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Synthesis and properties of ditelluroether complexes of osmium, *trans*-$[OsCl_2(L\text{-}L)_2]$ and *trans*-$[OsCl(PPh_3)(L\text{-}L)_2]PF_6$ (L-L = *o*-$C_6H_4(TeMe)_2$, $RTe(CH_2)_3TeR$ (R = Ph or Me))

Andrew J. Barton, William Levason *, Gillian Reid, Vicki-Anne Tolhurst

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

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Abstract

The complexes *trans*-$[OsCl_2(L\text{-}L)_2]$ (L-L = *o*-$C_6H_4(TeMe)_2$, $RTe(CH_2)_3TeR$ (R = Ph or Me)) have been prepared from *trans*-$[OsCl_2(dmso)_4]$ and the ditelluroethers in ethanol. The reaction of $[OsCl_2(PPh_3)_3]$ with the ditelluroethers or $MeSCH_2CH_2SMe$ or $MeSe(CH_2)_3SeMe$ in ethanol in the presence of NH_4PF_6 gave *trans*-$[OsCl(PPh_3)(L\text{-}L)_2]PF_6$. The complexes have been characterised by analysis, IR, UV–Vis and multinuclear NMR spectroscopy. The reaction of OsO_4–HCl–EtOH with $PhTe(CH_2)_3TePh$ results in chlorination of the ligand to $PhTeCl_2(CH_2)_3TePhCl_2$, identified by single-crystal X-ray study. The X-ray structure for *trans*-$[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ is reported. The reaction of $[OsCl_2(dmso)_4]$ with the distibine $Ph_2Sb(CH_2)_3SbPh_2$ affords *trans*-$[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]$ which has also been characterised crystallographically.

Keywords: Osmium; Ditelluroether; X-ray structures

1. Introduction

Osmium forms compounds in formal oxidation states ranging from 8 to −2 and as a consequence has an extremely rich coordination chemistry [1]. However, the absence of labile osmium precursors in the medium oxidation states can make some types of complex difficult to prepare. For example, whilst a wide range of bidentate and polydentate phosphine and arsine complexes of Os(II), Os(III) and Os(IV) are readily made starting from OsO_4–HX–ROH (X = Cl, Br or I) or $[OsX_6]^{2-}$ [1], obtaining complexes with Group 16 donors has proved considerably more difficult. Direct reaction of $[OsX_6]^{2-}$ with dithioethers [2] or diselenoethers [3] generates $[OsX_4(L\text{-}L)]$ type complexes in poor yield, whilst from OsO_4–HX–EtOH and the ligands at low temperatures unstable osmyl complexes $[OsO_2X_2(L\text{-}L)]$ form [4,5]. Further reduction to, for example, $[OsX_2(L\text{-}L)_2]$ does not appear possible by this route. We were interested in extending our previous studies of ditelluroether complexes with platinum group metals, Pt or Pd [6–8], Ir [6,7], Ru or Rh [8], to osmium and report our investigations below.

* Corresponding author. Tel.: +44-1703-543792; fax: +44-1703-593781; e-mail: wxl@soton.ac.uk

2. Results and discussion

The reaction of OsO_4–conc. HCl–EtOH with the three ditelluroether ligands (L-L = *o*-$C_6H_4(TeMe)_2$, or $RTe(CH_2)_3TeR$ (R = Me or Ph)) at 0°C gave brownish-purple solids leaving a dark red solution. These solids lacked the very strong $\nu(OsO_2)$ IR vibration at ca. 850 cm^{-1} typical of *trans*-$[OsO_2Cl_2(L'\text{-}L')]$ (L′-L′ = dithioether or diselenoether) [4,5], ruling out the formation of osmyl species. A similar result was reported with Me_2Te [4,5]. Since telluroethers are both stronger reducing agents and less able to stabilise high oxidation states than their lighter analogues [6–8], their failure to stabilise Os(VI) is not unexpected, but it was hoped that reduction would lead to Os(III) or Os(IV) complexes. The brownish-purple solids have UV–Vis spectra typical of Os(IV), in fact the major features are very similar to those of $[OsCl_6]^{2-}$ [9] and were weakly paramagnetic, which would suggest either Os(IV) and/or Os(III) compounds were present. However, after long accumulations each sample gave a single sharp ^{125}Te NMR resonance at very high frequencies (δ (^{125}Te) ca. 800–900) which would seem to indicate that at least some of the tellurium was present in a diamagnetic material, the shifts being in the range [10] typical of R_2TeCl_2 species. A pale brown crystal was grown (from MeCN) from the $PhTe(CH_2)_3TePh$ reaction and the

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structure solution revealed the diamagnetic tellurium compound to be $PhCl_2Te(CH_2)_3TePhCl_2$.MeCN [1]. The structure is shown in Fig. 1 and selected bond length and angle data are in Table 1. The structure is typical of R_2TeCl_2 type compounds, with $PhCl_2TeCH_2TePhCl_2$ the closest structurally characterised example [11]. The environment about each Te is based upon a distorted trigonal bipyramid with axial $TeCl_2$ groups and with one equatorial position vacant, presumably occupied by the lone pair. The Te–Cl bonds 2.504(2)–2.524(1) Å lie within the usual range [11], and the structure is unexceptional, but serves to identify unequivocally a significant product of the reactions described above.

Similar brownish-purple materials are formed on refluxing $[NH_4]_2[OsCl_6]$ with the ditelluroethers in alcohols. Notably none of the crude materials gave ^{125}Te NMR resonances in the ranges we subsequently observed for the $[OsCl_2(L\text{-}L)_2]$ complexes (below). Although we have been unable to separate any pure osmium species from these reactions, it is clear that the target $[OsCl_2(L\text{-}L)_2]$ are not present in significant amounts.

An alternative route to *trans*-$[OsCl_2(L\text{-}L)_2]$ from Os(II) starting materials was sought, although as indicated in Section 1, most Os(II) materials are kinetically very inert and introducing moderate donor ligands like telluroethers is not easy. We found that the recently characterised [12] *trans*-$[OsCl_2(dmso)_4]$ (dmso = dimethylsulfoxide) reacted with the ditelluroethers under reflux in ethanol to produce poor to moderate yields of *trans*-$[OsCl_2(L\text{-}L)_2]$ as orange or red solids. The isolated complexes are air stable and generally poorly soluble in chlorocarbons or MeCN, which to some extent limited solution spectroscopic studies. Red crystals of $[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ were obtained by evaporation of a $CHCl_3$ solution of the complex, and the structure solution (Table 2, Fig. 2) revealed a *trans* pseudo-octahedral molecule with the osmium on the inversion centre and with both ditelluroethers in *meso* form. Although the crystals are not isomorphous, the structure is very similar to that previously found in *trans*-$[RuCl_2\{PhTe(CH_2)_3TePh\}_2]$ [8]. The Os–Cl bond length, 2.450(4) Å, is comparable with those found in $[OsCl_2\{Ph_2PCH_2CH_2PPh_2\}_2]$ (2.434(1) Å) [13] and $[OsCl_2\{H_2C{=}C(PPh_2)_2\}_2]$ (2.431(1) Å) [14]. There are no literature data on Os^{II}–TeR_2 bonds, but those in the present complex (2.616(1), 2.6135(9) Å) are, as might be expected, similar to the Ru–Te bonds in the Ru^{II} analogue (2.6247(3), 2.6194(3) Å) [8].

[1] Although $RCl_2Te(CH_2)_nTeRCl_2$ prepared from $RTe(CH_2)_nTeR$ and Cl_2 are white or cream, our crystals were brown, presumably owing to traces of an osmium species.

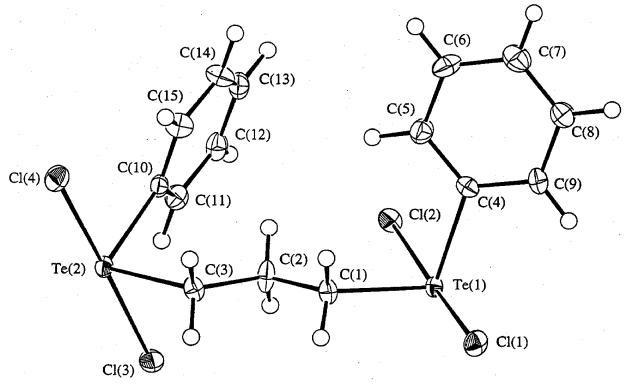

Fig. 1. View of the structure of $PhTeCl_2(CH_2)_3TePhCl_2$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

Table 1
Selected bond lengths (Å) and angles (°) for $PhCl_2Te(CH_2)_3TePhCl_2 \cdot MeCN$

Te(1)–Cl(1)	2.507(1)	Te(1)–Cl(2)	2.524(1)
Te(1)–Cl(1)	2.169(5)	Te(1)–C(4)	2.131(6)
Te(2)–Cl(3)	2.520(2)	Te(2)–Cl(4)	2.504(2)
Te(2)–C(3)	2.169(6)	Te(2)–C(10)	2.150(6)
Cl(1)–Te(1)–Cl(2)	175.01(5)	Cl(1)–Te(1)–C(1)	85.3(2)
Cl(1)–Te(1)–C(4)	89.3(2)	Cl(2)–Te(1)–C(1)	93.1(2)
Cl(2)–Te(1)–C(4)	86.2(2)	C(1)–Te(1)–C(4)	99.1(2)
Cl(3)–Te(2)–Cl(4)	176.54(5)	Cl(3)–Te(2)–C(3)	88.1(2)
Cl(3)–Te(2)–C(10)	91.3(2)	Cl(4)–Te(2)–C(3)	89.7(2)
Cl(4)–Te(2)–C(10)	91.5(2)	C(3)–Te(2)–C(10)	94.6(2)
Te(1)–C(1)–C(2)	114.7(4)	C(1)–C(2)–C(3)	110.8(5)
Te(2)–C(3)–C(2)	112.3(4)		

Table 2
Selected bond lengths (Å) and angles (°) for $[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$

Os(1)–Te(1)	2.6135(9)
Os(1)–Te(2)	2.616(1)
Os(1)–Cl(1)	2.450(4)
Te(1)–C(1)	2.18(1)
Te(1)–C(11)	2.13(1)
Te(2)–C(3)	2.18(1)
Te(2)–C(21)	2.14(1)
Te(1)–Os(1)–Te(2)	86.65(3)
Te(1)–Os(1)–Cl(1)	93.15(8)
Te(2)–Os(1)–Cl(1)	93.12(9)

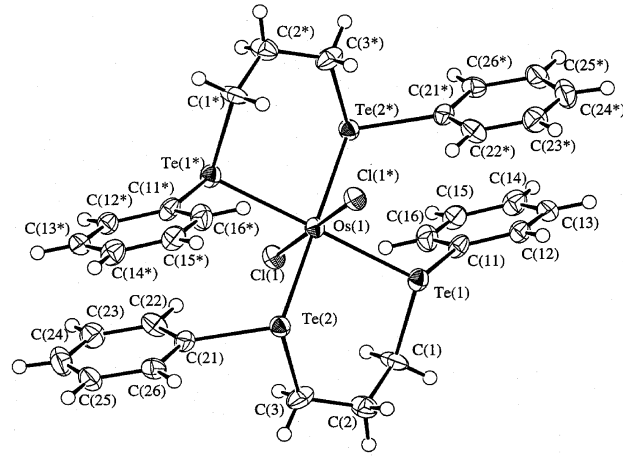

Fig. 2. View of the structure of $[OsCl_2\{PhTe(CH_2)_3TePh_2\}$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. Atoms marked * are related by a crystallographic inversion centre. H-atoms are omitted for clarity.

The three $[OsCl_2(L\text{-}L)_2]$ complexes have very similar spectroscopic properties (Section 3) including two d–d bands in the range 21000–26000 cm^{-1} as expected for a low spin d^6 complex with local D_{4h} symmetry [9]. The poor solubility made it very difficult to obtain ^{125}Te NMR spectra, but after very long accumulations several resonances were present in each complex, consistent with a mixture of invertomers, showing that pyramidal inversion is slow on the NMR time scale in these systems. As we have discussed elsewhere [8], it is not possible to assign resonances to individual isomers. Notably, for comparable complexes, the $\delta(^{125}Te)$ are found at considerably higher frequency in the ruthenium complexes [8] compared with the present osmium examples, an effect also found for corresponding ruthenium and osmium phosphines [15]. Cyclic voltammetry of the complexes in CH_2Cl_2 revealed a single reversible oxidation for each ($[OsCl_2\{MeTe(CH_2)_3TeMe\}_2]$ +0.35 V versus SCE; $[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ +0.18 V; $[OsCl_2\{o\text{-}C_6H_4(TeMe)_2\}_2]$ +0.43 V), which contrasts with the quasi-reversible or irreversible oxidations observed in the ruthenium analogues [8], reflecting the expected greater stability of the M(III) state for osmium.

Although $[OsCl_2(dmso)_4]$ provided a satisfactory starting material for the synthesis of the ditelluroether complexes it is still not ideal, and attempts to prepare $[OsCl_2(L'\text{-}L')_2]$ (L′-L′ dithioether or diselenoether) similarly usually result in mixtures containing $[OsCl(dmso)(L'\text{-}L')_2]^+$, $[OsCl_2(dmso)_2(L'\text{-}L')]$ and $[OsCl_2(L'\text{-}L')_2]$, which are not readily separated, and we have not obtained useful amounts of the last complexes.

The reactions of $[OsCl_2(PPh_3)_3]$ with 2 equiv. of the Group 16 ligands in EtOH in the presence of $[PF_6]^-$ gave moderate yields of $[OsCl(PPh_3)(L\text{-}L)_2]PF_6$ (L-L = $RTe(CH_2)_3TeR$, R = Me or Ph), $[OsCl(PPh_3)(MeSCH_2CH_2SMe)_2]PF_6$ and $[OsCl(PPh_3)\{MeSe(CH_2)_3SeMe\}_2]PF_6$ as yellow or brown solids. The complexes are air stable solids which show $[OsCl(PPh_3)(L\text{-}L)_2]^+$ as the highest mass ions in their ES^+ mass spectra. The UV–Vis spectra are uninformative, showing only the $\pi \rightarrow \pi^*$ transitions of the Ph-groups and charge transfer transitions in the near-UV which tail into the visible obscuring the d–d bands, although the absence of significant features below 20000 cm^{-1} confirms the oxidation state as Os(II). The ^1H NMR spectra of the ditelluroether compounds are complex and not very helpful, but the $^{31}P\{^1H\}$ NMR spectra are more useful. For $[OsCl(PPh_3)\{PhTe(CH_2)_3TePh\}_2]PF_6$, in addition to the septet at δ −145 due to $[PF_6]^-$ there are two singlets at −10.5 and −11.8 with approximate intensities 2:1 showing the presence of two major invertomers. The corresponding $^{125}Te\{^1H\}$ NMR spectrum showed five doublets in the range δ 450–565 with $^2J(^{125}Te\text{–}^{31}P)$ of ca. 60–90 Hz. In the case of $[OsCl(PPh_3)\{MeTe(CH_2)_3TeMe\}_2]PF_6$ the $^{31}P\{^1H\}$ NMR spectrum reveals one major invertomer δ −14.5 and there are four doublets in the $^{125}Te\{^1H\}$ NMR spectrum and four δ(Me) resonances in the ^1H NMR spectrum. This is consistent with one invertomer as the major solution form with one *meso* and one *DL* ditelluroether. The pattern of invertomers in these two cases is very similar to that observed in the ruthenium analogues [8]. For the $[OsCl(PPh_3)\{MeSe(CH_2)_3SeMe\}_2]PF_6$ the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −14.0 and the septet at −145. There are singlets for the Me and CH_2 groups of the diselenoether in the ^1H NMR spectrum. Whilst at first sight this might be taken to indicate one isomer with high symmetry, we were unable to observe a ^{77}Se NMR spectrum from this complex, which suggests that pyramidal inversion is occurring. Finally, for $[OsCl(PPh_3)\{MeS(CH_2)_2SMe\}_2]PF_6$ there is a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −15.1, and broad singlets at δ 2.44 and 2.7 (in addition to the Ph multiplet) in the ^1H NMR spectrum, consistent with fast inversion in the dithioether complex. The poor solubility and the number of possible invertomers make these systems poorly suited to VT NMR studies, but comparison of the room temperature spectra shows the usual trends [16,17] in pyramidal inversion barriers Te > Se > S are present.

The reaction of $[OsCl_6]^{2-}$ with Ph_3Sb in alcohols readily yields *mer*-$[OsCl_3(Ph_3Sb)_3]$ which can be reduced by excess ligand and $NaBH_4$ to *trans*-$[OsCl_2(Ph_3Sb)_4]$ [18,19], but attempts to carry out corresponding reactions with ditertiary stibines failed. As a further test of the usefulness of $[OsCl_2(dmso)_4]$ we reacted this with $Ph_2Sb(CH_2)_3SbPh_2$ in ethanol, and readily obtained good yields of yellow *trans*-$[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]$. The spectroscopic data (Section 3) are unexceptional and compare well with the corresponding data on *trans*-$[OsCl_2(Ph_3Sb)_4]$ [18,19] and *trans*-$[OsCl_2(diphosphine)_2]$ [20]. Yellow crystals of *trans*-$[OsCl_2(Ph_2Sb(CH_2)_3SbPh_2)_2]$ were obtained from CH_2Cl_2, and the structure determined. The molecule is shown in Fig. 3 and significant bond lengths and angles are in Table 3. The structure reveals a centrosymmetric molecule, with the d(Os–Cl) 2.477(2) Å typical of an Os(II) centre [13,14]. The d(Os–Sb) 2.5933(8), 2.6030(4) Å are very similar to those in *trans*-$[OsCl_2(Ph_3Sb)_4]$ (2.611(2)–2.630(2) Å) [21].

3. Experimental

Physical measurements were made as described previously [8].

3.1. *[Os{MeTe(CH$_2$)$_3$TeMe}$_2$Cl$_2$]*

$[Os(dmso)_4Cl_2]$ (151 mg, 0.155 mmol), $MeTe(CH_2)_3TeMe$ (100 mg, 0.307 mmol) in MeOH (70 cm^3) were refluxed for 16 h. The solvent was removed in vacuo and CH_2Cl_2 added (2 cm^3). The orange solution was filtered and Et_2O added to precipitate an orange solid. Yield: 0.05 g, 36%. *Anal*. Found: C, 12.9; H, 2.6. Calc. for $C_{10}H_{24}Cl_2OsTe_4$: C, 13.1; H, 2.6%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.94–3.15 (m, $CH_2 + CH_3$). $^{125}Te\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$, 113 MHz): δ 236, 267, 274, 286, 293, 329, 339. IR spectrum

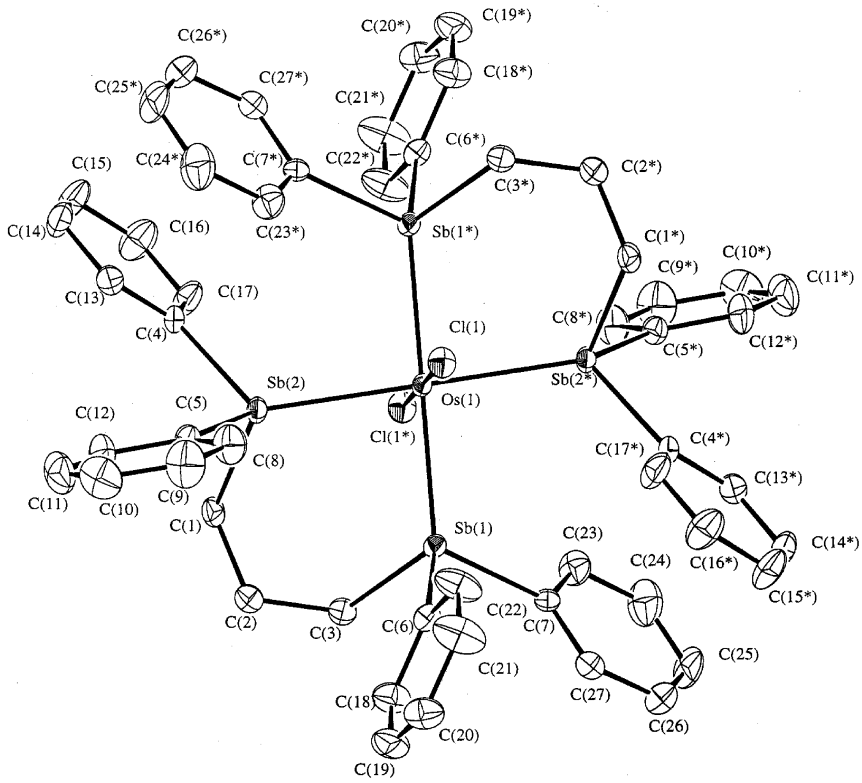

Fig. 3. View of the structure of $[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]$ with number scheme adopted. Ellipsoids are drawn at 40% probability. Atoms marked * are related by a crystallographic inversion centre. H-atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for $[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]\cdot 2CH_2Cl_2$

Os(1)–Sb(1)	2.5933(8)
Os(1)–Sb(2)	2.6030(4)
Os(1)–Cl(1)	2.477(2)
Sb(1)–C(3)	2.154(7)
Sb(1)–C(6)	2.137(7)
Sb(1)–C(7)	2.149(7)
Sb(2)–C(1)	2.143(7)
Sb(2)–C(4)	2.137(7)
Sb(2)–C(5)	2.144(7)
Sb(1)–Os(1)–Sb(2)	85.73(1)
Sb(1)–Os(1)–Cl(1)	95.53(4)
Sb(2)–Os(1)–Cl(1)	96.76(4)
Os(1)–Sb(1)–C(3)	114.2(2)
Os(1)–Sb(1)–C(6)	124.2(2)
Os(1)–Sb(1)–C(7)	117.1(2)
C(3)–Sb(1)–C(6)	100.1(3)
C(3)–Sb(1)–C(7)	96.9(3)
C(6)–Sb(1)–C(7)	99.7(3)
Os(1)–Sb(2)–C(1)	114.3(2)
Os(1)–Sb(2)–C(4)	118.9(2)
Os(1)–Sb(2)–C(5)	123.6(2)
C(1)–Sb(2)–C(4)	95.7(3)
C(1)–Sb(2)–C(5)	98.5(3)
C(4)–Sb(2)–C(5)	100.8(3)

(CsI disc): 2922 (m), 2855 (w), 1358 (s), 1262 (w), 1091 (s), 1068, 920 (w), 835 (m), 615 (w), 598 (w), 430 (w), 297 (m), 224 (w). UV–Vis spectrum (CH_2Cl_2): $\nu_{max}=22125$ ($\varepsilon_{mol}=330$), 20580 (sh) cm^{-1} (250 $dm^3\,mol^{-1}\,cm^{-1}$).

3.2. *[Os{PhTe(CH$_2$)$_3$TePh}$_2$Cl$_2$]*

The method used was the same as for the previous complex, giving a red powder. Yield: 40 mg, 32%. *Anal*. Calc. for $C_{30}H_{32}Cl_2OsTe_4$: C, 31.0; H, 2.8. Found: C, 30.8; H, 2.9%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.0–3.5 (6H, CH_2), 7.4–7.9 (10H, Ph). ^{125}Te{^{1}H} NMR ($CDCl_3/CH_2Cl_2$ 113 MHz): δ 478, 489, 513, 523, 548. IR spectrum (CsI disc): 3042 (m), 2921 (w), 1571 (m), 1474 (s), 1433 (s), 1415 (m), 1396 (m), 1359 (s), 1200 (m), 1061 (m), 1018 (m), 996 (m), 754 (w), 730 (s), 691 (s), 614 (w), 490 (w), 453 (w), 259 (w), 227 (w). UV–Vis spectrum (MeCN): $\nu_{max}=21000$ ($\varepsilon_{mol}=180$), 24600 (540), 38300 cm^{-1} (18235 $dm^3\,mol^{-1}\,cm^{-1}$).

3.3. *[Os{o-C$_6$H$_4$(TeMe)$_2$}$_2$Cl$_2$]*

The method used was the same as for the previous complex, giving an orange powder. Yield: 29%. *Anal*. Calc. for $C_{16}H_{20}Cl_2OsTe_4$: C, 19.5; H, 2.1. Found: C, 19.4; H, 1.9%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.05–2.3 (6H, CH_3), 7.2–7.8 (4H, C_6H_4). ^{125}Te{^{1}H} NMR ($CDCl_3/CH_2Cl_2$ 113 MHz): δ 656, 663, 671, 672, 673. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 992, 948; calc. for $[^{192}Os\{C_6H_4(^{130}TeMe)\}_2{}^{35}Cl+MeCN]^+$ 1000, $[^{192}Os$-

$\{C_6H_4(^{130}TeMe)\}_2{}^{35}Cl]^+$ 959. IR spectrum (CsI disc): 2923 (w), 2851 (w), 1358 (s) 1260 (w), 1080 (s), 1019 (m), 835 (m), 753 (m), 685 (w), 614 (w), 548 (w), 427 (w), 326 (w), 302 (w). UV–Vis spectrum (MeCN): $\nu_{max}=22600$ cm^{-1} ($\varepsilon_{mol}=590$), 33200 (sh) cm^{-1} (6300 dm^{3}mol^{-1}cm^{-1}).

3.4. $[OsCl(PPh_3)(MeSCH_2CH_2SMe)_2]PF_6$

$[OsCl_2(PPh_3)_3]$ (0.1 g, 0.095 mmol) and $MeSCH_2CH_2SMe$ (0.06 g, 0.29 mmol) were refluxed together in ethanol (10 cm^3) for 2 h, during which time the colour changed from green to orange. After cooling to room temperature, NH_4PF_6 (0.06 g, 0.32 mol) was added and the solution concentrated to 3 cm^3 to give an orange solid, which was filtered off and recrystallised from CH_2Cl_2–Et_2O. Yield: 0.069 g, 70%. *Anal*. Calc. for $C_{26}H_{35}ClF_6OsP_2S_4$: C, 35.5; H, 4.0. Found: C, 35.0; H, 3.3%. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 734; calc. for $[^{192}Os^{35}Cl(PPh_3)(MeSCH_2CH_2SMe)_2]^+$ 733. IR (CsI disc): 2930 (w), 1435 (m), 1357 (m), 1091 (m), 839 (s), 750 (m), 699 (s), 516 (m), 504 (m). ^{1}H NMR (300 MHz $CDCl_3$): δ 2.6 (s), 2.74 (s). $^{31}P\{^1H\}$ (145 MHz, $CH_2Cl_2/CDCl_3$): δ −15.1 (s), −147 (septet).

3.5. $[OsCl(PPh_3)(MeSeCH_2CH_2CH_2SeMe)_2]PF_6$

The method used was similar to that described in Section 3.4, giving a brown solid. Yield: 70%. *Anal*. Calc. for $C_{28}H_{39}ClF_6OsP_2Se_4$: C, 30.9; H, 3.2. Found: C, 30.2; H, 3.0%. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 949; calc. for $[^{192}Os^{35}Cl(PPh_3)(Me^{80}SeCH_2CH_2{}^{80}SeMe)_2]^+$ 753. IR (CsI disc): 2927 (w), 2850 (w), 1434 (w), 1413 (w), 1089 (m), 999 (w), 840 (s), 751 (m), 699 (s), 558 (s), 537 (m), 499 (w), 440 (w). ^{1}H NMR (300 MHz $CDCl_3$): δ 1.72 (q), 2.25 (s), 2.85 (t), 7.4–7.7 (m). $^{31}P\{^1H\}$ (145 MHz, $CH_2Cl_2/CDCl_3$): δ −14.0(s), −147 (septet).

3.6. $[OsCl(PPh_3)\{MeTe(CH_2)_3TeMe\}_2]PF_6$

The method used was the same as described in Section 3.4, giving a yellow solid. Yield: 75%. *Anal*. Calc. for $C_{28}H_{39}ClF_6OsP_2Te_4$: C, 26.1; H, 3.0. Found: C, 26.5; H, 2.1%. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 1143; calc. for $[^{192}Os^{35}Cl(PPh_3)(Me^{130}Te(CH_2)_3Me)_2]^+$ 1153. IR (CsI disc): 2921 (w), 1634 (w), 1417 (w), 1201 (w), 1088 (m), 841 (s), 753 (w), 688 (m), 556 (m), 539 (m), 517 (w), 278 (w). ^{1}H NMR (300 MHz $CDCl_3$): δ 1.57 (m), 1.78 (s), 1.96 (s), 2.02 (s), 2.25 (s), 3.2–3.4 (m), 7.4–7.6 (m). $^{31}P\{^1H\}$ (145 MHz, $CH_2Cl_2/CDCl_3$): δ −13.0 (s), −147 (septet). $^{125}Te\{^1H\}$ NMR (114 MHz, $CH_2Cl_2/CDCl_3$): δ 361, 411, 422, 430.

3.7. $[OsCl(PPh_3)\{PhTe(CH_2)_3TePh\}_2]PF_6$

The method used was the same as described in Section 3.4, giving a yellow solid. Yield: 87%. *Anal*. Calc. for $C_{48}H_{47}ClF_6OsP_2Te_4$: C, 37.5; H, 3.0. Found: C, 37.9; H, 2.4%. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 1391; calc. for $[^{192}Os^{35}Cl(PPh_3)(PhTe(CH_2)_3TePh)_2]^+$ 1401. IR (CsI disc): 3050 (w), 2932 (w), 1477 (w), 1435 (m), 1362 (m), 1088 (m), 1017 (w), 938 (s), 735 (s), 688 (s), 558 (m), 536 (m), 454 (w), 250 (m). ^{1}H NMR (300 MHz $CDCl_3$): δ 2.2 (m), 2.9–3.3 (m), 7.0–7.8 (m). $^{31}P\{^1H\}$ (145 MHz, $CH_2Cl_2/CDCl_3$): δ −10.5(s), −11.8(s), −145 (septet). $^{125}Te\{^1H\}$ NMR (114 MHz, $CH_2Cl_2/CDCl_3$): δ 454, 463, 499, 540, 565.

3.8. $[OsCl_2(Ph_2Sb(CH_2)_3SbPh_2)_2]$

$[OsCl_2(dmso)_4]$ (0.05 g, 0.09 mmol) and $Ph_2Sb(CH_2)_3SbPh_2$ (0.16 g, 0.27 mmol) were refluxed together in ethanol (10 cm^3) for 3 h. The solvent was removed in vacuo, CH_2Cl_2 added to the residue, the solution filtered and the orange product precipitated with Et_2O. Yield: 0.045 g, 35%. *Anal*. Calc. for $C_{54}H_{52}Cl_2OsSb_4\cdot CH_2Cl_2$: C, 43.1; H, 3.4. Found: C, 43.1; H, 2.8%. Electrospray mass spectrum (MeCN) *m/z*: found M^+ 1450. calc. for $[^{192}Os^{35}Cl_2(Ph_2{}^{121}Sb(CH_2)_3{}^{121}SbPh_2)_2]^+$ 1446. IR (CsI disc): 3066 (m), 3049 (m), 1480 (w), 1432 (s), 1360 (m), 1102 (m), 1069 (s), 998 (m), 727 (s), 695 (s), 451 (s), 267 (m). UV–Vis spectrum (CH_2Cl_2): $\nu_{max}=30860$ (sh), ($\varepsilon_{mol}=2200$), 22230 (sh) cm^{-1} (250 dm^3 mol^{-1} cm^{-1}). $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): δ 15.8, 24.3, 128–137. CV CH_2Cl_2: reversible +0.3 V versus SCE.

3.9. X-ray structure determination of $PhTeCl_2(CH_2)_3TeCl_2Ph\cdot MeCN$, $[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ and $[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]\cdot 2CH_2Cl_2$

Details of the crystallographic data collection and refinement parameters are given in Table 4. Data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K (except for $PhCl_2Te(CH_2)_3TePhCl_2\cdot MeCN$, 295 K), using graphite-monochromated Mo Kα X-ray radiation ($\lambda=0.71073$ Å). For $PhCl_2Te(CH_2)_3TePhCl_2\cdot MeCN$ (295 K) preliminary psi-scans showed no significant absorption. The structure was solved by direct methods [22] and refined by iterative cycles of least-squares refinement [23]. All non-H atoms were refined anisotropically and H atoms were placed in fixed, calculated positions. Selected bond lengths and angles are given in Table 1. For $[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ preliminary psi scans did not provide a satisfactory absorption correction, hence, with the model at isotropic convergence, the data were corrected for absorption using DIFABS [24]. and for $[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]\cdot 2CH_2Cl_2$ the data were corrected for absorption using psi-scans. Both Os structures were solved by heavy atom methods [25] and developed by iterative cycles of full-matrix least-squares refinement [23] and difference Fourier syntheses. All fully occupied non-H atoms were refined anisotropically and H-atoms were placed in fixed, calculated positions (the H atoms associated with the disordered CH_2Cl_2

Table 4
Crystallographic data

	$PhTeCl_2(CH_2)_3TePhCl_2 \cdot MeCN$	$[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$	$[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2] \cdot 2CH_2Cl_2$
Formula	$C_{17}H_{19}Cl_4NTe_2$	$C_{30}H_{32}Cl_2OsTe_4$	$C_{56}H_{56}Cl_6OsSb_4$
FW	639.37	1164.09	1618.98
Crystal system	Monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
a (Å)	7.931(3)	8.684(5)	12.096(3)
b (Å)	26.889(4)	7.225(6)	12.226(3)
c (Å)	10.695(3)	25.205(2)	11.510(4)
α (°)	90	90	107.43(2)
β (°)	110.20(2)	94.00(2)	114.96(3)
γ (°)	90	90	96.17(2)
U (Å^3)	2140(1)	1577(1)	1417.4(9)
Z	4	2	1
D_{calc} (g cm^{-3})	1.968	2.451	1.897
μ(Mo Kα) (cm^{-1})	32.25	78.54	44.28
Absolute correction (max., min. transmission factors)		1.000, 0.559	1.000, 0.479
Unique observed reflections	3872	3040	4983
Observed reflections with $I_0 > 2\sigma(I_0)$	2785	2254	4308
No. of parameters	217	169	297
R [a]	0.027	0.052	0.036
R_w [b]	0.032	0.058	0.052

[a] $R = \sum(|F_{obs}|_i - |F_{calc}|_i) / \sum |F_{obs}|_i$.
[b] $R_w = \sqrt{[\sum w_i(|F_{obs}|_i - |F_{calc}|_i)^2 / \sum w_i |F_{obs}|_i^2]}$.

solvent molecules were omitted from the final structure factor calculation). In both cases the Os(II) species was found to have crystallographic inversion symmetry, with the Os atom occupying an inversion centre. Two half CH_2Cl_2 solvent molecules, disordered across crystallographic inversion centres, were also identified in the asymmetric unit in the structure of $[OsCl_2\{Ph_2Sb(CH_2)_3SbPh_2\}_2]$. Selected bond lengths and angles are given in Tables 2 and 3.

Supplementary data

Supplementary data have deposited at the Cambridge Crystallographic Data Centre, CCDC reference numbers 135001–135003.

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