Synthesis and properties of monometallic, homo- and heterobimetallic complexes based on $\{(\eta^6\text{-arene})\text{RuCl}\}^+$ and $\{(\eta^6\text{-arene})\text{OsCl}\}^+$ fragments with tetrathioether and tetraselenoether ligands

William Levason*, Catherine Marshall, Luke P. Ollivere, Gillian Reid, Nikolaos Tsoureas, Michael Webster

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

ABSTRACT

The reaction of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ with 2.0 mol equivalents of $C(CH_2SMe)_4$, $C(CH_2SeMe)_4$, $1,2,4,5\text{-}C_6H_2(CH_2SMe)_4$ or $1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4$ (L_4) and $[NH_4][PF_6]$ in ethanol solution forms the $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\kappa^2\text{-}L_4\}][PF_6]$ complexes. Similar Os(II) complexes are obtained starting with $[\text{Os}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$. Treatment of $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})\{\kappa^2\text{-}L_4\}][PF_6]$ with a further 0.5 mol equivalents of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ or reaction of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ directly with 1.0 mol equivalent of L_4 forms the homobimetalllic $[\{\text{RuCl}(\eta^6\text{-}p\text{-cymene})\}_2\{\kappa^2\kappa'^2\text{-}L_4\}][PF_6]_2$. Reaction of $[\text{OsCl}(\eta^6\text{-}p\text{-cymene})\text{-}\{\kappa^2\text{-}C(CH_2SeMe)_4\}][PF_6]$ with $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ or $[\text{PtCl}_2(\text{MeCN})]$ affords the heterobimetallic $[\{\text{OsCl}(\eta^6\text{-}p\text{-cymene})\}\{\text{RuCl}(\eta^6\text{-}p\text{-cymene})\}\{\kappa^2\kappa'^2\text{-}C(CH_2SeMe)_4\}][PF_6]_2$ and $[\{\text{OsCl}(\eta^6\text{-}p\text{-cymene})\}\{\text{PtCl}_2\}\{\kappa^2\kappa'^2\text{-}C(CH_2SeMe)_4\}][PF_6]$ respectively. The complexes have been characterised by multinuclear NMR and IR spectroscopy and X-ray crystallography.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Bimetallic complexes have been studied for a number of reasons, including metalloenzyme models, as mixed metal catalysts, molecular magnets and as reagents for producing alloys. The detailed behaviour of the species is determined by the ligand architecture, donor atom types and metal ion combinations [1].

Complexes of polydentate phosphine and arsine ligands have been studied in great detail and with a very wide variety of metals. In contrast similar studies of acyclic polydentate thio- or seleno-ethers are very limited [2]. Ligands with spirocyclic or 1,2,4,5-tet-rasubstituted aromatic backbones are sterically incapable of chelating as tetradentates to a single metal centre, but are suitable to bridge two metal centres, although only a small number of examples containing S or Se donor atoms have been described. These include complexes with Hg(II) and Ag(I) [3] and a highly unusual Co(II) complex $[\text{CoI}_2\{C(CH_2SMe)_4\}]$ which is a polymer containing octahedrally coordinated cobalt with bridging $\kappa^2\kappa'^2$ coordinated ligands in the solid state, but a tetrahedral monomer $[\text{CoI}_2\{\kappa^2\text{-}C(CH_2SMe)_4\}]$ in solution in chlorocarbon solvents [4]. We have recently described a range of substituted metal carbonyl complexes based upon the four ligands $C(CH_2SMe)_4$, $C(CH_2SeMe)_4$,

$1,2,4,5\text{-}C_6H_2(CH_2SMe)_4$ and $1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4$ [5] coordinated κ^2 or $\kappa^2\kappa'^2$ to one or two metal centres respectively. We have also described complexes $[\text{Mn}(CO)_3Cl\{(CH_2)_2C(CH_2EMe)_2\}]$ ($E =$ Se or Te) and $[\text{MCl}(\eta^6\text{-}p\text{-cymene})\{(CH_2)_2C(CH_2EMe)_2\}]\text{PF}_6$ (M = Ru or Os) of the cyclopropyl-backboned bidentates $(CH_2)_2C(CH_2EMe)_2$ [6]. We report here studies of the four tetradentates $C(CH_2SMe)_4$, $C(CH_2SeMe)_4$, $1,2,4,5\text{-}C_6H_2(CH_2SMe)_4$ and $1,2,4,5\text{-}C_6H_2(CH_2SeMe)_4$ with arene–ruthenium(II) and -osmium(II) centres and some homo- and heterobimetallic derivatives.

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates over the range $4000-200\ \text{cm}^{-1}$ using Perkin–Elmer 983 G or PE Spectrum100 instruments. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at ambient temperatures unless stated otherwise, using a Bruker AV300 or DPX400 spectrometer and referenced internally to the solvent resonance, and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra on a Bruker DPX400 spectrometer and referenced to external, neat SeMe_2. Mass spectra were obtained by positive ion electrospray (ES$^+$) in MeCN solution using a VG Biotech platform. Microanalyses were undertaken by Medac Ltd. All preparations were carried out under a N_2 atmosphere. The tetrathioether and tetraselenoether ligands were made as described [5] and $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2\}_2]$ and $[\{\text{Os}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2\}_2]$ [7] were prepared by literature methods.

---

* Corresponding author. Fax: +44 023 80593781.
E-mail address: wxl@soton.ac.uk (W. Levason).

2.1. [RuCl(η⁶-p-cymene){κ²-C(CH₂SMe)₄}][PF₆] (1)

[Ru(η⁶-p-cymene)Cl₂]₂ (0.100 g, 0.16 mmol) was dissolved in dry ethanol (20 mL). To this was added the tetrathioether (0.082 g, 0.32 mmol) in dry ethanol (15 mL). The reaction mixture was refluxed for 2 h. The reaction vessel was removed from the oil bath and while still hot, a solution of [NH₄][PF₆] (0.052 g, 0.32 mmol) in 10 mL ethanol was added. The mixture turned from dark orange to yellow and a yellow precipitate formed instantly. The reaction mixture was cooled to room temperature and stirred overnight. The yellow suspension was cannula filtered under nitrogen to leave a yellow solid which was washed twice in diethyl ether (50 mL) filtered, and dried in vacuo. Yield: 0.140 g, 66%. Anal. Calc. for $C_{19}H_{34}ClF_6PRuS_4$: C, 34.0; H, 5.1. Found: C, 33.4; H, 5.4%. ES⁺ (m/z): 527 $[Ru(p\text{-cymene})Cl\{C(CH_2SMe)_4\}]^+$. IR (Nujol)/cm⁻¹: 836 (PF₆ stretch), 557 (PF₆ bend). ¹H NMR (d⁶-acetone): 1.37 (d, [6H], $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 2.22, 2.25, 2.30 (3 × s each [3H], 2 × SCH₃ uncoord, aromatic CH₃), 2.61, 2.90 (2 × s each [2H], CH₂ uncoord), 2.75–3.05 (AB quartet, [4H], CH₂ coord), 2.82 (s, [6H], coord SCH₃), 2.95 (septet, [1H], $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 6.03 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH), 6.22 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH). ¹³C{¹H} NMR (d⁶-acetone): 17.53, 18.06, 18.37 (2 × SCH₃ uncoord, p-cymene CH₃), 22.42 (CH(CH₃)₂), 28.48 (coord SCH₃), 31.48 (CH (CH₃)₂), 38.82, 40.22 (2 × uncoord CH₂), 43.90 (C_quaternary), 46.40 (coord CH₂), 88.04, 88.62 (2 × aromatic CH), 107.84, 109.57 (2 × C_ipso). Yellow crystals were grown by slow evaporation of an acetone solution of the complex.

2.2. [RuCl(η⁶-p-cymene){κ²-C(CH₂SeMe)₄}][PF₆] (2)

Prepared as described for the thioether analogue above from [Ru (η⁶-p-cymene)Cl₂]₂ (0.08 g, 0.125 mmol) and the ligand (0.11 g, 0.25 mmol) in ethanol (15 mL). Addition of [NH₄][PF₆] (0.04 g, 0.25 mmol) in ethanol (10 mL), followed by stirring overnight gave a yellow precipitate. Yield 0.18 g, 83%. Anal. Calc. for $C_{19}H_{34}ClF_6PRuSe_4$: C, 26.5; H, 4.0 Found: C, 26.6; H, 3.7%. ES⁺ (m/z): 714 $[Ru(p\text{-cymene})Cl\{C(CH_2SeMe)_4\}]^+$. IR (Nujol)/cm⁻¹: 836 (PF₆ stretch), 557 (PF₆ bend). ¹H NMR (CDCl₃): 1.31 (d, [6H], $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 2.07, 2.11 (2 × s each [3H], SeCH₃ uncoord), 2.23 (s, [3H], aromatic CH₃), 2.47, 2.66 (2 × s each [2H], SeCH₂ uncoord), 2.54 (s, [6H] SeCH₃ coord), 2.74–3.05 (AB quartet, [4H], SeCH₂ coord), 2.78 (septet, [1H], CH(CH₃)₂), 5.69 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH), 5.80 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH). ⁷⁷Se{¹H} NMR (MeCN/ CD₃CN, 25 °C): 24.5, 25.0 (s, uncoordinated Se), 115.6 (s, coordinated Se). Yellow crystals suitable for X-ray diffraction studies were grown by slow evaporation of a chloroform solution.

2.3. [OsCl(η⁶-p-cymene){κ²-C(CH₂SMe)₄}][PF₆] (3)

[Os(η⁶-p-cymene)Cl₂]₂ (0.077 g, 0.097 mmol) in dry degassed ethanol (50 mL) was added dropwise over 1 h to a flask fitted with reflux apparatus, containing C(CH₂SMe)₄ (0.05 g, 0.2 mmol) in dry CH₂Cl₂ (50 mL). The dark yellow solution was then refluxed for 1 h [NH₄][PF₆] (0.032 g, 0.19 mmol) in dry degassed ethanol (15 mL) was added, the solution was then stirred overnight before filtering to remove small amounts of insoluble material. The filtrate was evaporated to dryness and the product recrystallised from aceto-nitrile-diethyl ether. The yellow solid deposited was filtered off, washed with ether (2 × 5 mL) and dried in vacuo. Yield: 0.054 g, 35%. Anal. Calc. for $C_{19}H_{34}ClF_6OsPS_4·CH_2Cl_2$: C, 28.3; H, 4.3. Found: C, 28.2; H, 4.3%. ES⁺ (m/z): 617 $[Os(p\text{-cymene})Cl\{C(CH_2SMe)_4\}]^+$. IR (Nujol)/cm⁻¹: 836 (PF₆ stretch), 557 (PF₆ bend). ¹H NMR (d⁶-acetone): 1.275 (d, 6[H], $^3J_{HH} = 8.0$ Hz, CH(CH₃)₂), 2.13, 2.17, 2.19 (3 × s each [3H], 2 × SCH₃ uncoord, aromatic CH₃), 2.65, 2.71 (2 × s each [2H], CH₂ uncoord), 3.01–3.34 (AB quartet, [4H], CH₂ coord),

2.72 (s, [6H], coord SCH₃), 2.75 (septet, [1H], $^3J_{HH} = 7.0$ Hz, CH (CH₃)₂), 5.79 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH), 6.03 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH), (also a resonance at 5.3 due to CH₂Cl₂). Much weaker resonances often nearly coincident with the peaks listed above (<5% intensity of the major peaks) were observed and are attributed to other invertomers, but it is not possible to assign these to specific forms.

2.4. [OsCl(η⁶-p-cymene){κ²-C(CH₂SeMe)₄}][PF₆] (4)

[Os(η⁶-p-cymene)Cl₂]₂ (0.089 g, 0.11 mmol) in dry degassed ethanol (50 mL) was added to a stirred solution of C(CH₂SeMe)₄ (0.10 g, 0.23 mmol) in dry degassed ethanol (50 mL). The dark yellow solution was then refluxed for 1 h, [NH₄][PF₆] (0.037 g, 0.23 mmol) in dry ethanol (15 mL) was added, the solution was then stirred overnight before filtering to remove small amounts of insoluble material. The solution was then evaporated to dryness and the product recrystallised from acetonitrile-diethyl ether. The yellow solid deposited was filtered off, washed with ether (2 × 5 mL) and dried in vacuo. Yield 0.069 g, 32%. Anal. Calc. for $C_{19}H_{34}ClF_6OsPSe_4$: C, 24.1; H, 3.6. Found: C, 24.2; H, 3.5%. ES⁺ (m/z): 809 $[Os(p\text{-cymene})Cl\{CCH_2SeMe)_4\}]^+$. IR (Nujol)/cm⁻¹: 836 (PF₆ stretch), 557 (PF₆ bend). ¹H NMR (CDCl₃): 1.26 (d, [6H], $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 2.05, 2.09 (2 × s each [3H], SeCH₃ uncoord), 2.17 (s, [3H], aromatic CH₃), 2.56, 2.69 (2 × s each [2H], SeCH₂ uncoord), 2.48 (s, [6H] SeCH₃ coord), 2.63–3.28 (AB quartet, [4H], SeCH₂ coord), 2.68 (septet, [1H], CH(CH₃)₂), 5.81 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH), 6.03 (d, [2H], $^3J_{HH} = 6$ Hz, aromatic CH). ⁷⁷Se{¹H} NMR (MeCN/ CD₃CN, 25 °C): 23.2, 25.1 (s, uncoordinated Se), 72.2 (s, coordinated Se); (−40 °C): 19.8, 20.7, 71.5. Three very minor ⁷⁷Se resonances were observed at 66.0, 73.4 and 78.4 with an overall intensity ∼5% of the major resonance at 72.2 and are tentatively attributed to minor amounts of the other invertomers. There are also associated weak features in the ¹H NMR spectrum (see text).

2.5. [RuCl(η⁶-p-cymene){κ²-C₆H₂(CH₂SMe)₄}][BPh₄] (5)

A Schlenk tube was charged with [Ru(η⁶-p-cymene)Cl₂]₂ (0.10 g, 0.16 mmol) and the contents were degassed. The orange solid was then dissolved in dry CH₂Cl₂ (5 mL), 1,2,4,5-C₆H₂(CH₂SMe)₄ (0.11 g, 0.32 mmol) in dry ethanol (15 mL) added and the mixture refluxed for 30 min. The reaction mixture was then removed from the oil bath and while still hot, an EtOH solution of Na[BPh₄] (0.11 g, 0.32 mmol) was added. The solution immediately turned from pale orange to yellow and a yellow precipitate formed. Stirring was continued for an hour at ambient temperature. Volatiles were removed on a rotary evaporator and the orange solid was dissolved in CH₂Cl₂ (20 mL) and filtered through a Celite pad. The solvent was removed under vacuum and the yellow oil was washed with n-pentane. It was then re-dissolved in CH₂Cl₂ (3 mL), n-pentane (50 mL) was added slowly to precipitate a yellow solid that was isolated by filtration. Yield: 0.15 g, 51%. Anal. Calc. for $C_{48}H_{56}BClRuS_4·1/2C_5H_{12}$: C, 64.2; H, 6.3. Found: C, 64.2; H, 6.7%. ES⁺ (m/z): 589 $[Ru(p\text{-cymene})Cl\{C_6H_2(CH_2SMe)_4\}]^+$. ¹H NMR (CD₂Cl₂): 0.95 (d, [6H], $^3J_{HH} = 7$ Hz, CH(CH₃)₂), 2.00 (s, [3H] p-cymene CH₃) 2.01 (s, [6H] SCH₃ uncoord), 2.46 (s, [6H], SCH₃ coord.), 2.95 (septet [H], $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 3.33 (d, [2H], $^2J_{HH} = 12$ Hz, CH₂S coord.), 3.78 (s, [4H], CH₂S uncoord.), 4.41 (d, [2H], $^2J_{HH} = 12$ Hz, CH₂S coord.), 5.01 (d, [2H], $^3J_{HH} = 8$ Hz, p-cym-ene aromatics), 5.08 (d, [2H] $^3J_{HH} = 8$ Hz, p-cymene aromatics), 6.89 (m, [4H], aromatics), 7.02 (m, [8H], aromatics), 7.17 (s, [2H], C₆H₂(CH₂SMe)₄), 7.35 (br, [8H], aromatics), (also resonances due to C₅H₁₂). ¹³C{¹H} NMR (CD₂Cl₂): 15.56 (SCH₃ uncoord), 18.47 (aromatic-CH₃), 22.22 (CH(CH₃)₂), 30.89 (SCH₃ coord), 31.28 (CH (CH₃)₂), 35.56 (CH₂ uncoord), 37.22 (CH₂ coord), 86.98, 88.81

(2 × aromatic CH), 107.84, 109.57 (2 × C$_{ipso}$), 122.73, 126.51, 132.26, 134.23, 136.80, 139.35 (aromatics), 164.80 (quartet B–C$_{ipso}$ [1]J (^{11}B–^{13}C) = 50 Hz). Yellow crystals suitable for X-ray diffraction study were grown by layering a CH$_2$Cl$_2$ solution with hexane.

2.6. [RuCl(η^6-p-cymene){κ^2-C$_6$H$_2$(CH$_2$SeMe)$_4$}][BPh$_4$] (6)

[Ru(η^6-p-cymene)Cl$_2$]$_2$ (0.10 g, 0.16 mmol) was dissolved in dry CHCl$_3$ (5 mL) and added by syringe to the selenoether (0.16 g, 0.32 mmol) dissolved in dry ethanol (15 mL).. The reaction mixture was refluxed for 30 min removed from the oil bath and whilst hot, Na[BPh$_4$] (0.11 g, 0.32 mmol) was added in one portion. The solution immediately turned from pale orange to yellow and a yellow precipitate formed. The reaction mixture was cooled to room temperature and stirred overnight. The yellow suspension was concentrated under nitrogen to leave a yellow solid which was dried in vacuo. Yield: 0.17 g, 48%. Anal. Calc. for C$_{48}$H$_{60}$BClRuSe$_4$·CHCl$_3$: C, 50.2; H, 5.1. Found: C, 49.1, H, 5.0%. ES$^+$ (m/z): 778 [Ru(p-cymene)Cl{C$_6$H$_2$(CH$_2$SeMe)$_4$}]$^+$. ^{1}H NMR (CDCl$_3$): 1.09 (d, [6H], J = 7 Hz, CH(CH$_3$)$_2$), 1.90 (s, [3H], aromatic CH$_3$) 1.95 (s, 6[H], SeCH$_3$ uncoord), 2.64 (s, [6H], SeCH$_3$ coord), 3.50 (m, [H], CH(CH$_3$)$_2$), 3.52, 4.68 (AB quartet, 4[H], ^{2}J$_{HH}$ = 9 Hz, CH$_2$Se coord), 3.81 (s, CH$_2$Se uncoord), 5.56, 5.70 (2 × d each [2H] p-cymene aromatics), 6.84 (m), 6.99 (m), 7.27 (m), (total [22H], aromatic CH). ^{77}Se{^{1}H} NMR (MeCN/CD$_3$CN, 25 °C): 157.7 (s, Se uncoord), 183.9 (s, coord Se). Yellow crystals suitable for X-ray diffraction study were grown by slow evaporation of a chloroform solution.

2.7. [{RuCl(η^6-p-cymene)}$_2${κ^2 κ'^2-C(CH$_2$SMe)$_4$}][PF$_6$]$_2$. (7)

A Schlenk tube was charged with [Ru(η^6-p-cymene)Cl$_2$]$_2$ (0.15 g, 0.24 mmol) suspended in dry ethanol (15 mL) and C(CH$_2$SMe)$_4$ (0.06 g, 0.24 mmol) in ethanol (10 mL) was added. The mixture was refluxed for 30 min, and [NH$_4$][PF$_6$] (0.08 g, 0.49 mmol) was added to the hot solution. The mixture was allowed to cool, stirred overnight at room temperature, and the yellow precipitate removed by filtration, and dried in vacuo. Yield: 0.21 g, 80%. Anal. Calc. for C$_{29}$H$_{48}$Cl$_2$F$_{12}$P$_2$Ru$_2$S$_4$: C, 32.0; H, 4.5. Found: C, 31.3; H, 4.0%. ES$^+$ (m/z): 399 [{Ru(p-cymene)Cl}$_2${C(CH$_2$SMe)$_4$}]$^{2+}$. IR (Nujol)/cm^{-1}: 836 (PF$_6$ stretch), 557 (PF$_6$ bend). ^{1}H NMR (d^6-acetone): 1.35, 1.37 (2 × d each [6H], ^{3}J$_{HH}$ = 7.0 Hz, CH(CH$_3$)$_2$), 2.29 (br,s [3H], aromatic CH$_3$), 2.76, 2.83 (2 × s each [3H] SCH$_3$), 2.87–2.90 (m, [H], CH(CH$_3$)$_2$), 2.93–3.12 (overlapping m, [4H], CH$_2$), 6.03 (m, [2H], aromatic CH), 6.25 (m, [2H], aromatic CH). Much weaker resonances (<5%) at 2.27(s), 2.78(s), 2.82(s) are believed to be the aromatic CH$_3$ and SCH$_3$ resonances of other invertomer(s), other expected resonances are obscured by those of the major invertomer.

2.8. [{RuCl(η^6-p-cymene)}$_2${κ^2 κ'^2-C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (8)

Prepared as for the tetrathioether analogue above. Yield: 83%. Anal. Calc. for C$_{29}$H$_{48}$Cl$_2$F$_{12}$P$_2$Ru$_2$Se$_4$: C, 27.2; H, 3.8. Found: C, 27.3; H, 3.8%. ES$^+$ (m/z): 493 [{Ru(p-cymene)Cl}$_2${C(CH$_2$SeMe)$_4$}]$^{2+}$. IR (Nujol)/cm^{-1}: 840 (PF$_6$ stretch), 557 (PF$_6$ bend). ^{1}H NMR (CD$_3$CN): 1.26 (br, d [6H], ^{3}J$_{HH}$ = 6.0 Hz, CH(CH$_3$)$_2$), 2.17 (br,s [3H], aromatic CH$_3$), 2.45, 2.55, (2 s each [3H] SeCH$_3$), 2.72–2.90 (m, [H], CH(CH$_3$)$_2$), 2.88–3.01 (br AB quartet, [4H], CH$_2$), 5.73 (m, [2H], aromatic CH), 5.85 (m, [2H], aromatic CH). ^{77}Se{^{1}H} NMR (CH$_3$CN/CD$_3$CN, 25 °C): 120.5, 123.1 (coord. Se). Again, the spectra show very minor additional resonances near to those of the major form, including very weak resonances in the ^{77}Se NMR spectrum at 115.7 and 130.6, tentatively attributed to other invertomer(s).

2.9. [{OsCl(η^6-p-cymene)}$_2$ {κ^2 κ'^2-C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (9)

Method 1: [Os(η^6-p-cymene)Cl$_2$]$_2$ (0.178 g, 2.25 mmol) in dry degassed ethanol (50 mL) was added to a flask containing C(CH$_2$SeCH$_3$)$_4$ (0.10 g, 2.25 mmol) in dry degassed ethanol (50 mL). The dark yellow solution was then stirred at 70 °C for 1 h [NH$_4$][PF$_6$] (0.073 g, 4.5 mmol) in dry degassed ethanol (15 mL) was added, the solution was then stirred overnight before filtering to remove small amounts of insoluble material. The filtrate was taken to dryness and recrystallised from acetonitrile-diethylether. The yellow solid deposited was filtered off, washed with ether (2 × 5 mL) and dried in vacuo. Yield: 0.20 g, 63%.

Method 2: [OsCl(η^6-p-cymene){κ^2-C(CH$_2$SeMe)$_4$}][PF$_6$] (0.05 g, 0.052 mmol) in dry degassed ethanol (50 mL) was added to a flask containing [Os(η^6-p-cymene)Cl$_2$]$_2$ (0.02 g, 0.026 mmol) in dry degassed ethanol (50 mL). The dark yellow solution was then stirred at 70 °C for 1 h [NH$_4$][PF$_6$] (0.01 g, 0.06 mmol) in dry degassed ethanol (15 mL) was added, the solution was then stirred overnight before filtering to remove small amounts of insoluble material. The filtrate was taken to dryness and the product recrystallised from acetonitrile-diethyl ether. The yellow solid deposited was filtered off, washed with ether (2 × 5 mL) and dried in vacuo. Yield: 0.04 g, 53%. The products from the two routes were spectroscopically identical. Anal. Calc. for C$_{29}$H$_{48}$Cl$_2$F$_{12}$Os$_2$P$_2$Se$_4$: C, 24.0; H, 3.3. Found: C, 24.3; H, 3.5%. ES$^+$ (m/z): 581 [{Os(p-cymene)Cl}$_2${C(CH$_2$SeMe)$_4$}]$^{2+}$. IR (Nujol)/cm^{-1}: 840 (PF$_6$ stretch), 557 (PF$_6$ bend). ^{1}H NMR (CD$_3$CN): 1.28 (d, [6H], ^{3}J$_{HH}$ = 7.0 Hz, CH(CH$_3$)$_2$), 2.26 (s, [3H], aromatic CH$_3$), 2.61, 2.66 (2 × s each [3H] SeCH$_3$), 2.80–3.15 (AB quartet, [4H], SeCH$_2$), 2.82 (m, [H], CH(CH$_3$)$_2$), 6.12 (br d, [2H], ^{3}J$_{HH}$ = 6 Hz, aromatic CH), 6.34 (br d, [2H], ^{3}J$_{HH}$ = 6 Hz, aromatic CH). ^{77}Se{^{1}H} NMR (CH$_3$CN/CD$_3$CN, 25 °C): 66.6 (br s), 66.5(sh). As above, minor resonances in the ^{1}H NMR at 2.23, 2.60. 2.65 are respectively aromatic CH$_3$ and SeCH$_3$ of other forms, and these have associated very weak resonances in the ^{77}Se NMR spectrum at 69.6 and 66.1.

2.10. [{RuCl(η^6-p-cymene)}$_2${κ^2 κ'^2-C$_6$H$_2$(CH$_2$SMe)$_4$}][PF$_6$]$_2$ (10)

A Schlenk tube was charged with [Ru(η^6-p-cymene)Cl$_2$]$_2$ (0.38 g, 0.62 mmol) suspended in dry ethanol (15 mL) and the tetrathioether (0.2 g, 0.62 mmol) in ethanol (10 mL) added. The mixture was refluxed for 30 min, and [NH$_4$][PF$_6$] (0.20 g, 1.25 mmol) added to the hot solution. The mixture was allowed to cool, stirred overnight at room temperature, and the yellow precipitate removed by filtration, and dried in vacuo. Yield: 0.66 g, 91%. Anal. Calc. for C$_{34}$H$_{50}$Cl$_2$F$_{12}$P$_2$Ru$_2$S$_4$·C$_2$H$_5$OH: C, 36.2; H, 4.7. Found: C, 36.8; H 4.3%. ES$^+$ (m/z): 430 [{Ru(p-cymene) Cl}$_2${C$_6$H$_2$(CH$_2$SMe)$_4$}]$^+$. IR (Nujol)/cm^{-1}: 840 (PF$_6$ stretch), 557 (PF$_6$ bend). ^{1}H NMR (CD$_3$CN): 0.99 (d, [6H], ^{3}J$_{HH}$ = 9 Hz, CH(CH$_3$)$_2$), 2.10 (s, [3H] p-cymene CH$_3$), 2.67 (s, [6H], SCH$_3$), 2.85 (m [H], ^{3}J$_{HH}$ = 9.0 Hz, CH(CH$_3$)$_2$), 3.44 (d, [2H], ^{2}J$_{HH}$ = 12 Hz, CH$_2$S), 4.36 (d, [2H], ^{2}J$_{HH}$ = 12 Hz, CH$_2$S), 5.52 (d, [2H], ^{3}J$_{HH}$ = 8 Hz, p-cymene aromatics), 5.66 (d, [2H] ^{3}J$_{HH}$ = 8 Hz, p-cymene aromatics), 7.32 (s, [H], C$_6$H$_2$(CH$_2$SMe)$_4$) (and EtOH resonances at 1.12 (t), 3.54 (q) 2.63 (s)). Crystals were obtained from an MeCN solution by slow evaporation.

2.11. [{RuCl(η^6-p-cymene)}$_2${κ^2 κ'^2-C$_6$H$_2$(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (11)

A Schlenk tube was charged with [Ru(η^6-p-cymene)Cl$_2$]$_2$ (0.075 g, 0.12 mmol) and dry ethanol (15 mL) added, followed by a solution of the tetraselenoether (0.060 g, 0.12 mmol) in ethanol (10 mL). The mixture was refluxed for 30 min and the [NH$_4$][PF$_6$] (0.04 g, 0.24 mmol) added. The mixture was allowed to cool and stirred overnight. The yellow precipitate was filtered off and dried

in vacuo. Yield: 0.12 g, 75%. Anal. Calc. for $C_{34}H_{50}Cl_2F_{12}P_2Ru_2Se_4$: C, 30.5; H, 3.8. Found: C, 30.1, H, 4.1%. ES$^+$ (m/z): 523 [{Ru(p-cymene) Cl}$_2${C$_6$H$_4$(CH$_2$SeMe)$_4$}]$^{2+}$. IR (Nujol)/cm^{-1}: 836 (PF$_6$ stretch), 557 (PF$_6$ bend). The complex proved to be too poorly soluble for NMR studies.

2.12. [{RuCl(η^6-p-cymene)}{OsCl(η^6-p-cymene)κ^2 κ′^{2}-C(CH$_2$SeMe)$_4$}]-[PF$_6$]$_2$.(12)

[OsCl(η^6-p-cymene){κ^2-C(CH$_2$SeMe)$_4$}][PF$_6$] **(4)** (0.053 g, 0.056 mmol) was dissolved in ethanol (80 mL), [Ru(η^6-p-cymene) Cl$_2$]$_2$ (0.017 g, 0.028 mol) dissolved in ethanol (50 mL) was added dropwise over 1 h. The solution was then heated to 40 °C for 2 h [NH$_4$][PF$_6$] (0.01 g, 0.06 mmol) in ethanol was added to the warm solution and stirred for 48 h. The resulting solution was taken to dryness in vacuum and the residue recrystallised from MeCN and Et$_2$O to yield an orange solid. Crystals were grown from a solution of MeCN at room temperature. Yield: 0.047 g, 62%. Anal. Calc. for $C_{29}H_{48}Cl_2F_{12}OsP_2RuSe_4$: C, 25.5; H, 3.7. Found: C, 25.5, H, 3.6%. ES$^+$ (m/z): 538 [{Os(p-cymene)Cl}{Ru(p-cymene)Cl}{C(CH$_2$SeMe)$_4$}]$^{2+}$. IR (Nujol)/cm^{-1}: 842 (PF$_6$ stretch), 577 (PF$_6$ bend). ^{1}H NMR (CD$_3$CN): 1.27 (br, d [12H], $^3J_{HH}$ = 6.0 Hz, CH(CH$_3$)$_2$), 2.18, 2.20 (2 × br,s each [3H], aromatic CH$_3$), 2.45, 2.46, 2.55, 2.57, (4 × s, each [3H], SeCH$_3$), 2.72–2.90 (m, [2H], CH(CH$_3$)$_2$), 2.72–3.21 (br multiplets, [8H], CH$_2$), 5.72 (m, [2H], aromatic CH), 5.86 (m, [4H], aromatic CH), 6.06 (m, [2H], aromatic CH). ^{77}Se{^{1}H} NMR (CH$_3$CN/CD$_3$CN, 25 °C): 124.0, 117.0, 76.9 (sh), 78.8 (minor features at 80.0, 73.1)

2.13. [{OsCl(η^6-p-cymene)}PtCl$_2$ {κ^2 κ′^{2}-C(CH$_2$SeMe)$_4$}][PF$_6$] (13)

PtCl$_2$ (0.013 g, 0.05 mol) was suspended in MeCN (50 mL) and refluxed for 1.5 h, then the solution was allowed to cool to room temperature. [OsCl(η^6-p-cymene){κ^2-C(CH$_2$SeMe)$_4$}][PF$_6$] **(4)** (0.05 g, 0.052 mmol) dissolved in MeCN (50 mL) was added drop-wise over 10 min, and the mixture was stirred for 48 h. The resulting solution was the taken to dryness in vacuum and the residue recrystallised from MeCN and Et$_2$O to yield a dark yellow solid, which was rinsed with n-hexane and dried in vacuo. Yield: 0.022 g, 46%. Anal. Calc. for $C_{19}H_{34}Cl_3F_6OsPPtSe_4$.1/2C$_6H_{14}$ for C, 21.0; H, 3.3. Found: C, 20.6; H, 3.3%. ES$^+$ (m/z): 1072 [{Os(p-cymene) Cl}PtCl$_2${C(CH$_2$SeMe)$_4$}]$^+$, also m/z 803 [M–PtCl$_2$]$^+$. IR (Nujol)/cm^{-1}: 840 (PF$_6$ stretch), 577 (PF$_6$ bend). ^{195}Pt NMR (CH$_3$CN/CD$_3$CN, 25 °C): −3686 (minor resonances at −3667, −3753). ^{77}Se{^{1}H} NMR (CH$_3$CN/CD$_3$CN, 25 °C): 167.1 ($^1J_{PtSe}$ = 572 Hz), 162.9 ($^1J_{PtSe}$ = 467 Hz), 82.5, 75.0 (minor resonances at 83.2, 72.1).

2.14. X-ray crystallography experimental

Details of the crystallographic data collection and refinement are given in Table 1. The crystallisation details are provided under the section for each compound. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated Mo Kα X-radiation (λ = 0.71073 Å), and with the crystals held at 120 K in a dinitrogen gas stream. Structure solution and refinement were straightforward [8–10], except as described below, and H atoms were introduced into the model in calculated positions using the default C–H distances. [Ru(η^6-p-cymene)Cl{C$_6$H$_2$(CH$_2$SMe)$_4$}]BPh$_4$ had a disordered i-propyl group on the cymene residue which was modelled as two sites (A/B) with a refined population and the use of DFIX commands to control C–C distances. The major component (A, 0.68) is shown in Fig. 2. In [Ru(η^6-p-cymene)Cl{C(CH$_2$SMe)$_4$}] PF$_6$ the adp values of the anion F atoms used EADP constraints on trans F atoms together with a common refined P–F distance (DFIX/FVAR). Selected bond lengths and angles are given in Tables 2–5.

3. Results and discussion

3.1. Synthesis

The reaction of [Ru(η^6-p-cymene)Cl$_2$]$_2$ with 2 M equivalents of the ligands C(CH$_2$SMe)$_4$, C(CH$_2$SeMe)$_4$, 1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$ or 1,2,4,5-C$_6$H$_2$(CH$_2$SeMe)$_4$ (L_4) in ethanol, followed by addition of [NH$_4$][PF$_6$], produced good yields of yellow [RuCl(η^6-p-cymene)(κ^2-L_4)]PF$_6$. Treatment of these complexes with a further 0.5 equivalents of [Ru(η^6-p-cymene)Cl$_2$]$_2$, or direct reaction of [Ru(η^6-p-cymene)Cl$_2$]$_2$ with L_4 in a 1:1 M ratio, gives the corresponding diruthenium species [{RuCl(η^6-p-cymene)}$_2$(κ^{2}κ′^{2}-L_4)][PF$_6$]$_2$ (see Scheme 1). A more limited number of osmium(II) examples were obtained similarly from [Os(η^6-p-cymene)Cl$_2$]$_2$. All the complexes are air-stable solids, mostly relatively poorly soluble in chlorocarbons or acetone and more soluble in MeCN. Solubility is less for the 2:1 complexes than the 1:1, and the spirocyclic ligand complexes are markedly more soluble than those with the aromatic backbone. The solubility can also be improved by replacing the [PF$_6$]$^-$ anions by [BPh$_4$]$^-$. The complexes can also be isolated as chloride salts by omitting the large anion, but these were not obtained analytically pure, and the NMR spectra of their solutions suggest a equilibrium in solution with chloride anion partially displacing a thio- or selenoether group from the ruthenium, as observed in the [RuCl(η^6-p-cymene)(R$_2$S)$_2$]Cl complexes [11].

3.2. [M(η^6-p-cymene)Cl(L_4)]PF$_6$ (M = Ru or Os, L_4 = C(CH$_2$SMe)$_4$ or C(CH$_2$SeMe)$_4$)

It is convenient to discuss the structures of representative examples first. Both [RuCl(η^6-p-cymene)(κ^2-L_4)]$^+$ (**1,2**) cations (L_4 = C(CH$_2$SMe)$_4$, C(CH$_2$SeMe)$_4$) were structurally characterised (Table 2, Fig. 1). Both contain six-coordinate ruthenium with the arene formally occupying one triangular face of the octahedron, and with the chelating chalcogenoether and a chloride ligand completing the octahedron. The κ^2–chalcogenoethers are both meso forms with the S(Se)Me groups on the same side of the RuS(Se)$_2$ plane as the chlorine and anti to the p-cymene ^{i}Pr group. The S(Se)–Ru–S(Se) angles are slightly less than 90° in the six-membered rings produced by the spirocyclic linkages with E···E within the chelate ring 3.344(1) (E = S) or 3.472(1) (E = Se) Å, contrasting with the E···E distances of the uncoordinated groups which are some 1.5 Å greater due to the substituents being bent away to minimise lone pair repulsions. The bond lengths are unexceptional and the Ru–C and Ru–Cl little different between the two complexes.

The ES$^+$ mass spectra of all the complexes show ions with the correct isotope pattern for the cations present. The low symmetry of the complexes results in relatively complicated NMR spectra and slow pyramidal inversion at the chalcogen atom (if present) should lead to further resonances due to the different invertomers.[1] Taking the 1:1 ruthenium complexes first, the ruthenium centres are equatorially coordinated to two chalcogen groups in six-membered chelate rings, and since the ruthenium lacks axial symmetry, this leads to three possible invertomers: a DL form and two meso forms (with the MeS(Se) groups syn or anti to the RuCl group). In fact, the ^{1}H, ^{13}C{^{1}H} and where appropriate the ^{77}Se{^{1}H} NMR spectra show only single resonances for the coordinated MeS(Se) groups, consistent either with fast pyramidal inversion or with the presence of only one of the meso forms in significant amounts (the DL forms would

---

[1] The rates of pyramidal inversion vary with the metal, metal oxidation state, donor atom (S or Se), co-ligands, chelate ring size and substituents at E [12]. Investigation of the inversion processes is not relevant to the present study, but their effect on the observed NMR spectra needs to be taken into account.

Table 1
Crystal data and structure refinement details.[a]

Complex	[RuCl(η^6–p-cymene){C(CH$_2$SMe)$_4$}]PF$_6$	[RuCl(η^6–p-cymene){C(CH$_2$SeMe)$_4$}]PF$_6$	[RuCl(η^6–p-cymene){C$_6$H$_2$(CH$_2$SMe)$_4$}]BPh$_4$	[RuCl(η^6–p-cymene)–{C$_6$H$_2$(CH$_2$SeMe)$_4$}]BPh$_4$	[{RuCl(η^6–p-cymene)}$_2${C(CH$_2$SMe)$_4$}] [PF$_6$]$_2$	[{RuCl(η^6–p-cymene)}$_2$–{C$_6$H$_2$(CH$_2$SMe)$_4$}][PF$_6$]$_2$·2MeCN
Formula	C$_{19}$H$_{34}$ClF$_6$PRuS$_4$	C$_{19}$H$_{34}$ClF$_6$PRuSe$_4$	C$_{48}$H$_{56}$BClRuS$_4$	C$_{48}$H$_{56}$BClRuSe$_4$	C$_{29}$H$_{48}$Cl$_2$F$_{12}$P$_2$Ru$_2$S$_4$	C$_{38}$H$_{56}$Cl$_2$F$_{12}$N$_2$P$_2$Ru$_2$S$_4$
M	672.19	859.79	908.50	1096.10	1087.89	1232.07
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group (no.)	Pna2$_1$ (#33)	Pna2$_1$ (#33)	P2$_1$/n (#14)	P2$_1$/n (#14)	P-1 (#2)	C2/c (#15)
a (Å)	12.957(2)	13.0594(15)	9.4108(10)	9.378(2)	10.047(3)	25.274(3)
b (Å)	12.2813(15)	12.4383(15)	22.201(3)	22.445(7)	12.941(4)	9.9679(10)
c (Å)	16.5845(15)	16.893(3)	21.410(2)	21.649(7)	16.904(5)	19.698(3)
α (°)	90	90	90	90	71.299(15)	90
β (°)	90	90	91.900(6)	91.056(18)	79.89(2)	95.144(6)
γ (°)	90	90	90	90	80.07(2)	90
U (Å^3)	2639.1(6)	2744.1(6)	4470.6(8)	4556(2)	2033.6(10)	4942.4(10)
Z	4	4	4	4	2	4
μ(Mo Kα) (mm^{-1})	1.122	6.081	0.630	3.630	1.236	1.029
F(000)	1368	1656	1896	2184	1092	2488
Total no. of reflections	31 011	20 742	94 451	49 348	34 367	27 475
Unique reflections	5992	4978	10 248	8917	7906	5666
R$_{int}$	0.049	0.064	0.119	0.121	0.077	0.060
No. of parameters, constraints	303, 11	279, 1	522, 6	503, 0	470, 0	283, 0
R$_1$[b] [I$_o$ > 2σ(I$_o$)]	0.029	0.046	0.054	0.088	0.068	0.045
R$_1$ (all data)	0.039	0.059	0.096	0.146	0.113	0.060
wR$_2$[b] [I$_o$ > 2σ(I$_o$)]	0.054	0.093	0.105	0.143	0.121	0.101
wR$_2$ (all data)	0.057	0.100	0.118	0.167	0.144	0.109

[a] Common items: temperature = 120 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma || F_o| - |F_c||/\Sigma |F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$.

contain two resonances of equal intensity due to the lack of axial symmetry at the metal). The modest solubility of the complexes limited low temperature studies to CD$_3$CN/MeCN solutions (mp −48 °C), but the spectra of selected complexes were essentially unchanged on cooling, apart from a small temperature drift in the chemical shifts in the ^{77}Se NMR spectra. We note that the complexes of the cyclopropane-backboned ligands [MCl(η^6-p-cymene){(CH$_2$)$_2$C(CH$_2$SeMe)$_2$}]PF$_6$ (M = Ru or Os), where the ligands differ only in the substituents on the carbon backbone, show the presence (in very disparate amounts) of three invertomers, with one of the *meso* forms the major species in solution [6], and thus very disparate invertomer populations cannot be excluded (*vide infra*).

Looking first at the ^{1}H NMR spectrum of [Ru(η^6-p-cymene)Cl{C(CH$_2$SMe)$_4$}]$^+$ (**1**) the η^6-p-cymene group shows two doublets at δ 6.03, 6.22 $^3J_{HH}$ = 6 Hz, for the aromatic protons, a doublet at δ 1.37

$^3J_{HH}$ = 7 Hz for CH(CH$_3$)$_2$, and a septet at δ 2.95 for CH(CH$_3$)$_2$. There are three singlets of equal intensity at δ 2.22, 2.25, 2.30 assigned to the p-cymene Me group and to uncoordinated SMe groups (the tetrahedral disposition of the CH$_2$SMe groups about the quaternary carbon in the ligand backbone and the lack of axial symmetry at the ruthenium makes the uncoordinated SMe groups inequivalent − *syn* or *anti* to the arene), and a single resonance at δ 2.82 is the coordinated SMe. The ^{13}C{^{1}H} NMR spectrum (Section 2.1) is fully consistent with the presence of a single form of the complex. For the complex [Ru(η^6-p-cymene)Cl{C(CH$_2$SeMe)$_4$}]$^+$ (**2**) the assignment of the ^{1}H NMR spectrum (Section 2.2) follows that of the thioether analogue, and the ^{77}Se{^{1}H} spectrum shows resonances at δ 24.5, 25.0 due to the uncoordinated MeSe groups, and a singlet at 115.6 due to the coordinated SeMe groups. Careful examination of the spectra of the two ruthenium complexes failed to reveal any weak resonances which could be attributed to other invertomers.

The NMR spectra of the [Os(η^6-p-cymene)Cl{C(CH$_2$EMe)$_4$}]$^+$ (**3,4**) are generally similar to those of the ruthenium analogues,

Table 2
Selected bond lengths (Å) and angles (°) for [RuCl(η^6-p-cymene){C(CH$_2$EMe)$_4$}]PF$_6$, (E = S or Se).

	E = S (**1**)	E = Se (**2**)
Ru1−C(arene)	2.176(3)−2.267(3)	2.175(9)−2.225(9)
Ru1−Cl1	2.3891(8)	2.391(2)
Ru1−E1	2.3702(8)	2.4806(12)
Ru1−E2	2.3666(8)	2.4776(11)
E1···E2	3.344(1)	3.472(1)
E3···E4	4.849(1)	5.063(2)
E1−Ru1−E2	89.80(3)	88.89(4)
E1−Ru1−Cl1	88.19(3)	88.58(6)
E2−Ru1−Cl1	88.11(3)	88.63(6)
C2−E1−C6	97.4(2)	94.7(4)
C3−E2−C7	96.8(2)	94.5(4)
C4−E3−C8	102.8(2)	94.2(5)
C5−E4−C9	98.4(2)	100.8(5)

Table 3
Selected bond lengths (Å) and angles (°) for [RuCl(η^6-p-cymene){C$_6$H$_2$(CH$_2$EMe)$_4$}]BPh$_4$ (E = S or Se).

	E = S (**5**)	E = Se (**6**)
Ru1−C(arene)	2.167(4)−2.253(4)	2.174(9)−2.246(10)
Ru1−Cl1	2.3752(9)	2.382(2)
Ru1−E1	2.3766(9)	2.5138(15)
Ru1−E2	2.4044(9)	2.4799(15)
E1···E2	3.518(1)	3.637(2)
E3···E4	4.556(2)	4.765(2)
E1−Ru1−E2	94.75(3)	93.49(4)
Cl1−Ru1−E2	87.51(3)	87.91(7)
Cl1−Ru1−E1	87.40(3)	88.07(7)

Table 4
Selected bond lengths (Å) and angles (°) for [{RuCl(η^6-*p*-cymene)}$_2${C(CH$_2$SMe)$_4$}][PF$_6$]$_2$ (**7**).

Ru1–C(arene)	2.179(8)–2.218(8)	Ru2–C(arene)	2.175(8)–2.252(8)
Ru1–S1	2.366(2)	Ru2–S3	2.368(2)
Ru1–S2	2.363(2)	Ru2–S4	2.373(2)
Ru1–Cl1	2.402(2)	Ru2–Cl2	2.392(2)
S1⋯S2	3.323(3)	S3⋯S4	3.362(3)
S1–Ru1–S2	89.28(7)	S3–Ru2–S4	90.31(7)
S1–Ru1–Cl1	89.17(8)	S3–Ru2–Cl2	88.65(7)
S2–Ru1–Cl1	87.70(8)	S4–Ru2–Cl2	87.02(7)

with only very small differences in the ^{1}H chemical shifts. However, the ^{77}Se NMR spectra of [Os(η^6-*p*-cymene)Cl{C(CH$_2$SeMe)$_4$}]$^+$ show three very weak features at $\delta = 66.0$, 73.4 and 78.4 with an overall intensity 5% of the major resonance at $\delta = 72.2$ and we tentatively assign these to very minor amounts of the *DL* and the second *meso* invertomer. The smaller coordination shifts in the selenium spectra of the osmium compared to the ruthenium complexes reflects the usual trends between corresponding 4d and 5d metal centres [13]. Careful examination of the ^{1}H NMR spectrum of [Os(η^6-*p*-cymene)Cl{C(CH$_2$SeMe)$_4$}]$^+$ (**4**) shows very weak features mostly very close to the major resonances which we also attribute to very small amounts of other invertomers, although specific assignments are not possible. Somewhat larger amounts (<10% overall) of other invertomers are present in the ^{1}H NMR spectrum of [Os(η^6-*p*-cymene)Cl{C(CH$_2$SMe)$_4$}]$^+$ (**3**), but the complexity of the spectra preclude attribution to specific invertomers. Thus, we conclude that in this series of complexes pyramidal inversion is slow in the osmium complexes, but that the isomer distribution is very disparate, the dominant form being a *meso* invertomer, most probably the form present in the crystal structures. The disparate invertomer populations may well be largely due to steric factors in these crowded molecules. For the ruthenium complexes the spectra indicate that either only one form of each is present in detectable amounts or the inversion is fast and averaged resonances are observed.

3.3. [Ru(η^6-p-cymene)Cl(L$_4'$)]BPh$_4$ (L$_4'$ = 1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$ or 1,2,4,5-C$_6$H$_2$(CH$_2$SeMe)$_4$) (5,6)

The structures of both complexes were determined and are isomorphous, with very similar bond lengths and angles, the only significant differences being due to the larger covalent radius of Se over S (Table 3, Fig. 2). The seven-membered chelate rings result in rather wider E–Ru–E angles (by ~6°) than in the spirocyclic-backboned analogues which have six-membered chelate rings. The geometry at the ruthenium shows the two EMe groups (*meso* invertomer) and Cl occupying one face of the octahedron and again the ^{i}Pr group of the *p*-cymene is *anti* to the EMe groups.

The ^{1}H NMR spectrum of the [Ru(η^6-*p*-cymene)Cl{C$_6$H$_2$(CH$_2$SMe)$_4$}]$^+$ (**5**) differs from those of the spirocyclic linked ligands discussed in Section 3.2, in that replacement of the tetrahedrally coordinated quaternary carbon by a planar aromatic linker in the ligand backbone, means that the uncoordinated SMe groups are now equivalent by symmetry, and thus in the ^{1}H NMR spectrum

Table 5
Selected bond lengths (Å) and angles for [{RuCl(η^6-*p*-cymene)}$_2${C$_6$H$_2$(CH$_2$SMe)$_4$}][PF$_6$]$_2$·2MeCN (**10**).

Ru1–C(arene)	2.182(4)–2.237(4)	Ru1–S1	2.3925(10)
Ru1–Cl1	2.3915(9)	Ru1–S2	2.3934(9)
S1⋯S2	3.579(1)		
S1–Ru1–S2	96.80(3)	Cl1–Ru1–S2	87.52(3)
Cl1–Ru1–S1	87.43(3)		

occur as a singlet at δ 2.01, and the coordinated SMe are a singlet at δ 2.46. In the ^{13}C{^{1}H} NMR spectrum these groups give rise to single resonances at δ 15.56 and 30.89 respectively. Similar behaviour is seen in the spectra of [Ru(η^6-*p*-cymene)Cl{C$_6$H$_2$(CH$_2$SeMe)$_4$}]$^+$ (**6**) whilst in the ^{77}Se{^{1}H} NMR spectrum there are two resonances due respectively to uncoordinated and coordinated SeMe groups at δ 157.7 and 183.9. As we observed previously in their metal carbonyl complexes [5], the coordination shifts in the ^{77}Se NMR spectra of the 1,2,4,5-C$_6$H$_2$(CH$_2$SeMe)$_4$ complexes are much smaller than those in the spirocyclic-backboned analogues, possibly due to the larger chelate ring present. For both complexes the simple NMR spectra would suggest fast inversion, which might be expected to be a low energy process in the seven-membered chelate rings [12].

3.4. [{M(η^6-p-cymene)Cl}$_2$(L$_4$)][PF$_6$]$_2$ (M = Ru, L$_4$ = C(CH$_2$SMe)$_4$ or M = Ru or Os L$_4$ = C(CH$_2$SeMe)$_4$) (7–9)

The key structural features of these 2:1 complexes are illustrated in [{Ru(η^6-*p*-cymene)Cl}$_2${C(CH$_2$SMe)$_4$}][PF$_6$]$_2$ (**7**) (Fig. 3, Table 4). Although not related by crystallographic symmetry the two halves of the molecule are very similar, consisting of six-coordinate ruthenium centres bonded η^6 to the *p*-cymene and with a *fac* arrangement of one chloride and a chelating dithioether unit, again with *meso* SMe groups *syn* to the Cl. The Ru–S, Ru–Cl and Ru–C(arene) distances are not significantly different to those in the 1:1 complex above.

The ES$^+$ mass spectra show ions with the correct isotope structure at half-mass for the cations as expected due to the dipositive charge. The NMR spectra are again consistent with the presence of one major invertomer with *meso* EMe groups, the symmetry of the molecule now making the *E*Me resonances within each chelate ring inequivalent. The ^{1}H NMR spectrum of [{Ru(η^6-*p*-cymene)Cl}$_2${C(CH$_2$SMe)$_4$}][PF$_6$]$_2$ also shows inequivalent methyl resonances in the *p*-cymene ^{i}Pr group, possibly indicating restricted rotation, although this effect is not evident in either of the selenoether complexes. The ^{77}Se NMR spectrum of [{Ru(η^6-*p*-cymene)Cl}$_2${C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (**8**) shows two closely spaced resonances of equal intensity which correlate with the two SeMe resonances in the ^{1}H spectrum, but in the ^{77}Se NMR spectrum of [{Os(η^6-*p*-cymene)Cl}$_2${C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (**9**) only a broad single resonance with a clear shoulder was seen, which is attributed to accidental near coincidence of the signals. As observed in the spectra of the 1:1 osmium complexes described above, those of the 2:1 species exhibit very weak features attributable to minor amounts of the other invertomers, and this is particularly evident in the ^{77}Se NMR spectra of the two tetraselenoether complexes. The possibility that these minor resonances are due to small amounts of the 1:1 complexes is ruled out by the fact that the chemical shifts do not correspond to those of the 1:1 complexes (although as expected they are in relatively similar regions), but also by the absence of any features attributable to uncoordinated selenium groups.

3.5. [{Ru(η^6-p-cymene)Cl(L$_4'$)}$_2$][PF$_6$]$_2$ (L$_4'$ = 1,2,4,5-C$_6$H$_2$(CH$_2$SMe)$_4$ or 1,2,4,5-C$_6$H$_2$(CH$_2$SeMe)$_4$) (10,11)

The crystal structure of the tetrathioether complex (Fig. 4, Table 5) shows the now familiar geometry at ruthenium, and with the two ruthenium moieties related by a two-fold rotation axis lying through the central aromatic unit (C4–C5). The bond lengths are unexceptional. The ^{1}H NMR spectrum is simple showing only one SMe resonance present at room temperature, probably due to fast pyramidal inversion. There was no evidence for detectable amounts of the 1:1 complex. The tetraselenoether complex was very poorly soluble even in CD$_3$CN and useful NMR data were not obtained, although the microanalysis, ES$^+$ mass spectrum and the IR spectrum were consistent with the formulation.
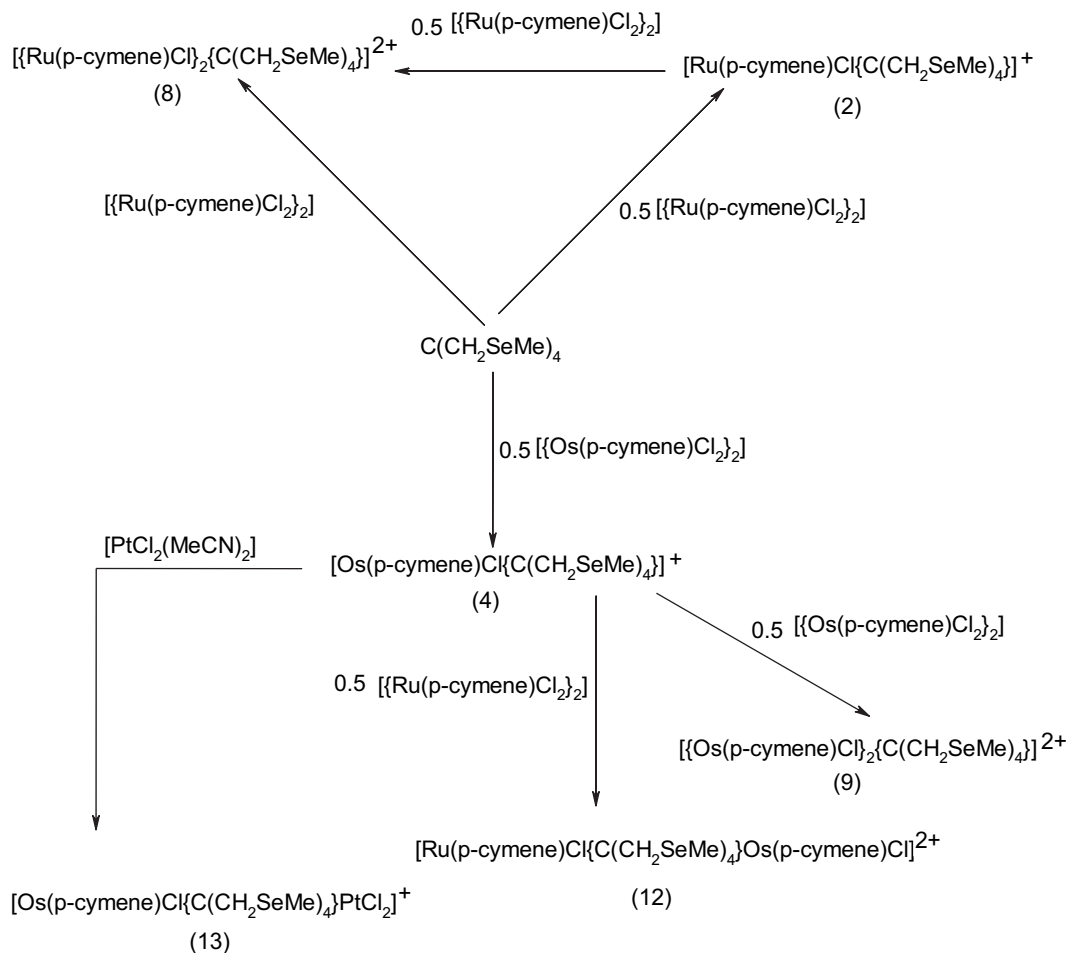
Scheme 1. Some reactions of $C(CH_2SeMe)_4$ with Ru and Os arene reagents.

3.6. Heterobimetallic complexes

Based upon the successful isolation of 1:1 and 2:1 homometallic complexes of the tetradentates (obtained by stepwise introduction of the metals), we explored the synthesis of several

heterobimetallic complexes. Studies were focussed on the tetraselenoethers which would permit use of ^{77}Se NMR as a useful spectroscopic probe, since the ^1H NMR spectra were expected to be of limited use due to their complexity. Initially the reactions of $[Ru(\eta^6\text{-}p\text{-cymene})Cl\{\kappa^2\text{-}C_6H_2(CH_2SMe)_4\}]PF_6$ and $[Ru(\eta^6\text{-}p\text{-cymene})Cl\{\kappa^2\text{-}C(CH_2SeMe)_4\}]PF_6$ with 0.5 equivalent of $[\{Os(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$ in ethanol were explored using a range of reaction conditions and times, but examination of the products by ES^+ mass
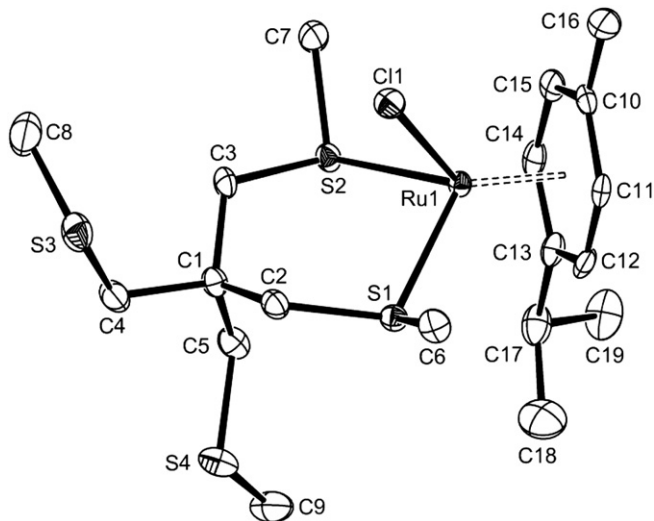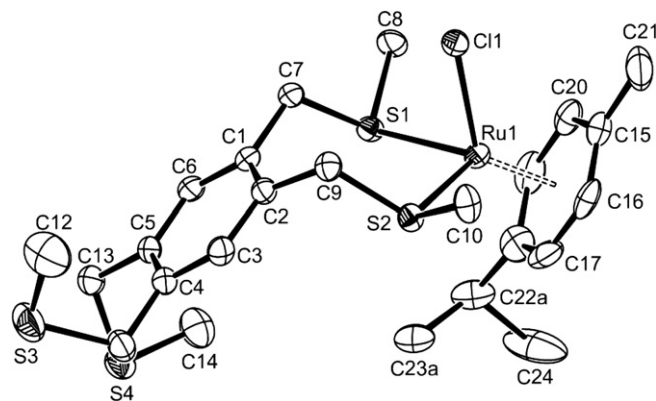

Fig. 1. Structure of the cation in $[(RuCl(\eta^6\text{-}p\text{-cymene})\{C(CH_2SMe)_4\}]PF_6$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. The structure of the cation in $[RuCl(\eta^6\text{-}p\text{-cymene})\text{-}\{C(CH_2SeMe)_4\}]PF_6$ is similar and has the same numbering scheme.

Fig. 2. Structure of the cation in $[RuCl(\eta^6\text{-}p\text{-cymene})\{C_6H_2(CH_2SMe)_4\}]BPh_4$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. There is disorder in the ^iPr group, modelled as two components (A/B). The figure shows the major component. The same numbering scheme is used for $[RuCl(\eta^6\text{-}p\text{-cymene})\{C_6H_2(CH_2SMe)_4\}]BPh_4$.
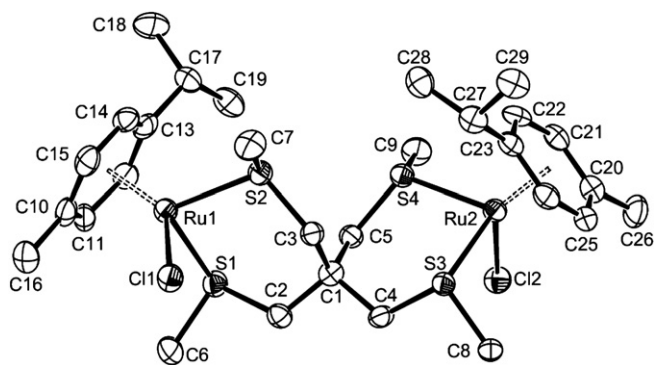
Fig. 3. Structure of the cation in [{RuCl(η^6-p-cymene)}$_2${C(CH$_2$SMe)$_4$}][PF$_6$]$_2$ showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

spectrometry showed ions corresponding to substantial amounts of diruthenium and diosmium complexes in addition to the targeted mixed RuOs species, indicative of substantial scrambling in the reactions. The products from the reactions using [Ru(η^6-p-cymene) Cl{κ^2-C$_6$H$_2$(CH$_2$SeMe)$_4$}]PF$_6$ were poorly soluble and hence subsequent efforts were concentrated upon the spirocyclic tetraselenoether. Reversing the order in which the metals were added, i.e. reacting [Os(η^6-p-cymene)Cl{κ^2-C(CH$_2$SeMe)$_4$}]PF$_6$ with 0.5 equivalent of [{Ru(η^6-p-cymene)Cl$_2$}$_2$] proved much more successful and produced an orange solid which showed [{Os(η^6-p-cymene)Cl}{Ru(η^6-p-cymene)Cl}{$\kappa^2\kappa'^2$-C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (**12**) as the dominant species in the ES$^+$ mass spectrum. The ^{77}Se NMR spectrum also showed strong resonances at 124.9 and 116.9 of equal intensity corresponding to ruthenium bound SeMe groups and a broad feature of twice the intensity at 76.8 assigned to osmium-bound SeMe groups, for the latter the expected (by symmetry) two resonances being near coincident as in [{Os(η^6-p-cymene)Cl}$_2${$\kappa^2\kappa'^2$C(CH$_2$SeMe)$_4$}][PF$_6$]$_2$ (above). There were also much weaker resonances at 130.1, 121.0, 77.9 and 73.2 which we attribute to minor amounts of other invertomers. Significantly, none of these resonances correlate with those observed in the 1:1 or the 2:1 homobimetallics, indicating these are not present in significant amounts. The ^{1}H NMR spectrum (Section 2.12) was very complicated due to the low symmetry and near coincidence of some resonances but is consistent with the formulation.

The reaction of [Os(η^6-p-cymene)Cl{κ^2-C(CH$_2$SeMe)$_4$}]PF$_6$ with [PtCl$_2$(MeCN)$_2$] in MeCN successfully proceeded to form [{Os(η^6-p-cymene)Cl}{PtCl$_2$}{κ^2,κ'^2-C(CH$_2$SeMe)$_4$}]PF$_6$ (**13**) in good yield, identified by an ES$^+$ ion multiplet at 1073 a.m.u.. The complex is insoluble in chlorocarbons and very poorly soluble in MeCN. After long accumulation (due to the poor solubility) the ^{195}Pt NMR spectrum contained a single broad peak at $\delta = -3686$, a typical
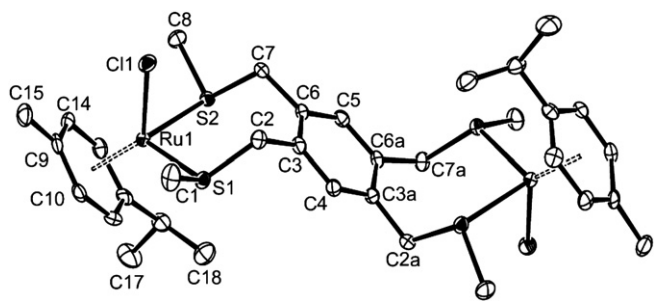
chemical shift for a planar PtSe$_2$Cl$_2$ unit [14,15], whilst the ^{77}Se NMR spectrum showed major resonances at $\delta = 167.1$ and 162.9 with ^{195}Pt satellites (^{1}J$_{Pt-Se} = 572$ and 467 Hz respectively), assignable to the same moiety, and at $\delta = 82.5$ and 75.0 attributable to the OsSe$_2$ unit. There are a number of other weak resonances in solution, none of which correspond to [Os(η^6-p-cymene)Cl{κ^2-C (CH$_2$SeMe)$_4$}]$^+$ and which may be of minor invertomers.

In contrast to the osmium reaction, attempts to combine [Ru(η^6-p-cymene)Cl{κ^2-C(CH$_2$SeMe)$_4$}]PF$_6$ with [PtCl$_2$(MeCN)$_2$] did not proceed cleanly, producing insoluble yellow products we were unable to separate or identify.

Based upon the successful isolation of [CoI$_2${κ^2-(C(CH$_2$SMe)$_4$)}] [4], we also attempted to incorporate CoI$_2$ into a heterobimetallic to afford an example of a 4d-3d metal combination. However, the yellow products isolated from reaction of either [Ru(η^6-p-cymene) Cl{C(CH$_2$SMe)$_4$}]PF$_6$ or [Ru(η^6-p-cymene)Cl{C$_6$H$_2$(CH$_2$SMe)$_4$}]BPh$_4$ with anhydrous CoI$_2$ in ^{n}BuOH were identified as the ruthenium starting materials. It is likely that successful isolation of [CoI$_2${κ^2-C (CH$_2$SMe)$_4$)}] [4] is attributable to its polymeric chain structure based upon octahedral Co(II) and that the assumed tetrahedral cobalt centre in the targeted [{Ru(η^6-p-cymene)Cl}{CoI$_2$}{$\kappa^2\kappa'^2$-C (CH$_2$SMe)$_4$}]PF$_6$ is too labile to permit isolation of the complex.

4. Conclusions

A series of complexes based upon κ^2-coordinated tetrathioether and tetraselenoether ligands with Ru(II) and Os(II) have been isolated and characterised spectroscopically and structurally. While the homo-bimetallic Ru$_2$ complexes have been obtained (either directly or stepwise) and their structures determined, attempts to introduce either Os(II) or Pt(II) to the Ru monomers to give Ru/Os or Ru/Pt heterobimetallics were not successful. However, the 5d^6 Os (II) species have been shown to be suitable synthons for formation of both homo- and heterobimetallic complexes with $\kappa^2\kappa'^2$-coordination. This is most likely attributable to the much slower kinetics of ligand substitution in Os(II).

Appendix. Supplementary data

CCDC 769,501−769,506 contain the supplementary crystallographic data for this paper: 769,501 (**1**); 769,502 (**2**); 769,503 (**5**); 769,504 (**6**); 769,505 (**7**); 769,506 (**10**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10. 1016/j.jorganchem 2010.050.010.

References

[1] J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Vol 9, Elsevier, Oxford, 2004.
[2] W. Levason, G. Reid, in: F.A. Devillanova (Ed.), Handbook of Chalcogen Chemistry, RSC, 2007 Chapter 2.2 and refs therein.
[3] . (a) J.D. Singh, M. Maheshwari, S. Khan, R.J. Butcher, Tetrahedron Lett. 49 (2008) 117;
(b) M. Maheshwari, S. Khan, J.D. Singh, Tetrahedron Lett. 48 (2007) 4737.
[4] J. Evans, W. Levason, J.M. Manning, G. Reid, N. Tsoureas, M. Webster, Dalton Trans. (2007) 1986.
[5] W. Levason, L.P. Ollivere, G. Reid, N. Tsoureas, M. Webster, J. Organometal. Chem. 694 (2009) 2299.
[6] W. Levason, L.P. Ollivere, G. Reid, M. Webster, J. Organometal. Chem. 695 (2010) 1346.
[7] J.P. Fackler, Inorg. Synth 21 (1982) 75;
J.A. Cabeza, P.M. Maitlis, J. Chem. Soc., Dalton Trans. (1985) 573.

Fig. 4. Structure of the cation in [{RuCl(η^6-p-cymene)}$_2${C$_6$H$_2$(CH$_2$SMe)$_4$}] [PF$_6$]$_2$·2MeCN showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Symmetry operation: a = − x, y, 1/2 − z.

[8] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution. University of Göttingen, Germany, 1997.

[9] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.

[10] H.D. Flack, Acta Crystallogr. Sect. A 39 (1983) 876.

[11] M. Gaye, B. Demerseman, P.H. Dixneuf, J. Organometal. Chem. 411 (1991) 263.

[12] E.W. Abel, S.K. Bhargava, K.G. Orrell, Progr. Inorg. Chem. 34 (1984) 1 and references therein.

[13] W. Levason, S.D. Orchard, G. Reid, Coord. Chem. Rev. 225 (2002) 159.

[14] D.J. Gulliver, E.G. Hope, W. Levason, S.G. Murray, G.L. Marshall, J. Chem, Soc., Dalton Trans. (1985) 1265.

[15] E.G. Hope, W. Levason, N.A. Powell, Inorg. Chim. Acta 115 (1986) 187.