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Platinum metal ditelluroether complexes: synthesis, spectroscopic and structural studies of $[M(L–L)_2][PF_6]_2$ [M = Pd or Pt, L–L = $RTe(CH_2)_3TeR$ (R = Me or Ph) or $C_6H_4(TeMe)_2$-*o*], $[Rh(L–L)_2Cl_2]PF_6$, $[Ru(L–L)_2X_2]$ (X = Cl, Br or I) and $[Ru(L–L)_2(PPh_3)Cl]PF_6$

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The reaction of $[MCl_2(MeCN)_2]$ (M = Pd or Pt) with L–L ($RTe(CH_2)_3TeR$ (R = Me or Ph) or $C_6H_4(TeMe)_2$-*o*) and $TlPF_6$ in a 1:2:2 ratio in MeCN gave planar $[M(L–L)_2][PF_6]_2$ which was confirmed by an X-ray crystallographic study of $[Pd\{meso\text{-}C_6H_4(TeMe)_2\text{-}o\}_2][PF_6]_2$. The complexes *trans*-$[Ru(L–L)_2X_2]$ (X = Cl, Br or I) were prepared from $[Ru(dmf)_6][CF_3SO_3]_3$, L–L and LiX, whilst $[Ru(PPh_3)_3Cl_2]$, L–L and NH_4PF_6 gave *trans*-$[Ru(L–L)_2(PPh_3)Cl]PF_6$. The crystal structure of $[Ru\{MeTe(CH_2)_3TeMe\}_2(PPh_3)Cl][PF_6]$ revealed one ditelluroether in the *meso* form and the other in the DL, the first time both stereoisomers have been crystallographically identified in the same compound. In contrast in *trans*-$[Ru\{PhTe(CH_2)_3TePh\}_2Cl_2]$ both ditelluroethers are *meso* forms. For Pd, Pt and Ru multinuclear NMR spectroscopy (^1H, ^{125}Te-$\{^1H\}$, ^{195}Pt) showed a mixture of stereoisomeric forms in solution, and for the compounds of Pd and Pt pyramidal inversion at Te is fast on the NMR timescales at ambient temperatures. Reaction of $RhCl_3\cdot 3H_2O$, L–L and NH_4PF_6 gave $[Rh(L–L)_2Cl_2]PF_6$ which appear to be predominantly *trans* isomers based upon their NMR and UV/vis spectra. Attempts to oxidise the complexes of Pt^{II} or Ru^{II} (to Pt^{IV} or Ru^{III}) with halogens or electrochemically were unsuccessful, contrasting with the successful oxidation of analogous complexes with dithioether or diselenoether ligands.

Introduction

Chelating ditelluroethers including $RTe(CH_2)_3TeR$ (R = Me or Ph) and $C_6H_4(TeMe)_2$-*o* (L–L) were first reported about 10 years ago,[1,2] and a range of platinum metal halide complexes with a 1:1 metal:ditelluroether ratio were subsequently characterised, including $[M(L–L)X_2]$ (M = Pd or Pt, X = Cl, Br or I),[3,4] $[Ir(L–L)X_4]^-$,[4] and $[\{Ir(L–L)Cl_3\}_n]$.[5] Far fewer complexes with a 2:1 ditelluroether:metal ratio are known, examples being limited to some unstable cobalt(III) complexes[6] and homoleptic compounds of Cu^I and Ag^I.[7] More recently, ditelluroether complexes of Group 6 metal carbonyls and Group 7 carbonyl halides have been obtained.[8] However it remains true that far less is known about tellurium donor ligands than their thio- or seleno-ether analogues. Here we report the synthesis of some complexes of Pd, Pt, Rh and Ru with a 2:1 ditelluroether:M ratio, their spectroscopic and structural characterisation, and an exploration of the redox chemistry of the platinum and ruthenium complexes. The ligand properties of the ditelluroethers are compared with those of Se, S and Group 15 donor analogues.

Results and discussion

Palladium and platinum

The reaction of $[MCl_2(MeCN)_2]$ (M = Pd or Pt) with a large excess of the ditelluroether affords only the $[M(L–L)Cl_2]$ complexes.[3,4] However, if the halide is removed with $TlPF_6$ the products are the yellow or orange $[M(L–L)_2][PF_6]_2$ (L–L = $RTe(CH_2)_3TeR$, R = Me or Ph, or $C_6H_4(TeMe)_2$-*o*). Coordinated ditelluroethers exist as two diastereoisomers, *meso* (with *syn* R groups) and DL (*anti* R groups).[9] Proton and especially ^{125}Te-$\{^1H\}$ NMR spectroscopies have proved very useful in assigning structures to many ditelluroether complexes,[3–8] but are rather less useful for the bis(ditelluroether) complexes in the present study. The possible combinations of *meso* or DL ditelluroethers for planar $M(L–L)_2$ or *trans* $M(L–L)_2X_2$ moieties result in five possible isomers (invertomers), containing eight distinct tellurium centres, although all possible isomers need not be present in significant amounts. For lower symmetry *trans* $M(L–L)_2XY$ or *cis* $M(L–L)_2X_2$ even more resonances are predicted. The isomers interconvert by pyramidal inversion at Te, a process whose energy depends upon the metal centre present, the ligand structure, chelate ring size, and ligands *trans* to Te.[9] The complexity of the spectra and in some cases the consequences of the onset of pyramidal inversion means that assignment of resonances to particular invertomers is not possible, although usually the geometric isomer(s) present can be identified. For the planar $[M(L–L)_2]^{2+}$ (M = Pd or Pt) the Te-*trans*-Te arrangement lowers inversion barriers due to the high *trans* influence of tellurium, and at room temperature the ^1H NMR spectra of all the complexes show broad features, sometimes with ill defined splittings, showing that inversion processes are present. Similarly at 300 K the ^{125}Te-$\{^1H\}$ NMR spectra show very broad features typical of systems near to coalescence. On cooling the spectra sharpen and for the platinum complexes individual resonances resolve, but even at 210 K inversion still leads to significant broadening and ^{195}Pt satellites are not resolved. Consistent with this, none of the platinum complexes exhibited a ^{195}Pt NMR spectrum at ambient temperatures, but on cooling a solution of $[Pt\{C_6H_4(TeMe)_2\text{-}o\}_2]^{2+}$ to 210 K broad resonances appeared at δ −4790 and −4760, which are entirely reasonable shifts for a $Pt^{II}Te_4$ centre. The structure of $[Pd\{C_6H_4(TeMe)_2\text{-}o\}_2][PF_6]_2\cdot MeCN$ reveals a square planar cation with the Pd on an inversion centre, coordinated to two *meso* ditelluroether ligands (Fig. 1, Table 1). The Te–Pd–Te angles are very close to 90°, with Pd–Te 2.5716(4)–2.5789(5) Å, markedly longer than Pd–Te in

Table 1 Selected bond lengths (Å) and angles (°) for [Pd{C_6H_4-$(TeMe)_2$-*o*}$_2$][PF_6]$_2$·MeCN

Te(1)–Pd(1)	2.5716(4)	Te(1)–C(3)	2.120(7)
Te(1)–C(4)	2.132(8)	Te(2)–Pd(1)	2.5789(5)
Te(2)–C(5)	2.112(9)	Te(2)–C(6)	2.116(7)
Te(3)–Pd(2)	2.5732(5)	Te(3)–C(12)	2.112(9)
Te(3)–C(13)	2.120(7)	Te(4)–Pd(2)	2.5781(5)
Te(4)–C(10)	2.118(7)	Te(4)–C(11)	2.136(8)
Pd(1)–Te(1)–C(3)	102.3(2)	Pd(1)–Te(1)–C(4)	98.3(2)
C(3)–Te(1)–C(4)	93.6(3)	Pd(1)–Te(2)–C(5)	100.5(2)
Pd(1)–Te(2)–C(6)	102.4(2)	C(5)–Te(2)–C(6)	92.8(3)
Pd(2)–Te(3)–C(12)	99.4(3)	Pd(2)–Te(3)–C(13)	103.2(2)
C(12)–Te(3)–C(13)	92.8(3)	Pd(2)–Te(4)–C(10)	102.7(2)
Pd(2)–Te(4)–C(11)	99.7(2)	C(10)–Te(4)–C(11)	93.6(3)
Te(1)–Pd(1)–Te(2)	89.98(1)	Te(3)–Pd(2)–Te(4)	89.67(1)

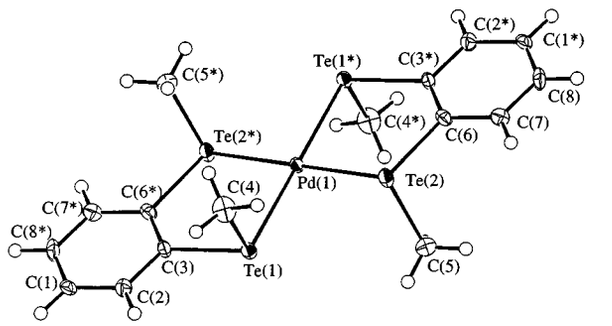

Fig. 1 View of the structure of one of the two independent [Pd{C_6H_4-$(TeMe)_2$-*o*}$_2$]$^{2+}$ cations with numbering scheme adopted (the other cation is essentially indistinguishable). Atoms marked * are related by a centre of inversion at Pd. Ellipsoids are drawn at 40% probability.

[Pd{$PhTe(CH_2)_3TePh$}Br_2][3] (2.528(1), 2.525(1) Å) and consistent with the relative *trans* influence Te > Br. Attempts to oxidise the [Pt(L–L)$_2$]$^{2+}$ to Pt^{IV} using Cl_2 were unsuccessful, causing decomposition of the complexes, and treatment of either the palladium or platinum cations with LiCl in MeCN resulted in displacement of one ditelluroether and the formation of the corresponding [M(L–L)Cl_2].[3,4]

Ruthenium

Direct reaction of the ditelluroethers with $RuCl_3$·*n*H_2O proved generally unsatisfactory, although one example *trans*-[Ru{C_6H_4-$(TeMe)_2$-*o*}$_2$$Cl_2$] has been obtained by this route.[10] Entry into the ruthenium chemistry was achieved by reaction of the ligands with [Ru$(PPh_3)_3Cl_2$] in the presence of NH_4PF_6, [Ru$(dmso)_4Cl_2$] or [Ru$(dmf)_6$][CF_3SO_3]$_3$.[11] The first reaction gave *trans*-[Ru(L–L)$_2$$(PPh_3)$Cl]$PF_6$ as orange-brown powders, whilst use of [Ru$(dmso)_4Cl_2$] afforded *trans*-[Ru(L–L)$_2$$Cl_2$]. A more general route to *trans*-[Ru(L–L)$_2$$X_2$] (X = Cl, Br or I) was reaction of [Ru$(dmf)_6$][CF_3SO_3]$_3$ with L–L and LiX in EtOH. The ruthenium(II) complexes are air-stable in the solid state; solubility in organic solvents decreases in the order Cl > Br > I with the iodides in particular very poorly soluble in chlorocarbons or MeCN, which limited solution spectroscopic studies.

The structure determination of a yellow crystal of [Ru{$MeTe(CH_2)_3TeMe$}$_2$$(PPh_3)$Cl]$PF_6$ revealed a *trans* cation with one *meso* and one DL form of the ditelluroether (Fig. 2, Table 2), the first time both forms have been identified crystallographically in one complex. The *d*(Ru–P) 2.304(4) Å and *d*(Ru–Cl) 2.467(4) Å are similar to those found[12] in *trans*-[Ru{[16]aneSe_4}-(PPh_3)Cl]PF_6 ([16]aneSe_4 = 1,5,9,13-tetraselenacyclohexadecane), 2.307(6), 2.499(5) Å respectively. The *d*(Ru–Te) lie in the range 2.636(1)–2.655(1) Å, the first examples of Ru^{II}–Te bond lengths reported. The ^{31}P-{^{1}H} NMR of this complex shows a strong resonance at δ 51.5 and the corresponding ^{125}Te-{^{1}H} NMR has four major resonances of similar intensities at δ 177, 262, 274 and 371 which show doublet splittings of 30–60 Hz attributable to ^2J(^{31}P–^{125}Te). Much weaker peaks at 53.1 (^{31}P) and 249 (^{125}Te) are assigned to a second isomer. The spectra are consistent with the form identified in the solid state being the major invertomer in solution: although there is no requirement that the form in the crystal should be the major solution form, studies of several diselenoether systems have shown this is often true in practice.[13] The *trans*-[Ru{$PhTe(CH_2)_3TePh$}$_2$$(PPh_3)$Cl]$PF_6$ shows two major ^{31}P NMR resonances of approximately equal intensity (δ 44.8, 46.0) and five ^{125}Te resonances in the range δ 500–550, suggesting two invertomers are present in significant amounts. In the case of *trans*-[Ru{$C_6H_4(TeMe)_2$-*o*}$_2$$(PPh_3)$Cl]$PF_6$ two ^{31}P resonances (δ 52.0, 44.8) are associated with five ^{125}Te resonances (δ 870–785), one of which (δ 842) is very much more intense than the rest, suggesting this is an invertomer with both ligands in the *meso* form. This complex also decomposes slowly on standing in CH_2Cl_2 solution in air, developing new ^{31}P resonances at δ 26.0 and 27.2. This is consistent with the co-ordinated PPh_3 being oxidised to $OPPh_3$, a reaction observed in other ruthenium complexes.[14] Cyclic voltammetry revealed that the complexes undergo irreversible oxidation at *ca.* 1.2 V in CH_2Cl_2 solution (*vs.* Fc–Fc^+ at 0.49 V), showing that Ru^{III} is not stable when surrounded by tellurium donors (Te_4PCl donor set).

Table 2 Selected bond lengths (Å) and angles (°) for [Ru{$MeTe(CH_2)_3TeMe$}$_2$$(PPh_3)$Cl]$PF_6$

Te(11)–Ru(1)	2.650(1)	Te(11)–C(11)	2.13(1)
Te(11)–C(12)	2.14(1)	Te(12)–Ru(1)	2.655(1)
Te(12)–C(14)	2.18(1)	Te(12)–C(15)	2.16(2)
Te(21)–Ru(1)	2.647(1)	Te(21)–C(21)	2.16(1)
Te(21)–C(22)	2.17(1)	Te(22)–Ru(1)	2.636(1)
Te(22)–C(24)	2.12(1)	Te(22)–C(25)	2.12(1)
Ru(1)–Cl(1)	2.467(4)	Ru(1)–P(1)	2.304(4)
Ru(1)–Te(11)–C(11)	105.2(5)	Ru(1)–Te(11)–C(12)	101.2(3)
C(11)–Te(11)–C(12)	90.7(6)	Ru(1)–Te(12)–C(14)	107.0(4)
Ru(1)–Te(12)–C(15)	108.0(4)	C(14)–Te(12)–C(15)	96.2(6)
Ru(1)–Te(21)–C(21)	114.3(4)	Ru(1)–Te(21)–C(22)	109.0(4)
C(21)–Te(21)–C(22)	91.8(6)	Ru(1)–Te(22)–C(24)	106.9(4)
Ru(1)–Te(22)–C(25)	109.2(4)	C(24)–Te(22)–C(25)	91.6(6)
Te(11)–Ru(1)–Te(12)	89.00(4)	Te(11)–Ru(1)–Te(21)	92.25(4)
Te(11)–Ru(1)–Te(22)	177.59(5)	Te(11)–Ru(1)–Cl(1)	87.47(9)
Te(11)–Ru(1)–P(1)	89.61(9)	Te(12)–Ru(1)–Te(21)	168.15(5)
Te(12)–Ru(1)–Te(22)	89.96(4)	Te(12)–Ru(1)–Cl(1)	90.09(9)
Te(12)–Ru(1)–P(1)	92.09(9)	Te(21)–Ru(1)–Te(22)	88.33(4)
Te(21)–Ru(1)–Cl(1)	78.21(9)	Te(21)–Ru(1)–P(1)	99.69(9)
Te(22)–Ru(1)–Cl(1)	90.35(9)	Te(22)–Ru(1)–P(1)	92.60(9)
Cl(1)–Ru(1)–P(1)	176.3(1)		

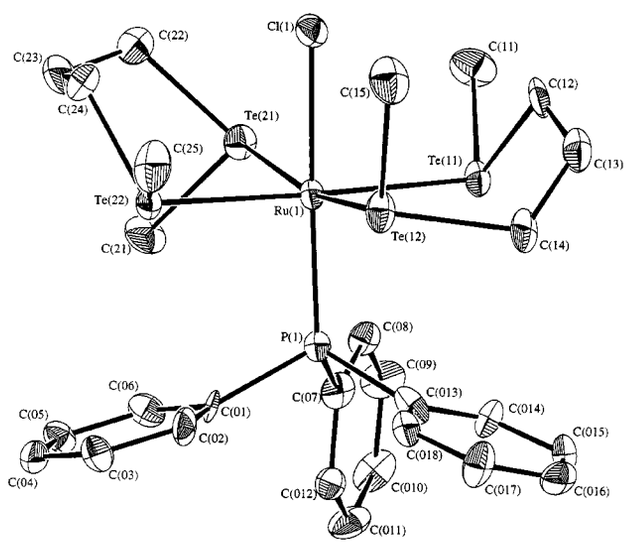

Fig. 2 View of the structure of [Ru{$MeTe(CH_2)_3TeMe$}$_2$$(PPh_3)$Cl]$^+$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

Table 3 Selected bond lengths (Å) and angles (°) for [Ru{PhTe-$(CH_2)_3TePh\}_2Cl_2$]

Te(1)–C(11)	2.142(5)	Te(1)–C(1)	2.153(6)
Te(1)–Ru(1)	2.6247(3)	Te(2)–C(21)	2.147(6)
Te(2)–C(3)	2.150(6)	Te(2)–Ru(1)	2.6194(3)
Ru(1)–Cl(1)	2.4389(13)		
C(11)–Te(1)–C(1)	89.9(2)	C(11)–Te(1)–Ru(1)	111.38(15)
C(1)–Te(1)–Ru(1)	105.15(17)	C(21)–Te(2)–C(3)	91.2(2)
C(21)–Te(2)–Ru(1)	110.93(14)	C(3)–Te(2)–Ru(1)	104.46(16)
Cl(1)–Ru(1)–Te(2)	87.62(3)	Cl(1)–Ru(1)–Te(1)	87.71(3)
Te(2)–Ru(1)–Te(1)	87.255(11)		

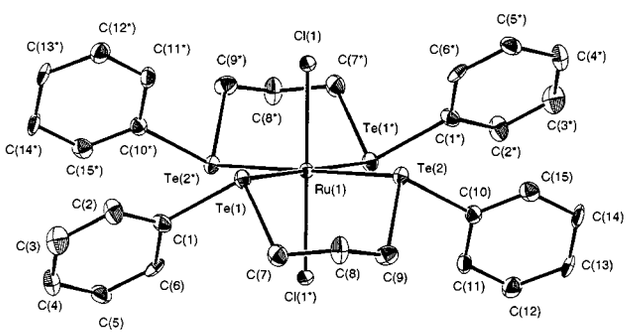

Fig. 3 View of the structure of $[Ru\{PhTe(CH_2)_3TePh\}_2Cl_2]$ with numbering scheme adopted. Atoms marked * are related by a centre of inversion at Ru. Ellipsoids are drawn at 40% probability.

The orange $[Ru(L–L)_2Cl_2]$ are air-stable solids, moderately soluble in chlorocarbons and poorly soluble in MeCN. The crystal structure of triclinic crystals of $[Ru\{PhTe(CH_2)_3TePh\}_2Cl_2]$ (Fig. 3, Table 3) revealed a *trans* geometry with the Ru on an inversion centre and the ditelluroether ligands have *meso* arrangements. The *d*(Ru–Cl) 2.4389(13) Å is shorter than that in the chlorophosphine complex (above), consistent with the expected *trans* influence order P > Cl, but is similar to those in other *trans* $Cl–Ru^{II}–Cl$ arrangements in for example *trans*-$[Ru(PhSeCH_2CH_2SePh)_2Cl_2]$ (2.413(1), 2.444(1) Å)[10] or *trans*-$[Ru\{H_2C{=}C(PPh_2)_2\}_2Cl_2]$ (2.431(1) Å).[15] The *d*(Ru–Te) (2.6194(3), 2.6247(3) Å) are slightly shorter than in the chlorophosphine. The ^1H and ^{125}Te-$\{^1H\}$ NMR spectra show that several diastereoisomers are present in solution, in particular the latter has a strong resonance at δ 638 due to a high symmetry form with all four tellurium sites identical (possibly the form present in the crystal), and six weaker resonances. The UV/vis spectra show two bands in the region 18 000–25 000 cm^{-1} as expected for low spin d^6 metal centres in local D_{4h} symmetry.[16] The characterisation of $[Ru(L–L)_2Cl_2]$ (L–L = $C_6H_4(TeMe)_2$-*o* or $MeTe(CH_2)_3TeMe$) and the corresponding bromo- and iodo-complexes was achieved by analysis and ES^+ mass spectrometry, and their assignment as *trans* isomers follows from the similar spectra to those of the dichloro-compounds. Multinuclear NMR spectroscopy was less successful due to their poor solubility, and convincing ^{125}Te NMR spectra were not observed from saturated CH_2Cl_2 solutions of the bromo- or iodo-complexes after *ca.* 2×10^6 scans. Cyclic voltammetry was used to study the oxidation of these complexes. In CH_2Cl_2 containing 0.1 mol dm^{-3} $NBu^n_4BF_4$ freshly prepared solutions of the dichloro-complexes showed irreversible or quasi-reversible oxidations at *ca.* +0.5–0.8 V (*vs.* $Fc–Fc^+$ at 0.49 V), the waves diminishing rapidly on repetitive scans consistent with deposition of material onto the electrodes. This behaviour contrasts with $[Ru(L–L)_2Cl_2]$ (L–L = various dithioether or diselenoether ligands)[10,17] which show reversible $Ru^{II}–Ru^{III}$ couples at less positive potentials, and for which the ruthenium(III) complexes can be isolated by halogen oxidation of the corresponding ruthenium(II) complex in CH_2Cl_2. Treatment of CH_2Cl_2 solutions of $[Ru(ditelluroether)_2Cl_2]$ with Cl_2 gave dark brownish solutions, which rapidly decomposed. Our inability to isolate ruthenium(III) ditelluroether complexes is a further example of the reduced ability of these ligands to stabilise higher oxidation states of transition metals compared to their lighter analogues. Phosphorus or arsenic donor ligands form quite stable ruthenium(III) complexes as *trans*-$[Ru(bidentate\ ligand)_2X_2]^+$ cations, and most exhibit electrochemically reversible $Ru^{II}–Ru^{III}$ couples.[17]

Rhodium

The reaction of $RhCl_3{\cdot}3H_2O$, L–L and NH_4PF_6 in EtOH gave deep orange $[Rh(L–L)_2Cl_2]PF_6$. The ES^+ mass spectra show ion multiplets with the correct isotope patterns for $[Rh(L–L)_2Cl_2]^+$, and the presence of PF_6^- anions is confirmed by the IR spectra which show the expected bands at *ca.* 840 (ν(P–F)) and *ca.* 560 cm^{-1} ($\delta(PF_2)$). We have been unable to grow crystals of any of these rhodium compounds, either with PF_6^- or ClO_4^- anions, suitable for an X-ray study. The UV/vis spectra each show a d–d band at *ca.* 21 000 cm^{-1} which is consistent with *trans* geometric isomers (*cis* isomers have d–d bands at higher energy, often obscured by charge-transfer transitions).[18] The ^1H NMR spectra are complex revealing a number of invertomers are present. Poor solubility made recording the ^{125}Te-$\{^1H\}$ NMR spectra difficult, but after very long accumulations the spectrum of $[Rh\{MeTe(CH_2)_3TeMe\}_2Cl_2]^+$ showed a number of doublets with δ 250–300 and with the $^1J(^{125}Te–^{103}Rh)$ couplings of 50–70 Hz. The spectrum of $[Rh\{PhTe(CH_2)_3TePh\}_2Cl_2]^+$ was similar. However, for $[Rh\{C_6H_4(TeMe)_2\text{-}o\}_2Cl_2]^+$ the ^{125}Te-$\{^1H\}$ NMR spectrum showed, in addition to seven major doublets, some evidence for a number of weaker features which may be due to the second geometric isomer (*cis*). It is notable that, for dithioether or diselenoether (L′–L′) ligands, direct reaction with $RhCl_3{\cdot}3H_2O$ leads to mixtures of *trans*- and *cis*-$[Rh(L'–L')_2Cl_2]Cl$ and $[\{Rh(L'–L')Cl_3\}_n]$[18] and pure *trans* isomers were obtained by oxidative addition to rhodium(I) analogues.[18,19]

Experimental

Infrared spectra were measured as CsI discs using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}, UV/vis spectra were recorded in solution using 1 cm path length quartz cells on a Perkin-Elmer Lambda19 spectrometer. 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 Mass Spectrometer or by positive electrospray (ES^+) using a VG Biotech Platform. The ^1H NMR spectra were recorded using a Bruker AM300 spectrometer operating at 300 MHz, ^{125}Te-$\{^1H\}$, ^{31}P-$\{^1H\}$ and ^{195}Pt NMR spectra on a Bruker AM360 spectrometer operating at 113.6, 145.8 and 77.4 MHz respectively and referenced to neat Me_2Te, 85% H_3PO_4 and aqueous $[PtCl_6]^{2-}$. Microanalyses were performed by the microanalytical service of Strathclyde University. Electrochemical studies used an Eco Chemi PGstat20 with Pt working and auxiliary electrodes.

Preparations

$[Pd\{MeTe(CH_2)_3TeMe\}_2][PF_6]_2$. The complex $[PdCl_2(MeCN)_2]$ (82 mg, 0.32 mmol) and $TlPF_6$ (226 mg, 0.65 mmol) were stirred in MeCN (30 cm^3) for 30 min under a dinitrogen atmosphere. The compound $MeTe(CH_2)_3TeMe$ (221 mg, 0.68 mmol) in MeCN (5 cm^3) was then added and the reaction stirred at room temperature for 18 h to give a yellow solution and fine white precipitate (TlCl). The solution was filtered to remove the TlCl, reduced to *ca.* 2 cm^3 *in vacuo* and diethyl ether (10 cm^3) added to precipitate a yellow solid. Yield: 220 mg, 65% (Found: C, 11.4; H, 2.3. $C_{10}H_{24}F_{12}P_2PdTe_4$ requires C, 11.4; H, 2.3%). ^1H NMR (CD_3CN): (CH_2CH_2) δ 2.3 (br) [1H]; ($TeCH_3$) 2.4 (s) [3H]; and (CH_2Te) 2.9 (m) [2H]. ^{125}Te-$\{^1H\}$ NMR (Me_2CO–$CDCl_3$, 300 K): δ 198–219 (vbr). IR/cm^{-1}: 2957w,

2924w, 1425w, 1357s, 1279s, 1212w, 1095m, 987m, 832s, 739w, 709m, 613w and 556s. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 26 660 (19 800).

The following complexes were prepared similarly.

[Pd{PhTe(CH$_2$)$_3$TePh}$_2$][PF$_6$]$_2$. Yield 70% (Found: C, 27.9; H, 2.3. $C_{30}H_{32}F_{12}P_2PdTe_4$ requires C, 27.7; H, 2.5%). ^{1}H NMR (CD_3CN): (CH_2CH_2) δ 2.6 (br) [1H]; (CH_2Te) 3.1 (br) [2H]; and (TePh) 7.58 (m) [5H]. ^{125}Te-{^{1}H} NMR (Me_2CO–$CDCl_3$, 300 K): δ *ca.* 485, 580 and 605. IR/cm^{-1}: 1570w, 1470w, 1432w, 1357s, 1260w, 1210w, 1093s, 1018w, 996m, 840s, 728m, 686m, 615w, 557s and 452w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 26 380 (33 300).

[Pd{C$_6$H$_4$(TeMe)$_2$-*o*}$_2$][PF$_6$]$_2$. Yield 80% (Found: C, 17.6; H, 1.8. $C_{16}H_{20}F_{12}P_2PdTe_4$ requires C, 17.2; H, 1.8%). ^{1}H NMR (CD_3CN): ($TeCH_3$) δ 2.6 (s) [3H] and (C_6H_4) 7.8 (m) [2H]. ^{125}Te-{^{1}H} (Me_2CO–$CDCl_3$, 300 K): δ 770–825 (br). IR/cm^{-1}: 1356s, 1093s, 985m, 834s, 756m, 613w and 556m. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 26 600 (23 900).

[Pt{MeTe(CH$_2$)$_3$TeMe}$_2$][PF$_6$]$_2$. Yield 80% (Found: C, 11.0; H, 2.0. $C_{10}H_{24}F_{12}P_2PtTe_4$ requires C, 10.5; H, 2.1%). ^{1}H NMR (CD_3CN): (CH_2CH_2) δ 2.24 (q) [1H]; ($TeCH_3$) 2.43 (s) [3H]; and (CH_2Te) 3.02 (t) [2H]. ^{125}Te-{^{1}H} NMR (Me_2CO–$CDCl_3$, 300 K): δ 195, 196, 200, 201 and 202. IR/cm^{-1}: 2922w, 2853w, 1357s, 1262vw, 1228w, 1205w, 1092s, 986w, 834s, 613w and 557s. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 30 770 (sh) (8300).

[Pt{PhTe(CH$_2$)$_3$TePh}$_2$][PF$_6$]$_2$. Yield 76% (Found: C, 26.0; H, 2.1. $C_{30}H_{32}F_{12}P_2PtTe_4$ requires C, 26.0; H, 2.3%). ^{1}H NMR (CD_3CN): (CH_2CH_2) δ 2.5 (br) [1H]; (CH_2Te) 3.0 (br) [1H]; 3.26 (br) [1H]; and (TePh) 7.58 (m) [5H]. ^{125}Te-{^{1}H} NMR (Me_2CO–$CDCl_3$, 300 K): δ 570–580 (br). IR/cm^{-1}: 3070w, 1569w, 1471w, 1357m, 1210w, 1093m, 1015w, 996m, 838s, 732m, 689m, 613w, 557s and 453w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 29 950 (8400) and 33 330 (16 600).

[Pt{C$_6$H$_4$(TeMe)$_2$-*o*}$_2$][PF$_6$]$_2$. Yield 75% (Found: C, 15.9; H, 1.6. $C_{16}H_{20}F_{12}P_2PtTe_4$ requires C, 15.9; H, 1.7%). ^{1}H NMR (CD_3CN): ($TeCH_3$) δ 2.6 (m) [3H]; and (C_6H_4) 7.84 (m) [2H]. ^{125}Te-{^{1}H} NMR (MeCN–CD_3CN, 300 K): δ 692 and 720 (m). ^{195}Pt-{^{1}H} (Me_2CO–$CDCl_3$, 210 K): δ −4790 and −4760. IR/cm^{-1}: 1357s, 1261w, 1092s, 987m, 839s, 743m, 613m and 557s. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 32 800 (14 700).

[Ru{MeTe(CH$_2$)$_3$TeMe}$_2$(PPh$_3$)Cl][PF$_6$]. The complex [$RuCl_2(PPh_3)_3$] (372 mg, 0.39 mmol) and $MeTe(CH_2)_3TeMe$ (274 mg, 0.84 mmol) were refluxed for 3 h under a dinitrogen atmosphere in EtOH (40 cm^3). The orange solution was cooled to room temperature after which NH_4PF_6 (221 mg, 1.36 mmol) was added. A light orange precipitate was formed immediately. The reaction mixture was refluxed for 10 min. After cooling, the solution was reduced to *ca*. 2 cm^3 *in vacuo* and the yellow-orange precipitate collected. Yield 428 mg, 92% (Found: C, 28.0; H, 3.3. $C_{28}H_{39}ClF_6P_2RuTe_4$ requires C, 28.1; H, 3.3%). ^{1}H NMR ($CDCl_3$): δ 1.2–2.6 (CH_2 + CH_3) and 7.4–7.6 (Ph). ^{31}P-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 51.5 (br, s), 53.1 (PPh_3) and −143 (septet, PF_6). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 177 (−), 249 (^2J(^{31}P–^{125}Te) = 50), 262 (^2J = 30), 274 (^2J = 60) and 371 (^2J = 55 Hz). ES$^+$ (MeCN): *m*/*z* = 1055, 833 and 792; calc. for [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{35}Cl(PPh_3)]$^+$ 1053, [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{35}Cl + MeCN]$^+$ 842 and [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{35}Cl]$^+$ 801. IR/cm^{-1}: 1581w, 1478w, 1430m, 1412m, 1357m, 1274w, 1219w, 1086m, 995w, 960w, 840s, 753w, 704m, 614w, 557s, 516s, 480w, 423w, 279w, 246w and 204w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 25 200 (630) and 37 740 (22 440).

[Ru{PhTe(CH$_2$)$_3$TePh}$_2$(PPh$_3$)Cl][PF$_6$]. Yield 89% (Found: C, 39.9; H, 3.4. $C_{48}H_{47}Cl_2F_6P_2RuTe_4$ requires C, 39.8; H, 3.3%). ^{1}H NMR ($CDCl_3$): δ 7.88–6.25 (Ph) and 2.96–2.23 (CH_2). ^{31}P-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 44.8, 46.0 (PPh_3) and −145 (septet, PF_6). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 500, 508.5, 511.5, 525.5 and 544 (^2J(^{31}P–^{125}Te) couplings poorly resolved). ES$^+$ (MeCN): *m*/*z* = 933, 893 and 852; calc. for [^{102}Ru{Ph^{130}Te(CH$_2$)$_3$^{130}TePh}^{35}Cl(PPh_3) + 2MeCN]$^+$ 937, [^{102}Ru{Ph^{130}Te(CH$_2$)$_3$^{130}TePh}^{35}Cl(PPh_3) + MeCN]$^+$ 896 and [^{102}Ru{Ph^{130}Te(CH$_2$)$_3$^{130}TePh}^{35}Cl(PPh_3)]$^+$ 855. IR/cm^{-1}: 1576w, 1479m, 1435m, 1358m, 1261w, 1085m, 1018w, 997w, 835s, 732m, 690m, 555m, 530m, 450w, 428w, 280w and 256w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 23 000 (300), 26 200 (1055) and 32 500 (6490).

[Ru{C$_6$H$_4$(TeMe)$_2$-*o*}$_2$(PPh$_3$)Cl][PF$_6$]. Yield 37% (Found: C, 32.0; H, 2.5. $C_{34}H_{35}ClF_6P_2RuTe_4$ requires C, 32.2; H, 2.8%). ^{1}H NMR ($CDCl_3$): δ 1.95–2.5 (m, CH_3) and 7.3–8.0 (m, C_6H_4). ^{31}P-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 44.8, 52.0 (PPh_3) and −143 (septet, PF_6). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 785, 797, 842 (major), 854 and 870 (^2J(^{31}P–^{125}Te) couplings of *ca.* 30–55 Hz poorly resolved). ES$^+$ (MeCN): *m*/*z* = 1123, 902 and 862; calc. for [^{102}Ru{C$_6$H$_4$(^{130}TeMe)$_2$-*o*}$_2$^{35}Cl(PPh_3)]$^+$ 1131, [^{102}Ru{C$_6$H$_4$(^{130}TeMe)$_2$}$_2$^{35}Cl + MeCN]$^+$ 910 and [^{102}Ru{C$_6$H$_4$(^{130}TeMe)$_2$}$_2$^{35}Cl]$^+$ 869. IR/cm^{-1} 1478m, 1431m, 1408m, 1356m, 1256w, 1217w, 1087s, 1024w, 998w, 957w, 840s, 747m, 697m, 615w, 557m, 526m, 462w, 428w, 327w, 298w, 216w and 201w.

[Ru{MeTe(CH$_2$)$_3$TeMe}$_2$Cl$_2$]. *Method 1.* The complex [Ru(dmf)$_6$][CF_3SO_3]$_3$ (151 mg, 0.155 mmol), $MeTe(CH_2)_3TeMe$ (100 mg, 0.307 mmol) and LiCl (42 mg, 0.991 mmol) in EtOH (70 cm^3) were refluxed for 4 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: 40 mg, 32% (Found: C, 13.9; H, 3.1. $C_{10}H_{24}Cl_2RuTe_4$ requires C, 14.5; H, 2.9%). ^{1}H NMR ($CDCl_3$): δ 2.0–3.32 (m). ES$^+$ (MeCN): *m*/*z* = 834, 793 and 754; calc. for [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{35}Cl + MeCN]$^+$ 842, [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{35}Cl]$^+$ 801 and [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$]$^+$ 766. IR/cm^{-1}: 2918w, 1356s, 1270m, 1227w, 1151m, 1090m, 1028m, 834w, 636m, 516w and 216w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 21 000 (180), 24 600 (540) and 38 300 (18 235).

Method 2. The complex [Ru(dmso)$_4$Cl$_2$] (71 mg, 0.129 mmol) and $MeTe(CH_2)_3TeMe$ (87 mg, 0.267 mmol) in MeOH were refluxed for 3 h. The solvent was reduced to *ca.* 1 cm^3 *in vacuo* and Et_2O added to afford a light orange precipitate. Yield 84 mg, 78%.

Unless indicated otherwise, the ruthenium complexes below were made by method 1 using the appropriate LiX.

[Ru{MeTe(CH$_2$)$_3$TeMe}$_2$Br$_2$]. Yield 49% (Found: C, 12.7; H, 2.5. $C_{10}H_{24}Br_2RuTe_4$ requires C, 13.1; H, 2.6%). ^{1}H NMR ($CDCl_3$): δ 1.98–2.93 (CH_2, CH_3). ES$^+$ (MeCN): *m*/*z* = 878 and 839; calc. for [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{79}Br + MeCN]$^+$ 886 and [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$^{79}Br]$^+$ 845. IR/cm^{-1} 2918w, 1357s, 1272m, 1092s, 1028m, 987w, 834m, 636m, 534w, 248w and 229w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}) 19 200 (570), 24 700 (1575) and 36 250 (1978).

[Ru{MeTe(CH$_2$)$_3$TeMe}$_2$I$_2$]. Yield 16% (Found: C, 11.3; H, 2.5. $C_{10}H_{24}I_2RuTe_4$ requires C, 11.9; H, 2.4%). ^{1}H NMR ($CDCl_3$): δ 2.02–2.32 (CH_2, CH_3). ES$^+$ (MeCN): *m*/*z* = 1053 and 884; calc. for [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$I + MeCN]$^+$ 1061 and [^{102}Ru{Me^{130}Te(CH$_2$)$_3$^{130}TeMe}$_2$I]$^+$ 893. IR/cm^{-1}: 2918w, 1358s, 1092m, 834m, 614w, 511w and 217w.

[Ru{PhTe(CH$_2$)$_3$TePh}$_2$Cl$_2$]. From [Ru(dmso)$_4$Cl$_2$] as above (82%) (Found: C, 33.0; H, 3.0. $C_{30}H_{32}Cl_2RuTe_4$ requires C, 33.5;

Table 4 Crystallographic data collection and refinement parameters

	[Pd{C_6H_4(TeMe)$_2$-*o*}$_2$]-[PF_6]$_2$·MeCN	[Ru{PhTe(CH_2)$_3$TePh}$_2$$Cl_2$]	[Ru{MeTe(CH_2)$_3$TeMe}$_2$(PPh$_3$)Cl]PF_6
Formula	$C_{18}H_{23}F_{12}NPdTe_4$	$C_{30}H_{32}Cl_2RuTe_4$	$C_{28}H_{39}ClF_6P_2RuTe_4$
M	1160.11	592.22	1198.48
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.9645(6)	10.3523(4)	9.296(3)
b/Å	18.896(2)	10.7860(4)	30.811(2)
c/Å	8.9325(5)	11.1139(5)	12.732(3)
α/°	94.536(6)	114.60(4)	
β/°	95.649(5)	107.14(4)	105.40(2)
γ/°	99.533(7)	102.42(4)	
U/Å^3	1478.0(2)	993.33(7)	3515(1)
Z	2	1	4
D_c/g cm^{-3}	2.607	2.203	2.264
μ(Mo-Kα)/cm^{-1}	46.94	38.35	39.18
Absorption correction (maximum and minimum transmission factors)	—	0.859, 0.458	1.000, 0.865
Unique obs. reflections	5223	5594	6316
Obs. reflections with [$I_o > 2\sigma(I_o)$]	4284		3723
No. parameters	355	206	379
R	0.031	0.050[a]	0.045
R′	0.035	0.118[a]	0.051

[a] *R*1, *wR*2 ($I > 2\sigma(I)$) 0.076, 0.013 (all data).

H, 3.0%). ^{1}H NMR ($CDCl_3$): δ 1.86–3.75 (12 H, m, CH_2) and 6.91–7.92 (10 H, m, C_6H_5). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 545.6, 587.7, 592.6, 606.9, 637.6, 644.5 and 653.4. ES$^+$ (MeCN): *m*/*z* = 1038; calc. for [^{102}Ru{Ph^{130}Te(CH_2)$_3$^{130}TePh}$_2$-^{35}Cl]$^+$ 1049. IR/cm^{-1}: 3049w, 2929w, 1572m, 1474m, 1432s, 1413m, 1359s, 1261w, 1195w, 1098m, 1018m, 997m, 875w, 793w, 727s, 690s, 530w, 453m, 305w, 258w and 225w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 20 600 (240) and 24 300 (750).

[Ru{PhTe(CH_2)$_3$TePh}$_2$$Br_2$]. Brown powder. Yield: 21% (Found: C, 31.3; H, 2.9. $C_{30}H_{32}Br_2RuTe_4$ requires C, 31.0; H, 2.8%). ^{1}H NMR ($CDCl_3$): δ 2.65–3.93 (12 H, m, CH_2) and 6.91–7.87 (20 H, m, C_6H_5). ES$^+$ (MeCN): *m*/*z* = 1083; calc. for [^{102}Ru{Ph^{130}Te(CH_2)$_3$^{130}TePh}$_2$^{79}Br]$^+$ 1093. IR/cm^{-1}: 1473w, 1433m, 1358m, 1198w, 1061m, 998w, 740m, 689m, 671m, 610m, 454m and 223w.

[Ru{C_6H_4(TeMe)$_2$-*o*}$_2$$Cl_2$]. Yield 78% (Found: C, 21.2; H, 2.4. $C_{16}H_{20}Cl_2RuTe_4$ requires C, 21.5; H, 2.3%). ^{1}H NMR ($CDCl_3$): δ 1.20–2.65 (6 H, m, CH_3) and 7.38–7.93 (4 H, m, C_6H_5). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 804, 885, 890, 893, 894, 914 and 917. ES$^+$ (MeCN): *m*/*z* = 901 and 859; calc. for [^{102}Ru-{C_6H_4(^{130}TeMe)$_2$}$_2$^{35}Cl + MeCN]$^+$ 910 and [^{102}Ru{C_6H_4-(^{130}TeMe)$_2$}$_2$^{35}Cl]$^+$ 869. IR/cm^{-1}: 1438w, 1410w, 1358s, 1260w, 1098m, 831w, 803w, 749m, 594s, 248w and 209w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 20 300 (110) and 25 900 (1300).

[Ru{C_6H_4(TeMe)$_2$-*o*}$_2$$Br_2$]. Yield 45% (Found: C, 18.9; H, 2.0. $C_{16}H_{20}Br_2RuTe_4$ requires C, 19.5; H, 2.1%). ^{1}H NMR ($CDCl_3$): δ 2.13–2.97 (6 H, m, CH_3) and 7.40–7.97 (4 H, m, C_6H_5). ES$^+$ (MeCN): *m*/*z* = 946 and 904; calc. for [^{102}Ru{C_6H_4(^{130}Te-Me)$_2$}$_2$^{79}Br + MeCN]$^+$ 954 and [^{102}Ru{C_6H_4(^{130}TeMe)$_2$}$_2$^{79}Br]$^+$ 913. IR/cm^{-1}: 2929w, 2852w, 1356s, 1256w, 1089m, 991w, 834w, 746w, 638w and 542w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 21 500 (800) and 25 840 (2520).

[Ru{C_6H_4(TeMe)$_2$-*o*}$_2$$I_2$]. Yield 32% (Found: C, 13.9; H, 3.1. $C_{16}H_{20}I_2RuTe_4$ requires C, 14.5; H, 2.9%). ^{1}H NMR ($CDCl_3$): δ 2.31–2.54 (6 H, CH_3) and 7.30–7.44 (4 H, m, C_6H_5). ES$^+$ (MeCN): *m*/*z* = 998 and 950; calc. for [^{102}Ru{C_6H_4(^{130}Te-Me)$_2$}$_2$I + MeCN]$^+$ 1002 and [^{102}Ru{C_6H_4(^{130}TeMe)$_2$}$_2$I]$^+$ 961. IR/cm^{-1}: 2929w, 1593s, 1358s, 1076m, 883w, 747w, 598w, 511w and 254m. UV/vis (diffuse reflectance)/cm^{-1}: 20 900, 25 200 and 31 200.

[Rh{MeTe(CH_2)$_3$TeMe}$_2$$Cl_2$]$PF_6$. The compounds $RhCl_3$·$3H_2O$ (51 mg, 0.194 mmol) and MeTe(CH_2)$_3$TeMe (125 mg, 0.384 mmol) in EtOH (30 ml) were refluxed for 30 min, NH_4PF_6 (41 mg, 0.252 mmol) was then added and stirred at room temperature for 1 h. The resulting orange precipitate was collected and washed with diethyl ether. Yield: 76 mg, 41% (Found: C, 12.3; H, 1.7. $C_{10}H_{24}Cl_2F_6PRhTe_4$ requires C, 12.4; H, 2.5%). ^{1}H NMR (CD_3CN): δ 2.7–2.9 (CH_3 + CH_2) and 3.0–3.1 (CH_2). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 250.5 (^1J(^{125}Te–^{103}Rh) 60), 259.5 (60), 283.4 (50), 292 (70), 300 (−) and 300.5 (68). ES$^+$ (MeCN): *m*/*z* = 831; calc. for [Rh{Me^{130}Te(CH_2)$_3$^{130}TeMe}$_2$-^{35}Cl_2]$^+$ 837. IR/cm^{-1}: 1359s, 1262w, 1220w, 1203m, 1090m, 994w, 837s, 745w, 612w, 558m, 331m and 203w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 21 800 (1250).

The following complexes were made similarly.

[Rh{PhTe(CH_2)$_3$TePh}$_2$$Cl_2$]$PF_6$. Yield 84% (Found: C, 29.7; H, 1.5. $C_{30}H_{32}Cl_2F_6PRhTe_4$ requires C, 29.5; H, 2.6%). ^{1}H NMR ($(CD_3)_2SO$): δ 2.9–3.5 (CH_2) and 7.1–7.8 (Ph). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 481.5 (^1J(^{125}Te–^{103}Rh) 75), 492 (72), 534 (70), 540 (−), 542 (75) and 558 (80). ES$^+$ (MeCN): *m*/*z* = 1077; calc. for [Rh{Ph^{130}Te(CH_2)$_3$^{130}TePh}$_2^{35}Cl_2$]$^+$ 1085. IR/cm^{-1}: 1571w, 1474m, 1434m, 1358m, 1264w, 1206w, 1091m, 1017w, 997m, 837s, 731m, 690m, 654w, 613w, 557m, 451m, 339w, 255w and 226w. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 21 350 (1700).

[Rh{C_6H_4(TeMe)$_2$-*o*}$_2$$Cl_2$]$PF_6$. Yield 65% (Found: C, 18.6; H, 1.7. $C_{16}H_{20}Cl_2F_6PRhTe_4$ requires C, 18.45; H, 1.9%). ^{1}H NMR ($(CD_3)_2SO$): δ 2.3–2.7 (Me) and 7.4–7.8 (C_6H_4). ^{125}Te-{^{1}H} NMR ($CDCl_3$–CH_2Cl_2): δ 799 (^1J(^{125}Te–^{103}Rh) 90), 814 (−), 840.3 (70), 840.5 (70), 848.5 (70), 861 (55), 869 (80) and 891.5 (70). ES$^+$ (MeCN): *m*/*z* = 898; calc. for [Rh{C_6H_4(^{130}TeMe)$_2$}$_2$-^{35}Cl_2]$^+$ 905. IR/cm^{-1}: 2935w, 1665w, 1355m, 1259w, 1087s, 992sh, 842s, 751m, 561m, 421m, 327w, 303w, 251w and 208m. UV/vis (MeCN)/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}): 21 400 (1380).

Crystal structures of $[Pd\{C_6H_4(TeMe)_2\text{-}o\}_2][PF_6]_2\cdot MeCN$, $[Ru\{PhTe(CH_2)_3TePh\}_2Cl_2]$ and $[Ru\{MeTe(CH_2)_3TeMe\}_2(PPh_3)Cl]PF_6$

Details of the crystallographic data collection and refinement parameters are given in Table 4. For $[Pd\{C_6H_4(TeMe)_2\text{-}o\}_2][PF_6]_2\cdot MeCN$ and $[Ru\{MeTe(CH_2)_3TeMe\}_2(PPh_3)Cl]PF_6$ data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K and graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). The data for $[Ru\{MeTe(CH_2)_3TeMe\}_2(PPh_3)Cl]PF_6$ were corrected for absorption using ψ-scans. The structures were solved by heavy atom methods[20] and developed by iterative cycles of full-matrix least-squares refinement[21] and Fourier-difference syntheses. All non-H atoms were refined anisotropically and H atoms were placed in fixed, calculated positions. The complex $[Pd\{C_6H_4(TeMe)_2\text{-}o\}_2][PF_6]_2\cdot MeCN$ shows two independent half-cations with inversion symmetry, two PF_6^- anions on general positions and two disordered half MeCN solvent molecules in the asymmetric unit. The latter are disordered across inversion centres such that the methyl C atom of one form is superimposed on the cyano C atom of the other form and *vice versa*, with the inversion centre at the midpoint of this C–C vector. The H atoms associated with the MeCN molecules were not located from the difference map and therefore were omitted from the final structure factor calculation.

For $[Ru\{PhTe(CH_2)_3TePh\}_2Cl_2]$ data collection used an Enraf-Nonius Kappa CCD diffractometer operating at 150 K and Mo-Kα X-radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption using SORTAV.[22] The structures were solved by heavy atom methods[20] and refined using SHELXL 97.[23] The molecule has crystallographic *i* symmetry (at Ru). All non-H atoms were refined anisotropically and H atoms were placed in fixed, calculated positions.

CCDC reference number 186/1454.

See http://www.rsc.org/suppdata/dt/1999/2071/ for crystallographic files in .cif format.

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