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Synthesis and complexation of a new facultative tridentate S_2Te donor ligand $MeS(CH_2)_3Te(CH_2)_3SMe$: crystal structures of $[Rh(Cp^*)(S_2Te)][PF_6]_2$ and $[PtCl(S_2Te)]PF_6$

Matthew Hesford, William Levason *, Simon D. Orchard, Gillian Reid

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

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Abstract

The syntheses and spectroscopic characterisation of the new facultative tridentate tellurium containing ligands $MeS(CH_2)_3Te(CH_2)_3SMe$ (S_2Te) and $H_2N(CH_2)_3Te(CH_2)_3NH_2$ are described. The complexes of the former, *fac*-$[Mn(CO)_3(S_2Te)]CF_3SO_3$, $[Rh(Cp^*)(S_2Te)][PF_6]_2$, $[MCl(S_2Te)]PF_6$ (M = Pd or Pt), $[Cu(S_2Te)]BF_4$ and $[Ag(S_2Te)]CF_3SO_3$ have been prepared and characterised by analysis, IR, ^{1}H-, $^{13}C\{^1H\}$-, ^{125}Te- and ^{195}Pt-NMR spectroscopy and mass spectrometry. The X-ray crystal structures of $[Rh(Cp^*)(S_2Te)][PF_6]_2$ and $[PtCl(S_2Te)]PF_6$ are described. The results are compared with those obtained from complexes of the related tridentates $Te\{(CH_2)_3TeR\}_2$, $Se\{(CH_2)_3SeMe\}_2$ and $S\{(CH_2)_3SR\}_2$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Telluroether; Thioether; Rhodium; Platinum; Copper

1. Introduction

We are currently exploring the synthesis and metal complexation of acyclic polydentate and macrocyclic ligands containing tellurium [1–4]. Recent work has included the preparation of the first facultative tritelluroethers $RTe(CH_2)_3Te(CH_2)_3TeR$ (R = Me or Ph) [5] and a variety of mixed donor macrocycles containing tellurium and sulphur, including 9, 11 and 12 membered ring S_2Te donor ligands [6]. In connection with these studies we prepared the new facultative tridentate 2,10-dithia-6-tellura-undecane, $MeS(CH_2)_3Te(CH_2)_3SMe$ and report here its synthesis and the preparation of some metal complexes which illustrate its coordination modes and allows comparisons with related Group 16 donor ligands. Relevant Group 16 ligands in addition to $RTe(CH_2)_3Te(CH_2)_3TeR$ [5], include $MeS(CH_2)_nS(CH_2)_nSMe$ ($n = 2$ or 3) [7,8], $MeSe(CH_2)_nSe(CH_2)_nSeMe$ [8,9] and $RS(CH_2)_3S(CH_2)_3SR$ (R = Et, Ph or ^{i}Pr) [10]. The dimethylene-linked $MeS(CH_2)_2Te(CH_2)_2SMe$, has been described, and is apparently unstable, with few complexes known [11]. The synthesis of a new N_2Te donor ligand is also described.

2. Experimental

Physical measurements were made as described elsewhere [1,3,5]. All preparations were carried out under dinitrogen.

2.1. $MeS(CH_2)_3Te(CH_2)_3SMe$

Finely ground tellurium powder (3.19 g, 0.025 mol) was added to a solution of NaOH (13 g) and Rongalite, $HOCH_2SO_2Na_2{\cdot}2H_2O$ (10 g) in water (50 ml) and the mixture refluxed for 30 min to produce a white suspension. A solution of $Br(CH_2)_3SMe$ [7] (8.45 g, 0.05 mol) in EtOH (25 ml) was added and the mixture refluxed for 1.5 h, after which it was stirred at room temperature overnight. The mixture was extracted with Et_2O (3 × 25 ml) and the organic extract was dried over $MgSO_4$. Filtration and removal of the solvent in vacuo left a

* Corresponding author. Tel.: +44-2380-593792; fax: +44-2380-593781.

E-mail address: wxl@soton.ac.uk (W. Levason).

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red–orange oil: 6.2 g, 81%. Anal. Found: C, 31.2; H, 5.6. Calc. for $C_8H_{18}S_2Te$: C, 31.4; H, 5.9%. ^{1}H-NMR ($CDCl_3$): 1.98 (quin, 2H, $CH_2CH_2CH_2$), 2.06 (s, 3H, SMe), 2.53 (t, 2H, SCH_2), 2.69 (t, 2H, CH_2Te). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 1.5 ($^1J_{Te-C} = 155$ Hz, CH_2Te), 15.7 (MeS), 31.6 (CH_2S), 36.2 ($CH_2CH_2CH_2$). $^{125}Te\{^1H\}$-NMR ($CDCl_3$): 238; (neat) 241. FABMS (3-NOBA); m/z: 308, 219; calc. for $[C_8H_{18}S_2^{130}Te]^+$ 308, $[C_4H_9S^{130}Te]^+$, 219.

2.2. $[Mn(CO)_3\{MeS(CH_2)_3Te(CH_2)_3SMe\}]CF_3SO_3$

A solution of $[Mn(CO)_5Cl]$ (0.10 g, 0.43 mmol) in acetone (30 ml) was refluxed with $AgCF_3SO_3$ (0.11 g, 0.44 mmol) for 1 h to form a solution of $[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$ and a precipitate of AgCl. The solution was transferred via a cannula to the ligand (0.13 g, 0.43 mmol). The solution was gently refluxed for 30 min, stirred overnight and then concentrated in vacuo to ca. 5 ml. Injection into ice-cold Et_2O (20 ml) precipitated a yellow–brown gum which was dried in vacuo: 0.22 g, 86%. IR (cm^{-1}, CH_2Cl_2): ν(CO) 2035, 1950. ES$^+$MS (MeCN); m/z: 447; calc. for $[C_{11}H_{18}MnO_3S_2^{130}Te]^+$ 447. ^{1}H-NMR ($CDCl_3$): 2.3–4.0 (br,m). $^{13}C\{^1H\}$-NMR (CH_2Cl_2): 217 (br, CO), 39.2 ($CH_2CH_2CH_2$), 25.9 (MeS), 25.4 (CH_2S), 15.5 (CH_2Te). $^{125}Te\{^1H\}$-NMR (CH_2Cl_2): 81. ^{55}Mn-NMR (CH_2Cl_2): -645. $W_{1/2} = 1850$ Hz.

2.3. $[PdCl\{MeS(CH_2)_3Te(CH_2)_3SMe\}]PF_6$

A solution of $[PdCl_2(MeCN)_2]$ (0.08 g, 0.32 mmol) in MeCN (5 ml), the ligand (0.1 g 0.34 mmol) and $TlPF_6$ (0.13 g, 0.35 mmol) was stirred overnight, filtered through celite and reduced in volume to ca. 10 ml. This was added to ice-cold Et_2O (20 ml), and the precipitate separated and recrystallised from Me_2CO–Et_2O to give a yellow solid. 0.09 g, 43%. Anal. Found: C, 17.4; H, 3.0; calc. for $C_8H_{18}ClF_6PPdS_2Te \cdot 1/4Et_2O$: C, 17.7; H, 3.3%. IR ($cm^{-1}$): 830, 559 ($PF_6$), 313 (Pd–Cl). ^{1}H-NMR ($(CD_3)_2CO$): 1.98 (m, $CH_2CH_2CH_2$), 2.6(s, SMe), 2.9 (m, SCH_2), 3.4 (m, CH_2Te). $^{125}Te\{^1H\}$-NMR (CH_2Cl_2): 379. ES$^+$ Mass spectrum MeCN; m/z: 449; calc. for $[C_8H_{18}^{35}Cl^{106}PdS_2^{130}Te]^+$ 449.

2.4. $[PtCl\{MeS(CH_2)_3Te(CH_2)_3SMe\}]PF_6$

$PtCl_2$ (0.05 g, 0.2 mmol) was refluxed in MeCN (30 ml) and when dissolution was complete, $TlPF_6$ (0.08 g, 0.21 mmol) was added followed by S_2Te (0.06 g, 0.2 mmol) and the mixture stirred for 18 h. The solvent was removed, the residue dissolved in acetone and filtered through celite. After reduction to ca. 5 ml, the product was precipitated with excess Et_2O: 0.05 g, 38%. Anal. Found: C, 14.6; H, 2.6; calc. for $C_8H_{18}ClF_6PPtS_2Te$: C, 14.1; H, 2.7%. IR (cm^{-1}): 838, 559 (PF_6), 306 (Pt–Cl). ^{1}H-NMR ($(CD_3)_2CO$): 2.6 (m, $CH_2CH_2CH_2$), 2.7, 2.85, 2.9 (SMe), 2.9 (m, SCH_2), 3.4 (m, CH_2Te). $^{125}Te\{^1H\}$-NMR ($(CH_3)_2CO$): 356, 348. ^{195}Pt-NMR ($(CH_3)_2CO$, -80 °C): -3079, -3140. ES$^+$ (MeCN); m/z: 537; calc. for $[C_8H_{18}^{35}Cl^{195}PtS_2^{130}Te]^+$ 538.

2.5. $[Rh(Cp^*)\{MeS(CH_2)_3Te(CH_2)_3SMe\}][PF_6]_2$

A MeOH solution (15 ml) of $[\{Rh(Cp^*)Cl_2\}_2]$ (0.08 g, 0.13 mmol), $TlPF_6$ (0.20 g, 0.575 mmol) and the ligand (0.08 g, 0.26 mmol) was refluxed for 2 h. The TlCl precipitate was removed and the solution concentrated to ca. 5 ml and the product precipitated with excess Et_2O: 0.03 g, 29%. Anal. Found: C, 25.8; H, 3.8; calc. for $C_{18}H_{33}F_{12}P_2RhS_2Te$: C, 25.9; H, 4.0%. IR ($cm^{-1}$): 840, 560 ($PF_6$). ^{1}H-NMR ($(CD_3)_2CO$): 2.2 (m, $CH_2CH_2CH_2$), 2.6 (s, MeC), 2.73 (s, SMe), 2.8–3.4 ($SCH_2 + CH_2Te$). $^{125}Te\{^1H\}$-NMR ($(CH_3)_2CO$): 191 ($^1J_{Rh-Te} = 94$ Hz). $^{13}C\{^1H\}$-NMR ($(CH_3)_2CO$): 106 (C_5), 36.8, 22.0 ($CH_2CH_2CH_2$), 25.0 (SMe), 22.0 (CH_2S), 9.1 (MeC), 14.0 (CH_2Te). ES$^+$ (MeCN); m/z: 273; calc. for $[C_{18}H_{33}RhS_2^{130}Te]^{2+}$ 273.

2.6. $[Cu\{MeS(CH_2)_3Te(CH_2)_3SMe\}]BF_4$

A CH_2Cl_2 solution (40 ml) of ligand (0.08 g, 0.25 mmol) and $[Cu(MeCN)_4]BF_4$ (0.08 g, 0.25 mmol) was stirred at room temperature for 1 h, then concentrated to ca. 5 ml and the product precipitated with Et_2O (30 ml): 0.09 g, 79%. Anal. Found: C, 23.2; H, 4.3; calc. for $C_8H_{33}BCuF_4S_2Te \cdot 1/2MeCN$: C, 22.7; H, 4.0%. IR ($cm^{-1}$): 2270 (MeCN), 1080 ($BF_4$). ^{1}H-NMR ($(CD_3)_2CO$): 1.98 MeCN, 2.2 (m, $CH_2CH_2CH_2$), 2.32 (s, SMe), 2.76 (m, SCH_2), 2.88 (m, CH_2Te). $^{125}Te\{^1H\}$-NMR ($(CH_3)_2CO$): 99. $W_{1/2} = 700$ Hz. ES$^+$ (MeCN); m/z: 371; calc. for $[C_8H_{18}^{63}CuS_2^{130}Te]^+$ 371.

2.7. $[Ag\{MeS(CH_2)_3Te(CH_2)_3SMe\}]CF_3SO_3$

$AgCF_3SO_3$ (0.09 g, 0.34 mmol) and ligand (0.10 g, 0.34 mmol) were stirred together in CH_2Cl_2 (30 ml) in the dark for 30 min. The solvent was reduced to ca. 10 ml, n-hexane (20 ml) added and the solution refrigerated to yield a white solid: 0.1 g, 64%. Anal. Found: C, 19.7; H, 2.6; calc. for $C_9H_{18}AgF_3O_3STe$: C, 19.2; H, 3.2%. ^{1}H-NMR (CD_2Cl_2): 1.90 (m, $CH_2CH_2CH_2$), 2.0 (s, SMe), 2.4 (m, SCH_2), 2.6 (m, CH_2Te). $^{125}Te\{^1H\}$-NMR ($(CH_3)_2CO$): 136. ES$^+$ (MeCN); m/z: 415; calc. for $[C_8H_{18}^{107}AgS_2^{130}Te]^+$ 415.

2.8. $H_2N(CH_2)_3Te(CH_2)_3NH_2$

A solution of Na_2Te prepared as in 2.1 was treated with a solution of 3-chloropropylamine hydrochloride (Aldrich) (6.5 g, 0.05 mol) in EtOH (40 ml), refluxed for 3 h , cooled and extracted with Et_2O (4×25 ml). The

organic layer was dried ($MgSO_4$), filtered, and the solvent removed in vacuo to yield an orange oil: 5.4 g, 89%. Anal. Found: C, 30.2; H, 6.9; N, 11.0. Calc. for $C_6H_{16}N_2Te$: C, 29.6; H, 6.6; N, 11.5%. ^{1}H-NMR ($CDCl_3$): 0.98 (s,br, 2H, H_2N), 1.64 (quin, 2H, $CH_2CH_2CH_2$), 2.42 (t, 2H, $TeCH_2$), 2.50 (t, 2H, CH_2N). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 2.4 ($^1J_{Te-C} = 156$ Hz, CH_2Te), 38.8 ($CH_2CH_2CH_2$), 46.8 (NCH_2). $^{125}Te\{^1H\}$-NMR ($CDCl_3$): 240. FABMS (3-NOBA); m/z: 246, 188; calc. for $[C_6H_{16}N_2^{130}Te]^+$ 246, $[C_3H_8N^{130}Te]^+$ 188.

2.9. X-ray crystallographic studies

Crystals were grown from vapour diffusion of Et_2O into acetone solutions of $[PtCl(S_2Te)]PF_6$ and $[Rh(Cp^*)(S_2Te)][PF_6]_2$. Crystallographic parameters are presented in Table 1. Data collection used an Enraf–Nonius Kappa CCD diffractometer operating at 120 K (Pt) or 150 K (Rh) with the data corrected for absorption by SORTAV [12]. For both structures, data solution and refinement were essentially routine [13,14]. For the platinum complex two independent cations and anions were identified in the asymmetric unit, and a higher symmetry cell could not be identified. One PF_6 group was disordered and this disorder was modelled reasonably successfully with split occupancies (65:35).

3. Results and discussion

The new ligand $MeS(CH_2)_3Te(CH_2)_3SMe$ was prepared in good yield as an air-sensitive red–orange oil by reaction of Na_2Te with $Br(CH_2)_3SMe$ in a 1:2 molar ratio in aqueous alkali–ethanol. The analogous reaction replacing $Br(CH_2)_3SMe$ with $Cl(CH_2)_3NH_3Cl$ gave the new N_2Te donor ligand 1,9-diaza-5-telluranonane, $H_2N(CH_2)_3Te(CH_2)_3NH_2$. Both ligands were thoroughly characterised by ^{1}H-, $^{13}C\{^1H\}$- and ^{125}Te-NMR spectroscopy, mass spectrometry and analysis. The NMR spectroscopic data provide clear evidence of the ligand structures, and no other significant Te-containing products were detected. However, attempts to carry out similar reactions using $Br(CH_2)_3SH$ to make $Te(CH_2CH_2CH_2SH)_2$ gave a mixture of products which could not be separated since they decomposed on attempted chromatography.

Several complexes of $MeS(CH_2)_3Te(CH_2)_3SMe$ were prepared to establish the coordination modes available, and to allow comparison with complexes of $RS(CH_2)_nS(CH_2)_nSR$, $MeSe(CH_2)_3Se(CH_2)_3SeMe$ and $MeTe(CH_2)_3Te(CH_2)_3TeMe$, so that the effects of changing the Group 16 donor atom(s) are revealed. *Fac*-$[Mn(CO)_3\{MeS(CH_2)_3Te(CH_2)_3SMe\}]CF_3SO_3$ was obtained as an orange gum by displacement of acetone from $[Mn(CO)_3(Me_2CO)_3]^+$. The *fac* geometry follows from comparison of the spectrum which exhibited two ν(CO) modes 2035, 1950 cm^{-1} with those of related tricarbonylmanganese cations [3,5]. The values may be compared with the corresponding values in $[Mn(CO)_3(L^3)]^+$ $L^3 = MeSe(CH_2)_3Se(CH_2)_3SeMe$ (2029, 1945) and $MeTe(CH_2)_3Te(CH_2)_3TeMe$ (2014, 1936) [3,5]. The corresponding complex of $MeS(CH_2)_3S(CH_2)_3SMe$ has not been described but that of the dimethylene-linked $MeS(CH_2)_2S(CH_2)_2SMe$ has ν(CO) at 2047 and 1957 cm^{-1} [3]. The fall in ν(CO) along the series $MeS(CH_2)_2S(CH_2)_2SMe > MeS(CH_2)_3Te(CH_2)_3SMe \geq MeSe(CH_2)_3Se(CH_2)_3SeMe > MeTe(CH_2)_3Te(CH_2)_3TeMe$, shows the trend observed elsewhere [5,15] of increasing σ donation as Group 16 is descended. The ^{55}Mn-NMR chemical shifts show a slightly different order $MeSe(CH_2)_3Se(CH_2)_3SeMe$ ($\delta = -560$) > $MeS(CH_2)_3Te(CH_2)_3SMe$ ($\delta = -645$) > $MeTe(CH_2)_3Te(CH_2)_3TeMe$ ($\delta = -1338$), but here we cannot make comparison with the complex of $MeS(CH_2)_2S(CH_2)_2SMe$ since the ^{55}Mn chemical shifts are known to be sensitive to chelate ring size as well as donor atoms [3,15]. The chiral centres in the coordinated tridentate, generate several invertomers for $[Mn(CO)_3(L^3)]^+$, specifically two *meso* and a DL form which are NMR distinguishable if pyramidal inversion is slow [5,15], although not all forms need be present in significant amounts in a particular complex. In the case of the manganese complex of $MeTe(CH_2)_3Te(CH_2)_3TeMe$ two invertomers were detected [5], but in the S_2Te complex only single ^{125}Te-and ^{55}Mn-NMR resonances were observed, which could be due to a single predominant isomer, but since inversion barriers at sulphur are much

Table 1
Crystal data and structure refinement parameters

	$[Rh(Cp^*)(S_2Te)][PF_6]_2$	$[PtCl(S_2Te)]PF_6$
Empirical formula	$C_{18}H_{33}F_{12}P_2RhS_2Te$	$C_8H_{18}ClF_6PPtS_2Te$
Formula weight	834.01	681.45
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.4602(1)	9.8028(1)
b (Å)	19.5063(3)	27.4365(5)
c (Å)	13.5739(2)	13.5436(2)
β (°)	93.6330(9)	109.0450(9)
U (Å^3)	2764.05(6)	3443.23(7)
Z	4	8
μ(Mo–K$_\alpha$) (cm^{-1})	20.07	103.12
Unique observed reflections	6476	7928
Observed reflections with $[I_o > 2\sigma(I_o)]$	4196	5159
R	0.047	0.061
R_w	0.056	0.064

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

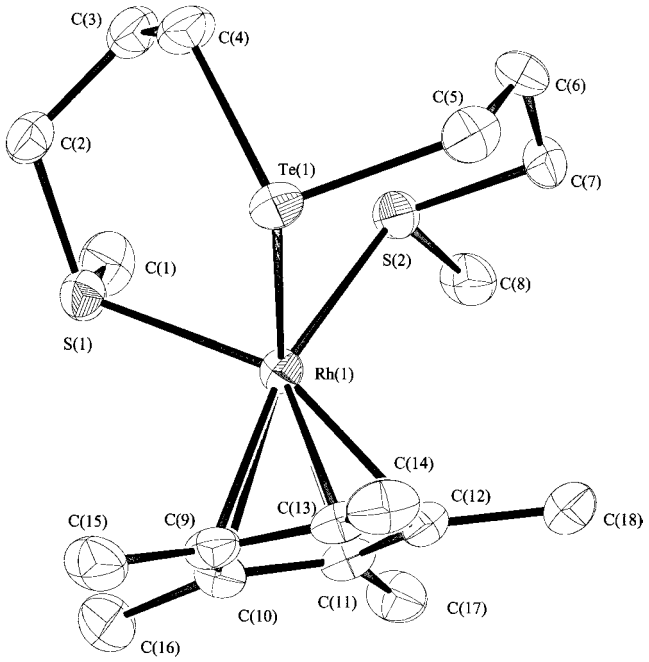

Fig. 1. A view of the cation in $[Rh(Cp^*)\{MeS(CH_2)_3Te(CH_2)_3SMe\}][PF_6]_2$. H atoms omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Rh(Cp^*)\{MeS(CH_2)_3Te(CH_2)_3SMe\}][PF_6]_2$

Bond lengths			
Rh(1)–Te(1)	2.6106(7)	Rh(1)–S(1)	2.364(2)
Rh(1)–S(2)	2.368(2)	Rh(1)–C(Me)	2.178(7)–2.232(8)
Te(1)–C(4)	2.157(8)	Te(1)–C(5)	2.140(8)
Bond angles			
Te(1)–Rh(1)–S(1)	93.14(5)	Te(1)–Rh(1)–S(2)	88.23(5)
S(1)–Rh(1)–S(2)	90.78(6)		

Table 3
Selected bond lengths (Å) and bond angles (°) for $[PtCl\{MeS(CH_2)_3Te(CH_2)_3SMe\}]PF_6$

Bond lengths			
Pt(1)–Te(1)	2.5258(11)	Pt(2)–Te(2)	2.5191(12)
Pt(1)–S(1)	2.310(4)	Pt(2)–S(3)	2.304(4)
Pt(1)–S(2)	2.288(4)	Pt(2)–S(4)	2.291(4)
Pt(1)–Cl(1)	2.358(4)	Pt(2)–Cl(2)	2.351(4)
Bond angles			
Te(1)–Pt(1)–Cl(1)	174.39(11)	Te(2)–Pt(2)–Cl(2)	175.73(12)
Te(1)–Pt(1)–S(1)	90.57(12)	Te(2)–Pt(2)–S(4)	91.26(11)
Te(1)–Pt(1)–S(2)	97.69(10)	Te(2)–Pt(2)–S(3)	97.39(11)
Cl(1)–Pt(1)–S(1)	87.9(2)	Cl(2)–Pt(2)–S(3)	86.3(2)
Cl(1)–Pt(1)–S(2)	83.9(1)	Cl(2)–Pt(2)–S(4)	84.9(2)
S(1)–Pt(1)–S(2)	171.7(1)	S(3)–Pt(2)–S(4)	170.2(2)

lower than at tellurium [3], fast pyramidal inversion (on the NMR timescale) is likely.

The $[Rh(Cp^*)\{MeS(CH_2)_3Te(CH_2)_3SMe\}][PF_6]_2$ was readily made from $[\{Rh(Cp^*)Cl_2\}_2]$, $TlPF_6$ and the ligand in methanol. The X-ray crystal structure of this complex shows a *fac* octahedral geometry with the S_2Te ligand in the DL form (Fig. 1). The bond lengths and angles (Table 2) may be compared with those in $[Rh(Cp^*)\{PhTe(CH_2)_3Te(CH_2)_3TePh\}][PF_6]_2$ [5] which also contained the DL invertomer. The d(Rh–Te) in the present case, 2.6106(8) Å, is identical with that in the tritelluroether complex (2.6016(7) Å), and the d(Rh–S) 2.364(2), 2.368(2) Å are much as expected. The Rh–C distances 2.207 Å (av) are also very similar to those in the tritelluroether complex [5]. In solution the ^{125}Te-NMR spectrum contains a single broad doublet at $\delta = 191$ ($^1J_{Rh-Te} = 94$ Hz), the coupling constant being typical for ^1J(Rh(III)–Te) [2,5]. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra show only single resonances for the –SMe groups, again almost certainly due to fast inversion at sulphur.

The reaction of the ligand with $[MCl_2(MeCN)_2]$ (M = Pd or Pt) and $TlPF_6$ in a 1:1:1 ratio gave planar $[MCl\{MeS(CH_2)_3Te(CH_2)_3SMe\}]PF_6$, the structure being confirmed for the platinum complex by an X-ray crystallographic study. The structure revealed two independent cations and anions in the asymmetric unit, with one of the PF_6 groups disordered. The small differences between the two cations (Table 3) are not chemically significant, and only one is shown in Fig. 2. The structure shows a planar cation with the DL form of the ligand, and with only small deviations from a regular geometry with unexceptional bond lengths, viz. $Pt–Cl_{trans\ Te} = 2.354$ Å (av), $Pt–S_{trans\ S} = 2.30$ Å (av), and $Pt–Te_{trans\ Cl} = 2.522$ Å (av). These may be com-

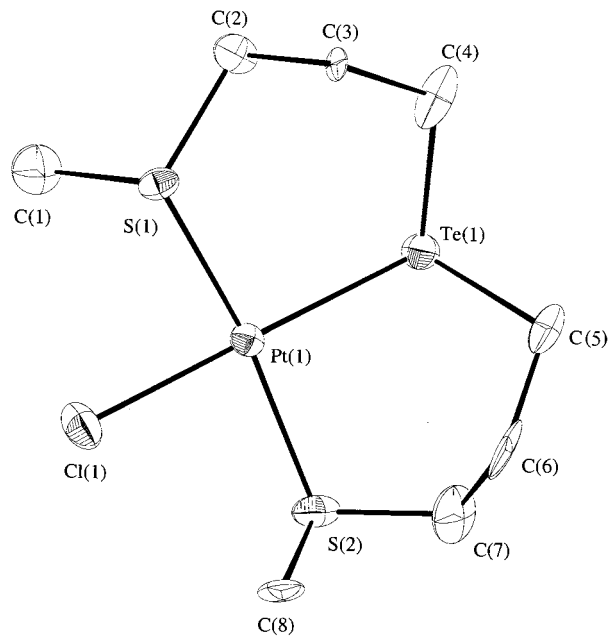

Fig. 2. A view of one of the independent cations in $[PtCl\{MeS(CH_2)_3Te(CH_2)_3SMe\}]PF_6$. H atoms omitted for clarity.

pared with Pt–$Cl_{trans\ Te}$ = 2.336(3) Å and Pt–$Te_{trans\ Cl}$ = 2.514(1) Å in *cis*-[$PtCl_2(EtOC_6H_4TeCH_2CH_2SMe)$] [16], and Pt–$S_{trans\ S}$ = 2.304 Å (av) in [PtCl{^{i}PrS-$(CH_2)_3S(CH_2)_3S^i$Pr}]BF_4 [10].

Pyramidal inversion at thioethers coordinated to palladium(II) is usually rapid on the NMR time-scales at room temperature [17], and this is clearly the case for [PdCl{$MeS(CH_2)_3Te(CH_2)_3SMe$}]PF_6 which shows a singlet in the ^{125}Te{^{1}H}-NMR spectrum at $\delta = 279$, a high frequency coordination shift of 140 ppm, and a single δ(MeS) in the ^{1}H-NMR spectrum. The NMR spectra obtained from [PtCl{$MeS(CH_2)_3Te(CH_2)_3$-SMe}]PF_6, however, are more complex: the ^{1}H-NMR at 300 K shows three rather broad δ(SMe) resonances and complex overlapping CH_2 resonances, with ill-defined ^{195}Pt satellites suggesting a system approaching coalescence. The ^{125}Te{^{1}H}-NMR spectrum at 300 K showed two very broad resonances consistent with the presence of *meso* and DL invertomers, the averaged coordination shift (ca. 113) being smaller than in the palladium analogue. No ^{195}Pt-NMR spectrum was observed at room temperature, but on cooling the solution two resonances at −3071, −3140 were observed, which are consistent with the two invertomers expected. The chemical shifts for this $PtTeS_2Cl$ system (ca. −3100), seem reasonable compared with $PtSe_3Cl$ (ca. −3700) [18] and $PtTe_3Cl$ (ca. −3900) [5].

The S_2Te ligand reacted with [$Cu(MeCN)_4$]BF_4 or $AgCF_3SO_3$ to give white complexes [$Cu(S_2Te)$]BF_4 and [$Ag(S_2Te)$]CF_3SO_3. Neither complex gave crystals suitable for X-ray studies and hence the structures are unclear, although probably oligomeric [6]. The ^{1}H-NMR spectra are simple showing resonances only little shifted from those of the 'free' ligand, and singlet ^{125}Te-NMR resonances to low frequency of the ligand resonance. Low frequency ^{125}Te-NMR shifts and very small ^{1}H-NMR coordination shifts are typical of group 16 donor ligand complexes of these two d^{10} metal centres [19,20].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 173953 and 173954 for [$PtCl(S_2Te)$]PF_6 and [$Rh(Cp^*)(S_2Te)$][PF_6]$_2$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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