiophene are indistinguishable from each other, however there is some evidence of bond length alternation in the arene ligand. Similarly, while the Os–C$_{thiophene}$ bonds span a small range, 2.22–2.27 Å, the range of lengths observed in the Os–C$_{arene}$ bonds is greater, 2.21–2.28 Å. The Os–S distance, 2.347(2) Å, is significantly shorter than that found for several ruthenium compounds with π-bonded tetramethylthiophene, e.g. 2.442(1) Å in [Ru(η^5-C$_4$Me$_4$S)Cl$_2$(PPhMe$_2$)] [25] and 2.414(4)–2.432(4) Å in [{Ru(η^5-C$_4$Me$_4$S)(μ-Cl)}$_3$(μ^3-S)] [13]. However, it is essentially indistinguishable from the Ru–S distance in the symmetrical sandwich compound [Ru(η^5-C$_4$Me$_4$S)$_2$][BF$_4$]$_2$, av. 2.355(2) Å [13].

Rauchfuss and co-workers have shown that the compounds [Ru(η^6-C$_6$Me$_6$)(η^5-thiophene)](OTf)$_2$ (thiophene = DMT, TMT) can be reduced both chemically, using cobaltocene, and electrochemically to the Ru(0) compounds [Ru(η^6-C$_6$Me$_6$)(η^4-thiophene)] [10]. The electrochemical process takes place in two clearly defined quasi-reversible one-electron steps, separated by ca. 160 mV. We have examined the electrochemical response of the three new osmium complexes by cyclic voltammetry at scan rates in the range 10–200 mV s^{-1} over the temperature range −40 to 30°C, using acetonitrile as solvent and tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. Both [Os(η^6-p-cymene)(η^5-C$_4$H$_4$S)](OTf)$_2$ and [Os(η^6-p-cymene)(η^5-DMT)](OTf)$_2$ exhibit a single irreversible reduction process under these experimental conditions, at potentials of −0.20 and −0.31 V, respectively. In contrast [Os(η^6-p-cymene)(η^5-TMT)](OTf)$_2$ exhibits a quasi-reversible peak at −0.37 V. The reversiblity of this process increases with increasing scan rate but even at 200 mV s^{-1} the ratio of peak currents is only 0.52. In contrast to the results obtained earlier on [Ru(η^6-C$_6$Me$_6$)(η^5-thiophene)](OTf)$_2$ [10] and [Ru(η^5-C$_4$Me$_4$S)$_2$][BF$_4$]$_2$ [13], two separate one-electron reduction processes are never resolved. It is notable that the reductions of [Os(η^6-p-cymene)(η^5-thio)]$^{2+}$ cations occur much more readily than that observed for the structurally related [Os(η^5-p-cymene)(η^5-C$_4$Me$_4$N)]$^+$ cation, −2.3 V [26].

Scheme 1.

Earlier we examined the reactions of $[Ru(\eta^5\text{-}TMT)(L_3)]^{2+}$ complexes $(L_3 = [2.2]\text{-paracyclophane}$, *tris*(pyrazolyl)methane, $[9]aneS_3$) with nucleophiles Y $(Y = H^-, CN^-, OR^-, SR^-)$ [16,17]. The nucleophile generally attacks at a carbon adjacent to the sulfur atom resulting in the formation of an $\eta^4\text{-}C_4R_4S\text{-}2\text{-}Y$ ligand on the metal. The attack is exclusively *exo*, as is demonstrated conclusively by the X-ray crystal structures of $[Ru(\kappa^3\text{-}[9]aneS_3)(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}OEt][PF_6]$ [16] and $[Ru(\kappa^3\text{-}[9]aneS_3)(\eta^4\text{-}C_4Me_4S\text{-}2\text{-}H)[PF_6]$ [27]. In contrast Rauchfuss and co-workers have shown that $[Ru(\eta^6\text{-arene})(\eta^5\text{-thiophene})]^{2+}$ complexes generally undergo attack by hydroxide ion at sulfur, to give $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_4R_4S\text{-}1\text{-}OH)]^+$ ions. These species may then subsequently react to give (i) an S-oxide $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_4R_4S\text{-}1\text{-}O)]$, which may rearrange to an acyl thiolate, or (ii) 2-hydroxythiopheneyl derivatives $[Ru(\eta^6\text{-arene})(\eta^4\text{-}C_4R_4S\text{-}2\text{-}OH)]^+$ [11].

The reaction of $[Os(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-thio})]^{2+}$ complexes with a number of nucleophiles (H^-, MeO^-, CN^-) in a range of solvents, including tetrahydrofuran and ethanol, gave yellow–brown solids on work-up. ^{1}H-NMR studies on these clearly indicated that reactions had occurred at both rings but that attack had generally occurred preferentially at the thiophene ligand, e.g. as evidenced by the appearance of thiophene methyl doublets in the compounds derived from the reaction of $[Os(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-}TMT)]^{2+}$ with hydride ion. However, our results also indicate that attack at the thiophene is not limited to a single site. Due to the complexity of these mixtures, we have been unable to separate and purify the compounds derived from these reactions satisfactorily.

In contrast the reaction of $[Os(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-}thio)]^{2+}$ complexes with hydroxide proceeds smoothly to give essentially single products, perhaps as a consequence of the initial attack being directed specifically towards the thiophene sulfur [11]. The ^{1}H-NMR spectrum of the yellow oil obtained by reaction of the cation $[Os(\eta^6\text{-}p\text{-cymene})(\eta^5\text{-}DMT)]^{2+}$ and KOH in methanol gave the expected five signals for the *p*-cymene ligands, one singlet, at δ 1.82 ppm, for the two equivalent methyl groups on the heterocyclic ligand, and a second singlet, at δ 4.85 ppm, for the protons of the thiophene derived ligand, consistent with a symmetrical product. An infrared spectrum contains a band at 998 cm^{-1}, due to a ν(S–O) stretch, closely similar to that observed for $[Ru(\eta^5\text{-}p\text{-cymene})(\eta^4\text{-}C_4Me_2H_2S\text{-}1\text{-}O)$, 1011 cm^{-1} [11], but does not contain bands due to a counterion. The compound extracts into hexane, consistent with it being neutral. Hence, we deduce that this species is a neutral S-oxide $[Os(\eta^6\text{-}p\text{-cymene})(\eta^4\text{-}C_4Me_2H_2S\text{-}1\text{-}O)]$ (Scheme 1) analogous to those described by Rauchfuss and co-workers in related ruthenium chemistry [11]. The sample obtained directly from the reaction mixture contained small amounts of a number of impurites and in an attempt to remove these it was chromatographed on a silca column. When the proton spectrum of the chromatographed sample was run it was immediately apparent that a chemical transformation had taken place. The appearance of diastereotopic signals from the *p*-cymene isopropyl group, together with two signals from the methyl groups of the sulfur containing ligand, δ 2.09 and 2.23 ppm, clearly indicate the loss of the plane of symmetry in the product. In addition the ^{13}C-{^{1}H}-NMR spectrum of the recovered sample contains 16 resonances, consistent with the loss of symmetry, and most notably exhibts a carbonyl signal, at δ 206.8 ppm. Infrared spectroscopy confirms the presence of the carbonyl functionality, ν(C=O) 1654 cm^{-1}. Thus, we are led to conclude that the final product is the acyl thiolate $[Os(\eta^6\text{-}p\text{-cymene})(\sigma,\eta^3\text{-}SCMeC_2H_2C(O)Me)]$ (Scheme 1) analogous to compounds described for ruthenium by Rauchfuss and co-workers [11]. Interestingly, while the ruthenium analogue of this compound was described as being obtained in two isomeric forms, the osmium compound shows no tendency to isomerism, even at elevated temperatures, where it decomposes, depositing a polymeric film in the process. Thiophene and tetramethylthiophene analogues of $[Os(\eta^6\text{-}p\text{-cymene})(\sigma,\eta^3\text{-}SCMeC_2H_2C(O)Me)]$ were obtained
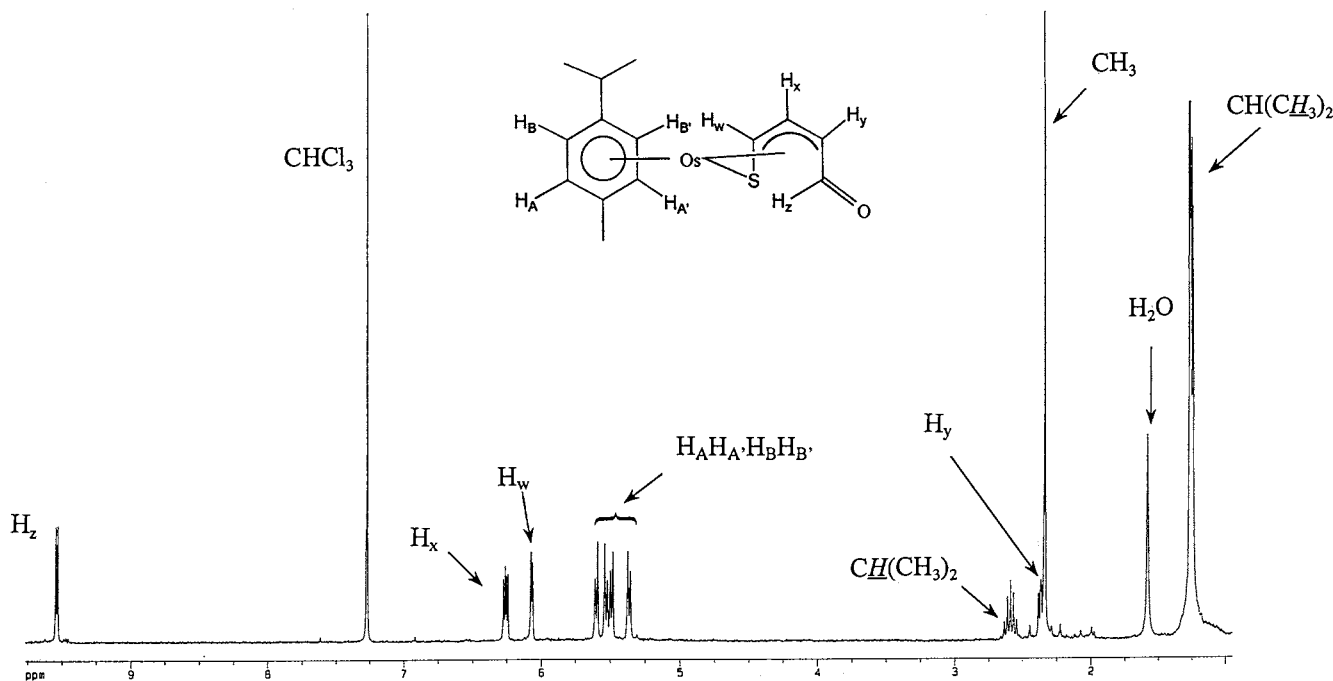
Fig. 2. The ^{1}H-NMR spectrum of [Os(η^6-p-cymene)(σ,η^3-SC$_3$H$_3$C(O)H)] illustrating the absence of symmetry in this compound. Complete assignment of the spectrum is made on the basis of a ^{1}H–^{1}H COSY experiment.

similarly and show the characteristic loss of symmetry in their NMR spectra (see Section 2 and Fig. 2). While the acyl thiolate derivatives of thiophene and 2,5-dimethylthiophene show no tendency to isomerism the compound [Os(η^6-p-cymene)(σ,η^3-SC$_3$Me$_3$C(O)Me)] is dynamic on the NMR timescale, as found for the ruthenium analogue [11]. The absence of any isomerism leads us to speculate that the isomeric form of the osmium compounds corresponds to the structural arrangement of Rauchfuss's 'thermodynamic' isomer [11].

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132395. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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