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Synthesis, spectroscopic and redox properties of ruthenium complexes with selenoether macrocycles: crystal structures of *cis*-$[RuCl_2([16]aneSe_4)]$ and *trans*-$[RuCl(PPh_3)([16]aneSe_4)]PF_6$ ($[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane)

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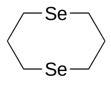
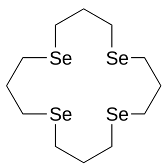
Reaction of $[Ru(dmf)_6]Cl_3$ (dmf = dimethylformamide) with 1 molar equivalent of $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) or 2 molar equivalents of $[8]aneSe_2$ (1,5-diselenacyclooctane) in refluxing EtOH yielded *cis*-$[RuCl_2([16]aneSe_4)]$ or *cis*-$[RuCl_2([8]aneSe_2)_2]$. Reaction of $[Ru(dmf)_6][CF_3SO_3]_3$ with $[16]aneSe_4$ in the presence of either LiBr or NaI in refluxing EtOH yielded *cis*-$[RuBr_2([16]aneSe_4)]$ or $[RuI_2([16]aneSe_4)]$ respectively. The *cis* arrangements have been confirmed in solution by $^{77}Se\text{-}\{^1H\}$ NMR studies on the dichloro and dibromo derivatives, and in the solid state by a single-crystal structure determination on *cis*-$[RuCl_2([16]aneSe_4)]$. Refluxing *cis*-$[RuX_2([16]aneSe_4)]$ (X = Cl or Br) in $MeNO_2$ yielded the *trans*-dihalogeno species exclusively. The compounds $[MCl_2(PPh_3)_3]$ (M = Ru or Os) react with $[16]aneSe_4$ to give *trans*-$[MCl(PPh_3)([16]aneSe_4)]^+$ which can be isolated by addition of PF_6^- counter ion. The single-crystal structure of $[RuCl(PPh_3)([16]aneSe_4)]^+$ confirms the *trans* chlorophosphine arrangement, with the Se-based lone pairs of the macrocycle adopting the *all-up* configuration, such that the methylene groups of the ligand backbone are all directed to the opposite side of the $RuSe_4$ plane from the PPh_3 ligand. Electrochemical studies on the metal(II) compounds have been conducted, and the macrocyclic complexes all exhibit reversible M^{II}–M^{III} redox couples. The ruthenium(III) species $[RuBr_2([16]aneSe_4)]Br$ has been prepared by Br_2 oxidation and isolated. These are the first macrocyclic selenoether complexes involving Ru^{II}, Os^{II} or Ru^{III}.

As part of a study on selenoether macrocyclic chemistry we have been investigating the chemistry of the tetraselenoether ligand $[16]aneSe_4$ (1,5,9,13-tetraselenacyclohexadecane) and the small cyclic diselenoether $[8]aneSe_2$ (1,5-diselenacyclooctane) with the platinum group metals. In the course of this study we have reported the preparation and characterisation of derivatives of Pd^{II}, Pt^{II}, Pt^{IV}, Rh^{III} and Ir^{III} including, for example, *trans*-$[PtX_2([16]aneSe_4)]^{2+}$ and $[MX_2([16]aneSe_4)]^+$ (M = Rh, Ir; X = Cl or Br).[1–5] While several macrocyclic thioether ruthenium complexes are known, *e.g.* *cis*-$[RuCl_2([14]aneS_4)]^{0/+}$,[6] *cis*-$[RuCl(PPh_3)([14]aneS_4)]^+$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane),[7] $[Ru([9]aneS_3)_2]^{2+}$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane), $[Ru([12]aneS_3)_2]^{2+}$ ($[12]aneS_3$ = 1,5,9-trithiacyclododecane)[8] and $[Ru(PPh_3)([15]aneS_5)]^{2+}$ ($[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane),[9] there are no examples involving macrocyclic selenoethers, although Hanton and Kemmitt[10] have reported the synthesis of the cyclic diselenoether complex $[Ru(\eta^6\text{-}C_6H_6)(E\text{–}E)L]^{2+}$ and $[Ru(\eta^6\text{-}C_6H_6)(E\text{–}E)X]^+$ (E–E = 2,11-diselena[3.3]orthocyclophane, L = EtCN or MeCN, X = Cl or Br). In fact, only a few ruthenium-(II) and -(III) complexes with acyclic selenoether ligands have been reported previously. These include species of the form $[RuX_2(L\text{–}L)_2]$ [X = Cl, Br or I; L–L = $MeSe(CH_2)_2SeMe$ or $PhSe(CH_2)_2SePh$],[11] *trans*-$[RuX_2\{PhSe(CH_2)_2SePh\}_2]^+$ (X = Cl or Br),[12] and the crystal structure of the anionic ruthenium(III) species $[RuCl_4\{MeSe(CH_2)_2SeMe\}]^-$ has been reported.[13]

We now report the preparation and spectroscopic characterisation of a series of ruthenium(II) complexes involving $[16]aneSe_4$, including single-crystal structure determinations on *cis*-$[RuCl_2([16]aneSe_4)]$ and *trans*-$[RuCl(PPh_3)([16]aneSe_4)]PF_6$. The preparation of *cis*-$[RuCl_2([8]aneSe_2)_2]$ is also reported. Electrochemical studies on the ruthenium(II) compounds have been conducted, and the ruthenium(III) species $[RuBr_2([16]aneSe_4)]^+$ prepared by chemical oxidation and isolated. These are the first macrocyclic selenoether complexes involving Ru^{II} and Ru^{III}.



$[8]aneSe_2$



$[16]aneSe_4$

Results and Discussion

Reaction of $[Ru(dmf)_6]Cl_3$[14] (dmf = dimethylformamide) with 1 molar equivalent of $[16]aneSe_4$ in refluxing ethanol solution gave a light brown solution after 3 h from which a neutral fawn solid was obtained by filtration after concentrating the solution and adding diethyl ether. The electrospray mass spectrum recorded in MeCN solution showed peaks with the correct isotopic distributions at *m/z* 663 and 622 corresponding to $[RuCl([16]aneSe_4)(MeCN)]^+$ and $[RuCl([16]aneSe_4)]^+$ respectively. Infrared spectroscopy showed peaks consistent with the presence of co-ordinated selenoether and weak features at 295 and 280 cm^{-1} are tentatively assigned to ν(Ru–Cl), suggesting a *cis*-dichloro arrangement. We have demonstrated previously that $^{77}Se\text{-}\{^1H\}$ NMR spectroscopy (^{77}Se: 7.8%, $I = \frac{1}{2}$) is a convenient technique through which to determine the solution structures adopted by selenoether compounds, and data for the compounds in this study are presented in Table 1. The spectrum of the product from this reaction revealed two resonances at δ +254 and +196, also consistent with a *cis*-dichloro arrangement in solution, subsequently confirmed in the solid state by X-ray crystallography.

Similarly, reaction of $[Ru(dmf)_6]Cl_3$ with 2 molar equivalents of $[8]aneSe_2$ in refluxing EtOH solution yielded *cis*-$[RuCl_2([8]aneSe_2)_2]$ as a brown solid. This species was also characterised by a combination of spectroscopic methods, with $^{77}Se\text{-}\{^1H\}$ NMR spectroscopy showing two Se environments (1 : 1 ratio) at δ +244 and +197, *i.e.* similar chemical shifts to those observed

Table 1 ^{77}Se-{^{1}H} NMR[a] and electrochemical[b] data

Compound	δ(^{77}Se-{^{1}H})	$E_{\frac{1}{2}}$/V
cis-$[RuCl_2([8]aneSe_2)_2]$[c]	197, 244	+0.50[d]
cis$[RuCl_2([16]aneSe_4)]$	196, 254	+0.07
trans-$[RuCl_2([16]aneSe_4)]$	155	+0.00
trans-$[RuCl(PPh_3)([16]aneSe_4)]PF_6$	157[e]	+0.84
trans-$[OsCl(PPh_3)([16]aneSe_4)]PF_6$	97[f]	+0.44
cis-$[RuBr_2([16]aneSe_4)]$	151, 241	+0.10
trans-$[RuBr_2([16]aneSe_4)]$	188	+0.11

[a] At 68.68 MHz, referenced to neat external Me_2Se; solutions in CH_2Cl_2–$CDCl_3$. [b] *vs.* ferrocene–ferrocenium ($E_{\frac{1}{2}} = 0$ V), CH_2Cl_2 or MeCN solution (0.1 mol dm^{-3} $NBu^n{}_4BF_4$ supporting electrolyte, scan rate = 200 mV s^{-1}). [c] *trans*-$[RuCl_2([8]aneSe_2)_2]$: δ(^{77}Se-{^{1}H}) +134. [d] Irreversible; daughter product at −0.24 V *vs.* ferrocene–ferrocenium. [e] Doublet, $^{2}J_{PSe} = 26$ Hz, δ(^{31}P) +41, −146 (septet, PF_6^-). [f] Doublet, $^{2}J_{PSe} = 40$ Hz, δ(^{31}P) −15, −146 (septet, PF_6^-).

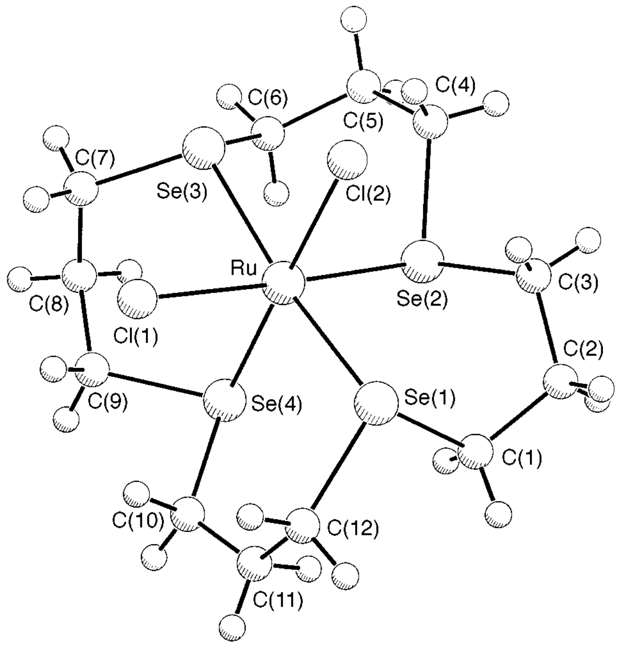


Fig. 1 View of the structure of *cis*-$[RuCl_2([16]aneSe_4)]$ with the numbering scheme adopted

for *cis*-$[RuCl_2([16]aneSe_4)]$. The EtOH solvent used in these reactions apparently facilitates reduction of the Ru^{III} to Ru^{II}.

With the exception of $[Cu_n([16]aneSe_4)_n]^{n+}$ (for which a polymeric structure has been observed[15]), the only structurally characterised examples of [16]aneSe$_4$ complexes with transition-metal ions to have been reported involve the metal ion occupying the cavity, with the Se donor atoms arranged around the four equatorial co-ordination sites; examples include *trans*-$[CoBr_2([16]aneSe_4)]^+$,[5] $[Pd([16]aneSe_4)]^{2+}$ (for which two different ligand configurations have been observed, both involving square-planar Pd$^{II\,2,16}$) and *trans*-$[PtCl_2([16]aneSe_4)]^{2+}$.[3]

Table 2 Selected bond lengths (Å) and angles (°) for *cis*-$[RuCl_2([16]aneSe_4)]$

Ru–Se(1)	2.465(1)	Ru–Se(2)	2.440(2)
Ru–Se(3)	2.453(1)	Ru–Se(4)	2.396(1)
Ru–Cl(1)	2.468(2)	Ru–Cl(2)	2.453(2)
Se(1)–C(1)	1.966(9)	Se(1)–C(12)	1.96(1)
Se(2)–C(3)	1.964(10)	Se(2)–C(4)	1.968(10)
Se(3)–C(6)	1.97(1)	Se(3)–C(7)	1.95(1)
Se(4)–C(9)	1.97(1)	Se(4)–C(10)	1.94(1)
C(1)–C(2)	1.52(1)	C(2)–C(3)	1.52(1)
C(4)–C(5)	1.52(2)	C(5)–C(6)	1.52(2)
C(7)–C(8)	1.50(2)	C(8)–C(9)	1.52(2)
C(10)–C(11)	1.38(2)	C(11)–C(12)	1.55(2)
Se(1)–Ru–Se(2)	89.23(4)	Se(1)–Ru–Se(3)	171.56(5)
Se(1)–Ru–Se(4)	93.50(4)	Se(1)–Ru–Cl(1)	93.11(6)
Se(1)–Ru–Cl(2)	86.23(6)	Se(2)–Ru–Se(3)	90.45(4)
Se(2)–Ru–Se(4)	88.47(4)	Se(2)–Ru–Cl(1)	177.61(7)
Se(2)–Ru–Cl(2)	90.79(7)	Se(3)–Ru–Se(4)	94.92(5)
Se(3)–Ru–Cl(1)	87.16(6)	Se(3)–Ru–Cl(2)	85.33(7)
Se(4)–Ru–Cl(1)	91.92(6)	Se(4)–Ru–Cl(2)	179.22(7)
Cl(1)–Ru–Cl(2)	88.82(8)	Ru–Se(1)–C(1)	105.3(3)
Ru–Se(1)–C(12)	111.2(3)	C(1)–Se(1)–C(12)	97.0(4)
Ru–Se(2)–C(3)	102.7(3)	Ru–Se(2)–C(4)	102.2(3)
C(3)–Se(2)–C(4)	96.5(4)	Ru–Se(3)–C(6)	106.0(3)
Ru—Se(3)–C(7)	110.4(4)	C(6)–Se(3)–C(7)	96.6(5)
Ru–Se(4)–C(9)	108.4(3)	Ru–Se(4)–C(10)	107.8(4)
C(9)–Se(4)–C(10)	92.1(6)	Se(1)–C(1)–C(2)	111.2(6)
C(1)–C(2)–C(3)	115.6(8)	Se(2)–C(3)–C(2)	111.0(7)
Se(2)–C(4)–C(5)	111.8(8)	C(4)–C(5)–C(6)	116.7(9)
Se(3)–C(6)–C(5)	112.5(7)	Se(3)–C(7)–C(8)	117.9(7)
C(7)–C(8)–C(9)	116.3(10)	Se(4)–C(9)–C(8)	114.5(8)
Se(4)–C(10)–C(11)	119(1)	C(10)–C(11)–C(12)	124(1)
Se(1)–C(12)–C(11)	116.0(8)		

A single-crystal structural study was therefore undertaken in order to confirm the *cis* stereochemistry around Ru^{II} in $[RuCl_2([16]aneSe_4)]$. This study should also provide an opportunity to probe the relative *trans* effect of Cl *vs.* Se. This can be established from the measured bond lengths. Suitable crystals were obtained by vapour diffusion of diethyl ether into a solution of the complex in CH_2Cl_2. The structure confirms (Fig. 1, Table 2) that the Ru^{II} ion is co-ordinated in a distorted octahedral arrangement to two mutually *cis* chlorine atoms and four Se donors of a folded [16]aneSe$_4$ molecule, Ru–Se(1) 2.465(1), Ru–Se(2) 2.440(2), Ru–Se(3) 2.453(1), Ru–Se(4) 2.396(1), Ru–Cl(1) 2.468(2) and Ru–Cl(2) 2.453(2) Å. The angles around the central metal lie in the ranges 86.23–94.92° for those involving mutually *cis* donor atoms and 171.56(5)–179.22(7)° for those involving mutually *trans* donor atoms. Thus, these do not deviate greatly from the 90 and 180° expected for a regular octahedron. The only other structurally characterised ruthenium(II) selenoether complex is *trans*-$[RuCl_2\{PhSe(CH_2)_2SePh\}_2]$ which shows *d*(Ru–Se) = 2.433(1)–2.460(1) and *d*(Ru–Cl) = 2.444(1) and 2.413(1) Å.[11] The structure of the anionic ruthenium(III) species $[RuCl_4\{MeSe(CH_2)_2SeMe\}]^-$ gave *d*(Ru–Se) = 2.446(1), 2.457(1), *d*(Ru–Cl) (*trans* Se) = 2.404(2), 2.386(2), *d*(Ru–Cl) (*trans* Cl) = 2.353(2), 2.344(2) Å.[13]

Examination of the Ru–Se bond lengths in *cis*-$[RuCl_2([16]aneSe_4)]$ reveals that *d*(Ru–Se) *trans* to Se [2.465(1), 2.453(1) Å] are marginally longer than *d*(Ru–Se) *trans* to Cl [2.440(2), 2.396(1) Å], indicating that Se has a slightly greater *trans* influence than Cl. The effect observed in this selenoether species is smaller than that seen in the thioether species *cis*-$[RuCl_2([14]aneS_4)]$, *d*(Ru–S) *trans* to Cl 2.262(1), *d*(Ru–S) *trans* to S 2.333(1) Å.[6]

Interconversion of geometric isomers of the form $[ML_4X_2]$ is usually expected to be a relatively high-energy process for low-spin d^6 transition-metal species, and where L is a mono- or bi-dentate ligand the product obtained is *usually* the thermodynamically favoured *trans* isomer. However, where L is a tetradentate macrocycle the main factor governing which particular isomer is formed is usually the balance between the metal-ion radius and the macrocyclic cavity size. Thus, it has been shown that for rhodium(III) complexes with tetrathioether ligands, $[RhCl_2([12]aneS_4)]^+$ ([12]aneS$_4$ = 1,4,7,10-tetrathiocyclododecane) and $[RhCl_2([14]aneS_4)]^+$ both adopt a *cis*-dichloro arrangement, while $[RhCl_2([16]aneS_4)]^+$, involving the larger 16-membered ring, adopts a *trans*-dichloro arrangement.[17] We have also shown recently that the tetraselenoether macrocyclic cations $[MX_2([16]aneSe_4)]^+$ (M = Rh or Ir, X = Cl or Br) exist in solution as a mixture of *cis* and *trans* isomers, although only the *trans* form has been observed in the solid state by X-ray crystallography, and we have been unable to obtain a pure sample of the *cis* isomer.[5] In contrast, we have shown here that in the case of the ruthenium(II) compound [RuCl$_2$([16]aneSe$_4$)] we can readily generate the pure *cis* form. Given that the ionic radii of Ru^{II} and Rh^{III} are very similar and that the M–Se bond lengths observed in *cis*-[RuCl$_2$([16]aneSe$_4$)] are very similar to those observed for *trans*-[RhCl$_2$([16]aneSe$_4$)]$^+$ [2.456(1), 2.461(1) Å] and some are marginally *shorter* than those in *trans*-[IrCl$_2$([16]aneSe$_4$)]$^+$ [2.461(3), 2.462(3), 2.470(3), 2.470(3) Å],[5] it does not seem likely that hole-size arguments govern the stereochemistry here.

Conversion of *cis*-[RuCl$_2$([16]aneSe$_4$)] into the *trans*-dichloro species can be achieved by refluxing a nitromethane solution of *cis*-[RuCl$_2$([16]aneSe$_4$)] for *ca.* 3 h, followed by precipitation with diethyl ether. The *trans* arrangement was confirmed by ^{77}Se-{^{1}H} NMR spectroscopy which showed a single resonance at δ +155 (with no evidence now for the *cis* form), while IR spectroscopy showed ν(Ru–Cl) 310 cm^{-1}. It seems likely that this conversion occurs as a result of the higher boiling point of MeNO$_2$ over EtOH. We cannot be certain which macrocyclic configuration (*all up* or *up,up,down,down* or *up,down,up,down*) is present in the *trans*-[RuCl$_2$([16]aneSe$_4$)] produced in this way, and unfortunately attempts to obtain crystals suitable for an X-ray analysis were unsuccessful. Surprisingly, attempts to convert *cis*-[RuCl$_2$([8]aneSe$_2$)$_2$] into the *trans* isomer by this route were not successful, with ^{77}Se-{^{1}H} NMR spectroscopy still showing only the *cis* isomer to be present in the product recovered. However, we have also found that an alternative reaction involving treatment of [RuCl$_2$(py)$_4$][18] (py = pyridine) with 2 molar equivalents of [8]aneSe$_2$ in refluxing toluene yields [RuCl$_2$([8]aneSe$_2$)$_2$] as a mixture of *cis* and *trans* isomers [*trans* isomer: δ (^{77}Se-{^{1}H}) 134] although the yield is rather poorer and significant amounts of unchanged starting material were also recovered.

Phosphine auxiliary ligands can also be introduced by treatment of [RuCl$_2$(PPh$_3$)$_3$][19] with 1 molar equivalent of [16]aneSe$_4$ in refluxing MeOH solution, followed by addition of an excess of NH$_4$PF$_6$, which afforded a yellow precipitate. Infrared spectroscopic measurements showed the presence of co-ordinated [16]aneSe$_4$, PF$_6^-$ anion and PPh$_3$ ligand. The FAB mass spectrum showed clusters of peaks with the correct isotopic distributions around m/z = 883 and 621, corresponding to [RuCl(PPh$_3$)([16]aneSe$_4$)]$^+$ and [RuCl([16]aneSe$_4$)]$^+$ respectively. The ^{31}P NMR spectrum showed a singlet at δ +41 with ^{77}Se satellites, giving $^2J_{PSe}$ = 26 Hz, and a septet at δ −146 due to the PF$_6^-$ anion (integrals 1 : 1). The ^{77}Se-{^{1}H} NMR spectrum showed a doublet at δ +157 ($^2J_{PSe}$ = 26 Hz). These data are consistent with the formulation *trans*-[RuCl(PPh$_3$)([16]aneSe$_4$)]PF$_6$ for this compound. In light of the *trans* arrangement predicted for this species in solution and to determine the configuration of the co-ordinated macrocycle, we undertook a structure determination on *trans*-[RuCl(PPh$_3$)([16]aneSe$_4$)]PF$_6$.

The quality of the crystals obtained was rather poor, resulting in a weak data set. Also, the PF$_6^-$ anion and some of the methylene C atoms of the macrocycle showed disorder. However, it is quite clear that the structure shows (Fig. 2, Table 3) the Ru^{II} co-ordinated in an endocyclic manner to the tetradentate selenoether ligand, with mutually *trans* Cl and PPh$_3$ ligands completing the distorted octahedral geometry, Ru–Se(1) 2.488(3), Ru–Se(2) 2.465(3), Ru–Se(3) 2.488(3), Ru–Se(4) 2.497(3), Ru–P(1) 2.307(6) and Ru–Cl 2.499(5) Å. All of the angles are close to octahedral at Ru^{II}. These Ru–Se bond distances compare well with those for *cis*-[RuCl$_2$([16]aneSe$_4$)] above and also *trans*-[RuCl$_2${PhSe(CH$_2$)$_2$SePh}$_2$].[11] Furthermore, the structure shows that the methylene groups are all directed to the opposite side of the RuSe$_4$ plane from the PPh$_3$ ligand, resulting in the Se-based lone pairs of the ligand adopting the *all up* arrangement. This is the first time that this ligand configuration had been observed in an octahedral complex of [16]aneSe$_4$, and probably arises as a result of the steric influence of the bulky PPh$_3$ ligand. Importantly also, the Ru atom lies almost exactly within the least-squares plane defined by the four selenoether donors, suggesting that there is a good size match between the ionic radius of the Ru^{II} and the macrocyclic cavity. This further supports our previous suggestion that hole size arguments are not important in governing the stereochemistries adopted by these particular ruthenium(II) complexes.

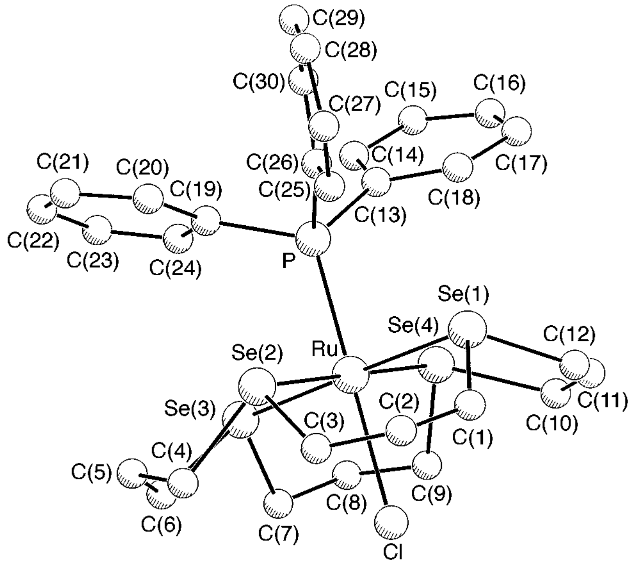


Fig. 2 View of the structure of *trans*-[RuCl(PPh$_3$)([16]aneSe$_4$)]$^+$ with the numbering scheme adopted

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-[RuCl(PPh$_3$)([16]aneSe$_4$)]$^+$

Ru–Se(1)	2.488(3)	Ru–Se(2)	2.465(3)
Ru–Se(3)	2.488(3)	Ru–Se(4)	2.497(3)
Ru–Cl	2.499(5)	Ru–P	2.307(6)
Se(1)–C(1)	1.96(6)	Se(1)–C(12)	1.92(4)
Se(2)–C(3)	2.03(6)	Se(2)–C(4)	1.95(3)
Se(3)–C(6)	1.94(4)	Se(3)–C(7)	1.93(3)
Se(4)–C(9)	1.95(2)	Se(4)–C(10)	2.04(4)
P–C(13)	1.82(2)	P–C(19)	1.85(2)
P–C(25)	1.86(2)	C(1)–C(2)	1.34(5)
C(2)–C(3)	1.40(6)	C(4)–C(5)	1.54(5)
C(5)–C(6)	1.42(5)	C(7)–C(8)	1.55(4)
C(8)–C(9)	1.45(3)	C(10)–C(11)	1.26(6)
C(11)–C(12)	1.28(6)		
Se(1)–Ru–Se(2)	90.9(1)	Se(1)–Ru–Se(3)	178.1(1)
Se(1)–Ru–Se(4)	92.7(1)	Se(1)–Ru–Cl	90.6(2)
Se(1)–Ru–P	89.2(2)	Se(2)–Ru–Se(3)	91.0(1)
Se(2)–Ru–Se(4)	176.4(1)	Se(2)–Ru–Cl	90.1(2)
Se(2)–Ru–P	89.6(2)	Se(3)–Ru–Se(4)	85.5(1)
Se(3)–Ru–Cl	89.0(2)	Se(3)–Ru–P	91.2(2)
Se(4)–Ru–Cl	90.3(2)	Se(4)–Ru–P	90.1(2)
Cl–Ru–P	179.6(2)	Ru–Se(1)–C(1)	107(1)
Ru–Se(1)–C(12)	113(1)	C(1)–Se(1)–C(12)	92(2)
Ru–Se(2)–C(3)	104(1)	Ru–Se(2)–C(4)	113.0(9)
C(3)–Se(2)–C(4)	86(1)	Ru–Se(3)–C(6)	113(1)
Ru–Se(3)–C(7)	110.7(9)	C(6)–Se(3)–C(7)	90(1)
Ru–Se(4)–C(9)	109.2(7)	Ru–Se(4)–C(10)	105(1)
C(9)–Se(4)–C(10)	90(1)	Ru–P–C(13)	114.4(7)
Ru–P–C(19)	116.0(7)	Ru–P–C(25)	121.4(7)
C(13)–P–C(19)	106.5(10)	C(13)–P–C(25)	98.4(9)
C(19)–P–C(25)	97.3(9)	Se(1)–C(1)–C(2)	124(4)
C(1)–C(2)–C(3)	130(4)	Se(2)–C(3)–C(2)	121(3)
Se(2)–C(4)–C(5)	107(2)	C(4)–C(5)–C(6)	122(4)
Se(3)–C(6)–C(5)	115(3)	Se(3)–C(7)–C(8)	111(1)
C(7)–C(8)–C(9)	119(2)	Se(4)–C(9)–C(8)	111(1)
Se(4)–C(10)–C(11)	127(3)	C(10)–C(11)–C(12)	142(6)
Se(1)–C(12)–C(11)	121(4)		

The yellow osmium(II) complex, [OsCl(PPh$_3$)([16]aneSe$_4$)]PF$_6$

has also been prepared by a similar method to that of the ruthenium(II) species, using [$OsCl_2(PPh_3)_3$], [16]aneSe_4 and NH_4PF_6 in refluxing EtOH. The electrospray mass spectrum (MeCN solution) of this compound shows a peak at *m*/*z* = 973, corresponding to [$OsCl(PPh_3)$([16]aneSe_4)]$^+$. Phosphorus-31 NMR spectroscopy confirms the presence of the co-ordinated PPh_3, with a resonance at δ −15 (as well as a septet at δ −146 due to the PF_6^- anion); ^{77}Se satellites are also evident, giving $^2J_{PSe}$ = 40 Hz. The ^{77}Se-{^{1}H} NMR spectrum shows a doublet at δ +97, indicative of a single environment for all four selenium donors, and hence consistent with a *trans* chlorophosphine arrangement at the octahedral Os^{II}, as seen for the ruthenium(II) analogue above.

The dibromo and diiodo compounds [RuX_2([16]aneSe_4)] (X = Br or I) were prepared by refluxing [$Ru(dmf)_6$](CF_3SO_3)$_3$,[14] [16]aneSe_4 and 2 molar equivalents of LiBr or NaI in EtOH solution. The brown product isolated was then washed with water to remove dmf and $CF_3SO_3^-$ impurities. In the case of [$RuBr_2$([16]aneSe_4)] a ^{77}Se-{^{1}H} NMR spectrum of the purified product showed two signals assigned to the *cis* isomer, δ +151 and +241. This species was also characterised by IR spectroscopy, electrospray mass spectrometry and microanalysis. Refluxing *cis*-[$RuBr_2$([16]aneSe_4)] in $MeNO_2$ for *ca.* 3 h resulted in complete conversion into *trans*-[$RuBr_2$([16]aneSe_4)], δ (^{77}Se-{^{1}H}) +188. The compound [RuI_2([16]aneSe_4)] {electrospray mass spectrometry: found *m*/*z* = 715; calculated for [^{102}Ru^{127}I([16]ane^{80}Se$_4$)]$^+$ *m*/*z* = 717} is very poorly soluble in common organic solvents and this has hindered our attempts to obtain ^{77}Se-{^{1}H} NMR data.

Electrochemistry

In order to establish whether the cyclic selenoether ligands [16]aneSe_4 and [8]aneSe_2 would stabilise other ruthenium oxidation states and to probe the effect that the auxiliary halogen or phosphine ligands have on the redox potentials, cyclic voltammetry measurements were undertaken on the newly prepared ruthenium(II) and osmium(II) species. The redox potentials measured are given in Table 1. With the exception of *cis*-[$RuCl_2$([8]aneSe_2)] (which shows an irreversible oxidation and subsequent formation of a daughter product), all of the dichloro, dibromo and chlorophosphine complexes exhibit a reversible Ru^{II}–Ru^{III} redox couple, *e.g.* Fig. 3. The oxidation potentials for the dihalogeno species appear to be essentially independent of X, and more surprisingly the variation in $E_{\frac{1}{2}}$ values between the *cis* and *trans* isomers is very small. This is in contrast to the observations for [MX_2(phosphine)$_4$] (M = Ru or Os). In these complexes the M^{II}–M^{III} redox couple is typically *ca.* 0.5 V more positive for the *cis*-dihalogeno species than the *trans*,[20] *e.g.* for [$RuCl_2(PMe_3)_4$]$^{0/+}$ *trans* isomer; $E_{\frac{1}{2}}$ = −0.13, *cis* isomer E_{pa} = +0.68 V (irreversible) *vs.* ferrocene–ferrocenium, [$OsCl_2(PMe_2Ph)_4$]$^{0/+}$ *trans* isomer $E_{\frac{1}{2}}$ = −0.31, *cis* isomer $E_{\frac{1}{2}}$ = +0.16 V, although the reason for this large variation is not really known.

The Ru^{II}–Ru^{III} couple for *trans*-[$RuCl(PPh_3)$([16]aneSe_4)]$^+$ occurs approximately 0.8 V higher than for *trans*-[$RuCl_2$([16]aneSe_4)], a consequence of the replacement of a hard anionic ligand with a soft, neutral phosphine ligand, and the increase in cationic charge on the complex associated with this. The compound *trans*-[$OsCl(PPh_3)$([16]aneSe_4)]PF_6 shows a reversible Os^{II}–Os^{III} redox couple at $E_{\frac{1}{2}}$ = +0.44 V. This is significantly less anodic compared to *trans*-[$RuCl(PPh_3)$([16]aneSe_4)]$^{+/2+}$, as expected for replacement of a 4d metal centre with the heavier 5d analogue.

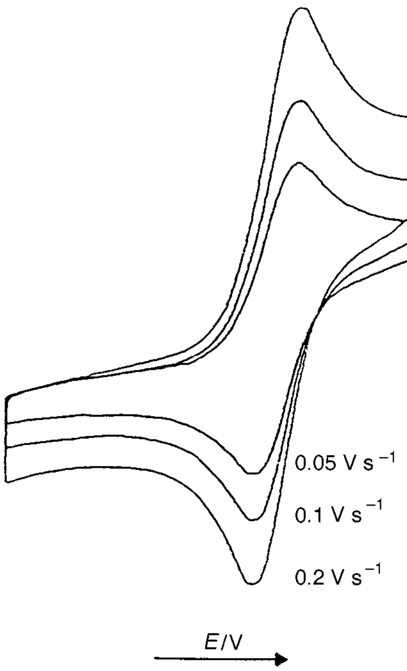


Fig. 3 Cyclic voltammogram of *cis*-[$RuCl_2$([16]aneSe_4)] showing the Ru^{II}–Ru^{III} redox couple (MeCN, 0.1 mol dm^{-3} $NBu^n_4BF_4$ supporting electrolyte)

In view of the low Ru^{II}–Ru^{III} redox potentials observed for the ruthenium(II) dihalogeno compounds, we also attempted chemically to oxidise *trans*-[RuX_2([16]aneSe_4)] (X = Cl or Br) to the corresponding ruthenium(III) species. For X = Br this was achieved by treating an MeCN solution of *trans*-[$RuBr_2$([16]aneSe_4)] with Br_2–CCl_4, giving a green solution which was concentrated and diethyl ether added to give a green solid. The electrospray mass spectrum (MeCN solution) showed clusters of peaks at *m*/*z* = 745 and 666, which are assigned to [$RuBr_2$([16]aneSe_4)]$^+$ and [$RuBr$([16]aneSe_4)]$^+$ respectively. The UV/VIS and IR spectroscopy and microanalytical measurements are also consistent with the assignment *trans*-[$RuBr_2$([16]aneSe_4)]Br. Similar treatment of *trans*-[$RuCl_2$([16]aneSe_4)] with Cl_2–CCl_4 in a variety of solvents gave red solutions. However, for reasons which we do not understand at present we have been unable to isolate a pure sample of the ruthenium(III) species [$RuCl_2$([16]aneSe_4)]$^+$.

Experimental

Infrared spectra were measured as KBr or CsI discs or as Nujol mulls using a Perkin-Elmer 983G spectrometer over the range 200–4000 cm^{-1}, UV/VIS spectra in solution using 1 cm path length quartz cells on a Perkin-Elmer Lambda19 spectrophotometer. Mass spectra were run by fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal geometry double focusing spectrometer or by positive electrospray (ES) using a VG Biotech Platform. Proton NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz, ^{77}Se-{^{1}H} and ^{31}P-{^{1}H} spectra using a Bruker AM360 spectrometer operating at 68.68 and 145.8 MHz respectively referenced to external neat Me_2Se [δ(^{77}Se) 0] or 85% H_3PO_4 [δ(^{31}P) 0]. Microanalyses were performed by the Imperial College microanalytical service. Cyclic voltammetry experiments used an EG&G Princeton Applied Research model 362 scanning potentiostat with 0.1 mol dm^{-3} $NBu^n_4BF_4$ supporting electrolyte, a double platinum electrode as working and auxiliary electrode and a standard calomel reference electrode. All potentials are quoted *versus* ferrocene–ferrocenium. The compounds [8]aneSe_2 and [16]aneSe_4 were prepared by the literature procedure.[21]

Preparations

***cis*-[$RuCl_2$([8]aneSe_2)$_2$].**The compound [8]aneSe_2 (140 mg, 0.58 mmol) was added to deoxygenated EtOH (75 cm^3) followed by [$Ru(dmf)_6$]Cl_3 in dmf (5 cm^3, *ca.* 0.048 mol dm^{-3}) and the mixture was refluxed under N_2 for 4 h, resulting in a change from yellow to light brown. After cooling the solution was filtered and the filtrate concentrated to *ca.* 2 cm^3 *in vacuo*. Deoxygenated diethyl ether (30 cm^3) was added with stirring to afford a light brown precipitate which was recrystallised from CH_2Cl_2 and dried *in vacuo*. Yield 43 mg (24%) (Found: C, 21.8; H, 3.5. Calc. for $C_{12}H_{24}Cl_2RuSe_4$: C, 21.9; H, 3.6%). Electrospray mass spectrum (MeCN): found *m*/*z* = 664, 623; calculated for $[^{102}Ru^{35}Cl([8]ane^{80}Se_2)_2(MeCN)]^+$ *m*/*z* 666, $[^{102}Ru^{35}Cl([8]ane^{80}Se_2)_2]^+$ *m*/*z* = 625. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 25 510 (ε_{mol} = 610 $dm^3\ mol^{-1}\ cm^{-1}$) and 23 365 (sh) cm^{-1}. ^1H NMR spectrum (300 MHz, CD_2Cl_2, 298 K): δ 2.3–3.2 (m, CH_2). IR spectrum (CsI disc): 2974w, 2927w, 2880m, 1413m, 1357m, 1233w, 1101m, 1021w, 995w, 954w, 879w, 833m, 614w, 532w, 298w, 244w and 220w cm^{-1}.

***cis*-RuCl₂([16]aneSe₄)].** Method as for *cis*-$[RuCl_2([8]aneSe_2)_2]$ above, but using $[16]aneSe_4$ (124 mg, 0.26 mmol) and $[Ru(dmf)_6]Cl_3$ in dmf (5.4 cm^3, *ca.* 0.048 mol dm^{-3}) giving a fawn precipitate which was recrystallised from CH_2Cl_2 and dried *in vacuo*. Yield 90 mg (54%) (Found: C, 22.0; H, 3.9. Calc. for $C_{12}H_{24}Cl_2RuSe_4$: C, 21.9; H, 3.6%). Electrospray mass spectrum (MeCN): found *m*/*z* = 663, 622; calculated for $[^{102}Ru^{35}Cl([16]ane^{80}Se_4)(MeCN)]^+$ *m*/*z* = 666, $[^{102}Ru^{35}Cl([16]ane^{80}Se_4)]^+$ *m*/*z* = 625. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 30 770 (sh, ε_{mol} = 520) and 24 750 cm^{-1} (380 $dm^3\ mol^{-1}\ cm^{-1}$). ^1H NMR spectrum (300 MHz, CD_2Cl_2, 298 K): δ 2.2–3.4 (m, CH_2). IR spectrum (CsI disc): 2960w, 2915w, 1461m, 1432m, 1356m, 1283w, 1218w, 1097w, 1021w, 979w, 891m, 856w, 787w, 743m, 574w, 295w, 280w and 218w cm^{-1}.

***trans*-[RuCl₂([16]aneSe₄)].** The compound *cis*-$[RuCl_2([16]aneSe_4)]$ (20 mg, 0.030 mmol) was added to deoxygenated $MeNO_2$ (25 cm^3). This solution was refluxed under N_2 for 3 h, cooled to room temperature and concentrated *in vacuo*. Diethyl ether was then added to afford a brown solid which was filtered off and dried *in vacuo*. Yield 12 mg (60%) (Found: C, 21.7; H, 3.5. Calc. for $C_{12}H_{24}Cl_2RuSe_4$: C, 21.9; H, 3.6%). Electrospray mass spectrum (MeCN): found *m*/*z* = 664, 621; calculated for $[^{102}Ru^{35}Cl([16]ane^{80}Se_4)(MeCN)]^+$ *m*/*z* = 666, $[^{102}Ru^{35}Cl([16]ane^{80}Se_4)]^+$ *m*/*z* = 625. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 33 330 (ε_{mol} = 3260) and 27 470 cm^{-1} (960 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum (CsI disc): 2960w, 2915w, 1461m, 1360m, 1245w, 1218w, 1080w, 979w, 891w, 856w, 787w, 750w, 580w and 310w cm^{-1}.

***trans*-[RuCl(PPh₃)([16]aneSe₄)]PF₆.** The compounds $[16]aneSe_4$ (60 mg, 0.12 mmol) and $[RuCl_2(PPh_3)_3]$ (118 mg, 0.12 mmol) were added to deoxygenated MeOH (60 cm^3). The mixture was refluxed under N_2 for 3.5 h, resulting in a change to yellow, and then left to stir at room temperature for 16 h. The salt NH_4PF_6 (60 mg, 0.36 mmol) was then added and the solution volume reduced to *ca.* 5 cm^3 to give a yellow precipitate which was filtered off, recrystallised from CH_2Cl_2 and dried *in vacuo*. Yield 80 mg (63%) (Found: C, 34.8; H, 3.6. Calc. for $C_{30}H_{39}ClPRuSe_4$: C, 34.9; H, 3.8%). FAB mass spectrum: found *m*/*z* = 883, 621; calculated for $[^{102}Ru^{35}Cl(PPh_3)([16]ane^{80}Se_4)]^+$ *m*/*z* = 887, $[^{102}Ru^{35}Cl([16]ane^{80}Se_4)]^+$ *m*/*z* = 625. UV/VIS spectrum (CH_2Cl_2 solution): $\tilde{\nu}$ = 28 090 (ε_{mol} = 583) and 25 000 cm^{-1} (sh, 340 $dm^3\ mol^{-1}\ cm^{-1}$). ^1H NMR spectrum (300 MHz, CD_2Cl_2, 298 K): δ 7.7–7.3 (m, 15 H, PPh_3) and 3.3–1.7 (m, CH_2, 24 H). IR spectrum (CsI disc): 3053m, 2922w, 2848w, 1584w, 1480m, 1432m, 1407m, 1248m, 1185w, 1161w, 1087m, 1025w, 999w, 984w, 838vs, 799m, 742m, 695m, 557s, 529s, 497w, 465w, 440w, 421w, 351w and 269w cm^{-1}.

***trans*-[OsCl(PPh₃)([16]aneSe₄)]PF₆.** The compounds $[16]aneSe_4$ (75 mg, 0.15 mmol) and $[OsCl_2(PPh_3)_3]$ (161 mg, 0.15 mmol) were added to deoxygenated EtOH (70 cm^3). The mixture was refluxed under N_2 for 3 h, resulting in a change from green to yellow. After cooling to room temperature, NH_4PF_6 (60 mg, 0.36 mmol) was added and the solution volume reduced to *ca.* 5 cm^3 to give a yellow precipitate which was filtered off, recrystallised from CH_2Cl_2 and dried *in vacuo*. Yield 65 mg, (39%) (Found: C, 32.6; H, 3.6. Calc. for $C_{30}H_{39}ClOsPSe_4$: C, 32.2; H, 3.5%). Electrospray mass spectrum (MeCN solution): found *m*/*z* = 973; calculated for $[^{190}Os^{35}Cl(PPh_3)([16]ane^{80}Se_4)]^+$ *m*/*z* = 975. ^1H NMR spectrum (300 MHz, CD_2Cl_2, 298 K): δ 7.9–7.3 (m, 15 H, PPh_3) and 3.8–2.4 (m, CH_2, 24 H). IR spectrum (CsI disc): 3056w, 2928w, 1584w, 1481m, 1431m, 1357m, 1247w, 1089m, 999w, 841vs, 747m, 697s, 614w, 557s, 531s, 464m and 427w cm^{-1}.

***cis*-[RuBr₂([16]aneSe₄)].** The compounds $[16]aneSe_4$ (120 mg, 0.25 mmol), $[Ru(dmf)_6][CF_3SO_3]_3$ (210 mg, 0.21 mmol) and LiBr (55 mg, 0.63 mmol) were added to deoxygenated EtOH (75 cm^3) and this mixture was refluxed under N_2 for 4 h, during which time a gradual change from yellow to brown was observed. After cooling to room temperature the solution was filtered and the filtrate evaporated to dryness. The resulting brown solid was then washed with water prior to recrystallisation from CH_2Cl_2. Yield 43 mg (27%) (Found: C, 19.4; H, 3.5. Calc. for $C_{12}H_{24}Br_2RuSe_4$: C, 19.3; H, 3.2%). Electrospray mass spectrum (MeCN): found *m*/*z* = 667; calculated for $[^{102}Ru^{79}Br([16]ane^{80}Se_4)]^+$ *m*/*z* = 669. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 19 650 (ε_{mol} = 190), 24 040 (330) and 41 670 cm^{-1} (14 910 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum (CsI disc): 2965w, 2961w, 1430m, 1356m, 1261w, 1097m, 1028m, 863w, 799m and 393m cm^{-1}.

***trans*-[RuBr₂([16]aneSe₄)].** Method as for *trans*-$[RuCl_2([16]aneSe_4)]$ above, but using *cis*-$[RuBr_2([16]aneSe_4)]$, giving a brown precipitate. Yield 30 mg (19%) (Found: C, 19.1; H, 3.0. Calc. for $C_{12}H_{24}Br_2RuSe_4$: C, 19.3; H, 3.2%). Electrospray mass spectrum (MeCN): found *m*/*z* = 667; calculated for $[^{102}Ru^{79}Br([16]ane^{80}Se_4)]^+$ *m*/*z* = 669. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 24 750 (ε_{mol} = 120) and 20 410 cm^{-1} (70 $dm^3\ mol^{-1}\ cm^{-1}$). ^1H NMR spectrum (90 MHz, CD_2Cl_2, 300 K): δ 2.1–3.6 (m, CH_2). IR spectrum (CsI disc): 2966w, 2919w, 1427m, 1398m, 1357m, 1280w, 1243w, 1216w, 1102w, 982w, 887w, 833w, 790w and 573w cm^{-1}.

***trans*-[RuI₂([16]aneSe₄)].** Method as for *cis*-$[RuBr_2([16]aneSe_4)]$ above, but using $[16]aneSe_4$ (155 mg, 0.32 mmol), $[Ru(dmf)_6][CF_3SO_3]_3$ (250 mg, 0.25 mmol) and NaI (115 mg, 0.76 mmol). Yield 38 mg (18%) (Found: C, 17.6; H, 3.1. Calc. for $C_{12}H_{24}I_2RuSe_4$: C, 17.2; H, 2.9%). Electrospray mass spectrum (MeCN): found *m*/*z* = 715; calculated for $[^{102}Ru^{127}I([16]ane^{80}Se_4)]^+$ *m*/*z* = 717. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 43 860 (ε_{mol} = 1942), 41 150 (1120), 34 840 (480) and 27 860 cm^{-1} (170 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum (CsI disc): 2960w, 2921w, 1423m, 1357m, 1315w, 1246w, 1096m, 983w, 834w, 614w and 510w cm^{-1}.

***trans*-[RuBr₂([16]aneSe₄)]Br.** The compound *trans*-$[RuBr_2([16]aneSe_4)]$ (40 mg, 0.05 mmol) was added to MeCN (5 cm^3) followed by Br_2–CCl_4 (5 drops) with stirring, producing a change from brown to dark green. The solution was concentrated to *ca.* 2 cm^3 and diethyl ether (10 cm^3) added to afford a green solid which was filtered off and dried *in vacuo*. Yield 15 mg (34%) (Found: C, 17.1; H, 3.2. Calc. for $C_{12}H_{24}Br_3RuSe_4$: C, 17.4; H, 2.9%). Electrospray mass spectrum (MeCN): found *m*/*z* = 745, 666; calculated for $[^{102}Ru^{79}Br_2([16]ane^{80}Se_4)]^+$ *m*/*z* = 748, $[^{102}Ru^{79}Br([16]ane^{80}Se_4)]^+$ *m*/*z* = 669. UV/VIS spectrum (MeCN solution): $\tilde{\nu}$ = 26 660 (ε_{mol} = 1550), 22 200 (sh) and 15 340 cm^{-1} (830 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum (CsI disc): 2917w, 1420m, 1356m, 1287w, 1250w, 1222w, 1106w, 982w, 884w, 833w, 789w, 741w, 532w and 240w cm^{-1}.

X-Ray crystallography

cis**-[RuCl$_2$([16]aneSe$_4$)].** Orange prisms of [RuCl$_2$([16]aneSe$_4$)] were obtained by vapour diffusion of Et$_2$O into a solution of the complex in CH$_2$Cl$_2$. The selected crystal (0.45 × 0.28 × 0.20 mm) was coated with mineral oil and mounted on a glass fibre under a cold stream of N$_2$ gas.

Crystal data. C$_{12}$H$_{24}$Cl$_2$RuSe$_4$, $M = 656.1$, monoclinic, space group $P2_1/n$, $a = 8.759(5)$, $b = 14.276(6)$, $c = 14.793(4)$ Å, $\beta = 99.80(3)°$, $U = 1822(1)$ Å^3 [from 2θ values of 25 reflections measured at ±ω (2θ = 38.3–44.1°, λ = 0.71 073 Å)], $Z = 4$, $D_c = 2.391$ g cm^{-3}, $\mu = 90.38$ cm^{-1}, $F(000) = 1240$.

Data collection and processing. Data collection used a Rigaku AFC7S diffractometer equipped with an Oxford Systems cryostream operating at 150 K, using graphite-monochromated Mo-Kα radiation (ω–2θ scan technique); 3572 data collected (2θ$_{max}$ 50.0°), 3343 unique ($R_{int} = 0.029$ based on F^2). As there were no identifiable faces an empirical absorption correction was applied using ψ scans (minimum and maximum transmission factors 0.628 and 1.000 respectively).

Structure solution and refinement. The structure was solved by heavy-atom Patterson methods[22] and expanded using Fourier techniques to locate all non-H atoms in the neutral [RuCl$_2$([16]aneSe$_4$)] molecule in the asymmetric unit.[23] All non-H atoms were refined anisotropically and hydrogen atoms were included in fixed calculated positions [with d(C–H) = 0.96 Å] but not refined. The final cycle of full-matrix least-squares refinement (on F) was based on 2287 observed reflections with [$I > 3\sigma(I)$] and 172 variable parameters and converged with $R = 0.036$, R' 0.035, using the weighting scheme $w^{-1} = \sigma^2(F)$. The maximum residual peak and minimum residual trough corresponded to +1.10 and −1.06 e Å^{-3}.

trans**-[RuCl(PPh$_3$)([16]aneSe$_4$)]PF$_6$.** Yellow, weakly diffracting, plate-like crystals of [RuCl(PPh$_3$)([16]aneSe$_4$)]PF$_6$ were obtained from a solution of the complex in CH$_2$Cl$_2$. The selected crystal (0.80 × 0.44 × 0.15 mm) was coated with mineral oil and mounted on a glass fibre under a cold stream of N$_2$ gas.

Crystal data. C$_{30}$H$_{39}$ClF$_6$P$_2$RuSe$_4$, $M = 1027.9$, monoclinic, space group $P2_1/c$, $a = 9.472(4)$, $b = 24.498(5)$, $c = 15.001(5)$ Å, $\beta = 98.40(3)°$, $U = 3443(1)$ Å^3 [from 2θ values of 20 reflections measured at ±ω (2θ = 19.0–21.0°, λ = 0.71 073 Å)], $Z = 4$, $D_c = 1.982$ g cm^{-3}, $\mu = 48.56$ cm^{-1}, $F(000) = 2000$.

Data collection and processing. Data collection used a Rigaku AFC7S diffractometer equipped with an Oxford Systems cryostream operating at 150 K, using graphite-monochromated Mo-Kα radiation (ω scan technique), 6624 data collected (2θ$_{max}$ 50.0°), 6230 unique ($R_{int} = 0.077$ based on F^2). As there were no identifiable faces an empirical absorption correction was applied using ψ scans (minimum and maximum transmission factors 0.390 and 1.000 respectively).

Structure solution and refinement. The structure was solved by heavy-atom Patterson methods[22] and expanded using Fourier techniques to locate all non-H atoms in the [RuCl(PPh$_3$)([16]aneSe$_4$)]$^+$ cation and PF$_6^-$ anion in the asymmetric unit.[23] During refinement it became apparent that the PF$_6^-$ anion was disordered. This was modelled using partial F atom occupancies such that the central P atom had twelve 50% occupied F atoms around it. This model still gave rather high thermal parameters for some of the F atoms, but resulted in an overall improvement in the structure. Also, some of the C atoms involved in the propyl linkages show high thermal parameters indicative of some disorder. However, efforts to identify alternative sites for these atoms were not successful and hence no further action was taken. The Ru, Se, P and Cl atoms were refined anisotropically and hydrogen atoms were included in fixed calculated positions [d(C–H) = 0.96 Å] but not refined. The final cycle of full-matrix least-squares refinement (on F) was based on 2693 observed reflections with [$I > 2.5\sigma(I)$] and 241 variable parameters and converged with $R = 0.083$, R' 0.085, using the weighting scheme $w^{-1} = \sigma^2(F)$. The maximum residual peak and minimum residual trough corresponded to +1.49 and −1.12 e Å^{-3}.

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