Articles

Synthesis, Properties, and Ligating Behavior of the First Facultative Tritelluroethers, $Te(CH_2CH_2CH_2TeR)_2$ ($R = Me$ or Ph)

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The first examples of linear tritelluroether ligands, $Te(CH_2CH_2CH_2TeR)_2$ [L, R = Me (L^1) or Ph (L^2)], have been prepared from Na_2Te and $RTeCH_2CH_2CH_2Cl$ and fully characterized spectroscopically and by quaternization with MeI to the corresponding telluronium salts, $MeITe(CH_2CH_2CH_2TeRMeI)_2$. A series of metal complexes have been prepared, the metal substrate being chosen to illustrate the ligating modes available to these ligands and to permit comparison with literature data on complexes of $Se(CH_2CH_2CH_2SeMe)_2$ and $MeC(CH_2TeR)_3$. In *fac*-$[Mn(CO)_3(L)]CF_3SO_3$ the ligands bind as tridentates facially to the metal center, whereas in $[PtCl(L)]PF_6$ the ligands occupy three positions on the square-planar metal center. The $[\{\eta^5\text{-}C_5Me_5\}Rh(L)](PF_6)_2$ contain tridentate L bound to one triangular face of the octahedron. The X-ray crystal structure of $[\{\eta^5\text{-}C_5Me_5\}Rh(L^2)](PF_6)_2\cdot MeOH$ shows tridentate telluroether coordination with the ligand adopting the DL configuration, giving a distorted pseudo-octahedral environment at Rh(III). A short contact between one C−H group in one of the phenyl rings and the centroid of the other phenyl ring (2.56 Å) helps to stabilize the adopted configuration. The metal complexes have been characterized by analysis, ES^+ or FAB mass spectrometry, and IR and multinuclear NMR (^1H, $^{13}C\{^1H\}$, ^{125}Te) spectroscopy. The invertomers present in coordinated L have been established by the multinuclear NMR studies.

Introduction

Although the synthesis and coordination chemistry of tellurium donor ligands has been developing rapidly in the last 10 or so years, studies are still far more limited than with sulfur and selenium analogues.[1,2] While this is in part due to less effort devoted to Te ligands, it also reflects the considerably greater problems in the synthesis of other than the simplest types. For example, the instability of the Te−H bond in tellurols (RTeH) makes these useless as synthons, while the weak Te−C bonds mean that bi- or polydentates with $-TeCH_2CH_2Te-$ or *cis*-TeCH═CHTe− linkages cannot be made.[3] These problems are particularly pronounced in the synthesis of polydentates or homoleptic tellurium macrocycles, where sequential generation of new Te−C bonds often competes with facile Te−C bond cleavage in precursors.[3] As a result of these problems, only two tritelluroethers, the tripodal $MeC(CH_2TeR)_3$ (R = Me[3] or Ph[4]), the spirocyclic $C(CH_2TePh)_4$,[3] and one macrocycle, 1,5,9-tritelluracyclododecane,[5] have been described. We report here the synthesis of the first linear tritelluroethers $Te(CH_2CH_2CH_2TeR)_2$ (R = Me, L^1 or Ph, L^2) and a representative range of transition metal complexes, which allow comparison of their ligating behavior with the previously reported tripods[4,6−10] and the selenoether analogue $Se(CH_2CH_2CH_2SeMe)_2$.[11,12]

Experimental Section

All preparations were conducted in good fume hoods under a dry dinitrogen atmosphere, and ligands and intermediates were stored under dinitrogen in a freezer. The tellurium ligands and intermediates have persistent, repulsive odors. Aqueous waste and used glassware was treated with aqueous NaOCl for 12 h to remove most of the odor. Tetrahydrofuran was distilled from sodium benzophenoneketyl before use, while

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other solvents were obtained commercially and used as supplied. Tellurium pieces were obtained from Aldrich and ground to a powder immediately before use.

^{1}H NMR spectra were obtained on a Bruker AC300 and ^{13}C{^{1}H} NMR on a Bruker AC300 or DPX400 and referenced via residual proton signals in the deuterated solvents to TMS. ^{125}Te, ^{55}Mn, and ^{195}Pt NMR spectra were obtained on a Bruker DPX400 and are referenced to (neat) Me_2Te, saturated aqueous $KMnO_4$, and aqueous $[PtCl_6]^{2-}$, respectively. Microanalyses were obtained from the University of Strathclyde Analytical Laboratory. Other measurements were made as in previous reports from these laboratories.[6-8,10]

1. $PhTe(CH_2)_3OH$. A freshly prepared solution of PhTeLi (0.05 mol) in thf[3] was frozen in liquid nitrogen and 3-bromopropan-1-ol (6.96 g, 0.05 mol) added. The mixture was allowed to thaw, warmed to room temperature, and stirred for 2 h. Water (100 cm^3) was added, and the organic phase separated and dried over magnesium sulfate. The drying agent was filtered off and the solvent removed in vacuo to leave a red oil. Yield: 11.5 g, 84%. APCI MS (MeCN): *m/z* 266, calcd for $C_9H_{12}O^{130}Te$ 266. ^{1}H NMR ($CDCl_3$): 7.72 (m) [2H], 7.18 (m) [3H], 3.64 (m, $^{3}J = 3.7$ Hz) [2H] CH_2O, 2.96 (t, $^{3}J = 7.4$ Hz) [2H] CH_2Te, 2.91 (s) [1H] OH, 2.03 (m) CH_2. ^{13}C{^{1}H} ($CDCl_3$): 138.3, 129.4, 127.3, 112.1 Ph, 63.8 CH_2OH, 34.4 CH_2, 3.5 ($^{1}J_{Te-C} = 156$ Hz) CH_2Te. ^{125}Te{^{1}H} (neat): 464.

2. $PhTe(CH_2)_3Cl$. To a solution of PPh_3 (2.09 g, 7.96 mmol) and $PhTe(CH_2)_3OH$ (2.0 g, 7.56 mmol) in MeCN (20 cm^3) was added CCl_4 (1 cm^3) and the mixture refluxed for 30 min. The solvent was removed in vacuo, and the residue extracted with *n*-hexane. Removal of the hexane in vacuo left an orange oil. Yield: 1.48 g, 68%. APCI MS (MeCN): *m/z* 284, calcd for $C_9H_{12}{}^{35}Cl^{130}Te$ 284. ^{1}H NMR ($CDCl_3$): 7.86 (m) [2H], 7.40 (m) [H], 7.31 (m) [2H], 3.65 (m, $^{3}J = 6.5$ Hz) [2H] CH_2Cl, 3.09 (t, $^{3}J = 7.4$ Hz) [2H] CH_2Te, 2.28 (m) [2H] CH_2. ^{13}C{^{1}H} ($CDCl_3$): 138.7, 129.6, 128.0, 111.8 Ph, 47.6 CH_2Cl, 34.6 CH_2, 5.1 ($^{1}J_{Te-C} = 162$ Hz) CH_2Te. ^{125}Te{^{1}H} (neat): 470.

3. $MeTe(CH_2)_3OH$. A solution of MeTeLi in thf[3] (0.05 mol) was frozen with liquid nitrogen, 3-chloropropan-1-ol (4.73 g, 0.05 mol) was injected in, and the mixture was allowed to warm to room temperature and stirred for 2 h. Water (100 cm^3) was added, the organic phase separated, and the water re-extracted with diethyl ether (3 × 50 cm^3). The combined organic phases were dried over magnesium sulfate. Filtration and removal of the solvent in vacuo left an orange oil. Yield: 8.1 g, 80%. APCI MS (MeCN): *m/z* 205, calcd for $C_4H_{10}O^{130}Te$ 205. ^{1}H NMR ($CDCl_3$): 4.09 (br) [H] OH, 3.65 (t, $^{3}J = 6.5$ Hz) [2H] CH_2O, 2.60 (t, $^{3}J = 7.4$ Hz) CH_2Te, 2.00 (m) [2H] CH_2, 1.90 (s) [3H] Me. ^{13}C{^{1}H} ($CDCl_3$): 63.7 CH_2OH, 34.5 CH_2, −1.6 ($^{1}J_{Te-C} = 150$ Hz) CH_2Te, −22.7 ($^{1}J_{Te-C} = 160$ Hz) TeMe. ^{125}Te{^{1}H} (neat): 113.

4. $MeTe(CH_2)_3Cl$. A mixture of PPh_3 (6.56 g, 25 mmol), $PhTe(CH_2)_3OH$ (4.0 g, 20 mmol), and CCl_4 (2 cm^3) was refluxed in MeCN (20 cm^3) for 30 min. The solvent was removed in vacuo and the residue extracted with *n*-hexane. Removal of the solvent in vacuo gave an orange oil. Yield: 2.64 g, 60%. APCI MS (MeCN): *m/z* 222, calcd for $C_4H_{10}{}^{35}Cl^{130}Te$ 222. ^{1}H NMR ($CDCl_3$): 3.44 (t $^{3}J = 6.5$ Hz) [2H] CH_2Cl, 2.53(t, $^{3}J = 7.0$ Hz) [2H] CH_2Te, 1.93 (m, $^{3}J = 7.0$ Hz) [2H] CH_2, 1.74 (s) [3H] Me. ^{13}C{^{1}H} ($CDCl_3$): 46.3 CH_2Cl, 34.3 CH_2, −0.4 ($^{1}J_{Te-C} = 157$ Hz) CH_2Te, −21.8 ($^{1}J_{Te-C} = 160$ Hz) TeMe. ^{125}Te{^{1}H} (neat): 112.5.

5. $Te(CH_2CH_2CH_2TePh)_2$, L^2. Sodium (0.41 g, 17.7 mmol) and tellurium powder (1.13 g, 8.9 mmol) were dissolved sequentially in liquid ammonia (200 cm^3), and $PhTe(CH_2)_3Cl$ (5.0 g, 17.7 mmol) in thf (75 cm^3) was added at −78 °C. The mixture was stirred at this temperature for 6 h, allowed to warm to room temperature, and then stirred for 16 h. The residue was treated with water (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3), and the organic phase was dried over magnesium sulfate. The solvent was removed in vacuo and the product purified by flash chromatography on silica, eluting with diethyl ether−hexane (1:10) to produce a red oil. Yield: 4.08 g, 62%. EI$^+$ MS: *m/z* 624, calcd for $C_{18}H_{22}{}^{130}Te_3$ 628. ^{1}H NMR ($CDCl_3$): 7.89 (m) [2H], 7.37 (m) [H], 7.32 (m) [2H], 3.24 (t, $^{3}J = 7.4$ Hz) [2H] CH_2TePh, 3.04 (t, $^{3}J = 7.4$ Hz) [2H] CH_2Te, 2.33 (m) [2H] CH_2. ^{13}C{^{1}H} ($CDCl_3$): 138.5, 129.4, 127.8, 112.4 Ph, 35.4 CH_2, 11.0 ($^{1}J_{Te-C} = 158$ Hz), 6.9 ($^{1}J_{Te-C} = 176$ Hz) CH_2Te. ^{125}Te{^{1}H} (neat): 465, 123.

The tris(methiodide) $\{MeIPhTe(CH_2)_3\}_2TeMeI$ was made by stirring the ligand (0.31 g, 0.5 mmol) in excess MeI (3 cm^3) in acetone (20 cm^3) for 1 h. The solution was concentrated to 5 cm^3 and cooled, and the white crystals were filtered off, rinsed with diethyl ether, and dried. Yield: 0.45 g, 85%. Anal. Calcd for $C_{21}H_{31}I_3Te_3$: C, 24.1; H, 3.0. Found: C, 23.7, 3.7. ^{125}Te NMR (Me_2CO): 484, 602.

6. $Te(CH_2CH_2CH_2TeMe)_2$, L^1, was made similarly to **5**, from Na (0.52 g, 23 mmol), Te (1.47 g, 11.5 mmol) in liquid ammonia (200 cm^3), and $MeTe(CH_2)_3Cl$ (5.0 g, 23 mmol) in thf (75 cm^3). Purification by chromatography with diethyl ether−hexane (1:10) gave an orange oil. Yield: 3.2 g, 56%. EI$^+$ MS: *m/z* 498, calcd for $C_8H_{18}{}^{130}Te_3$ 504. ^{1}H NMR ($CDCl_3$): 2.70 (t, $^{3}J = 6.5$ Hz) [2H] CH_2Te, 2.68 (t, $^{3}J = 6.5$ Hz) [2H] CH_2Te, 2.12 (m) [2H] CH_2, 1.92 (s) [3H] Me. ^{13}C{^{1}H} ($CDCl_3$): 33.9 CH_2, 5.4 ($^{1}J_{Te-C} = 145$ Hz), 4.9 ($^{1}J_{Te-C} = 140$ Hz) CH_2Te, −22.0 ($^{1}J_{Te-C} = 160$ Hz) MeTe. ^{125}Te{^{1}H} (neat): 116.8, 154.4.

The tris(methiodide) was made as for **5**: white crystals, 39%. Anal. Calcd for $C_{11}H_{27}I_3Te_3$ C, 14.3; H, 3.0. Found: C, 14.7; H, 2.9. ^{125}Te NMR (Me_2CO): 487, 522.

7. $[Rh(\eta^5\text{-}C_5Me_5)(L^1)][PF_6]_2$. A mixture of L^1 (0.15 g, 0.3 mmol), $TlPF_6$ (0.21 g, 0.6 mmol), and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ (0.09 g, 0.15 mmol) was refluxed together in MeOH (40 cm^3) for 18 h, resulting in a white precipitate (TlCl) and a yellow solution. The solution was filtered through Celite and the volume reduced to 2 cm^3. Addition of diethyl ether gave an orange solid. Yield: 0.27 g, 87%. The complex was analytically pure but could be recrystallized from acetone/diethyl ether. Anal. Calcd for $C_{18}H_{33}F_{12}P_2RhTe_3$: C, 21.1; H, 3.2. Found: C, 20.5; H, 3.1. ES$^+$ MS: *m/z* 368, calcd for $C_{18}H_{33}Rh^{130}Te_3$ 371. ^{1}H NMR (acetone-d_6): 2.06 (m) CH_2, 2.10 (s) C_5Me_5, 2.39 (d) 2.45 (d), 2.52 (d), 2.59 (d) Me, 3.1−3.4 (m) CH_2Te. ^{13}C{^{1}H} (acetone-d_6): 104.2, 103.7 (C_5Me_5), 33.3 CH_2, 11.4, 11.2, 10.5, 6.3 (CH_2Te), 9.6, 9.4, 9.1 (C_5Me_5), −7.5, −8.2, −10.4, −11.0 (MeTe). ^{125}Te{^{1}H} (acetone-d_6): 209.4 (d) ($^{1}J_{Rh-Te} = 80$ Hz), 235.5 (br, 4 lines?), 263.7 (d) ($^{1}J_{Rh-Te} = 89$ Hz), 264.1 ($^{1}J_{Rh-Te} = 95$ Hz).

8. $[Rh(\eta^5\text{-}C_5Me_5)(L^2)][PF_6]_2$. A mixture of L^2 (0.19 g, 0.3 mmol), $TlPF_6$ (0.21 g, 0.6 mmol), and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl_2\}_2]$ (0.09 g, 0.15 mmol) was refluxed together in MeOH (40 cm^3) for 18 h, resulting in a white precipitate (TlCl) and a yellow solution. The solution was filtered through Celite, and the volume reduced to 2 cm^3. Addition of diethyl ether gave an orange solid. Yield: 0.22 g, 64%. The complex was analytically pure but could be recrystallized from acetone/diethyl ether. Anal. Calcd for $C_{28}H_{37}F_{12}P_2RhTe_3$: C, 29.3; H, 3.3. Found: C, 29.5; H, 3.3%. ES$^+$ MS: *m/z* 430, calcd for $C_{18}H_{33}Rh^{130}Te_3$ 433. ^{1}H NMR (acetone-d_6): 1.85 (m) CH_2, 2.08 (s) C_5Me_5, 3.1−3.6 (m) CH_2Te, 7.2−7.7 (m) Ph. ^{13}C{^{1}H} (acetone-d_6): 134−129 (br) Ph, 100.7 C_5Me_5, 33.7 CH_2, 8.4 C_5Me_5, 5.0, 4.6, 3.0 CH_2Te. ^{125}Te{^{1}H} (acetone-d_6): 468.5 (d) ($^{1}J_{Rh-Te} = 80$ Hz), 455.1 (d) ($^{1}J_{Rh-Te} = 90$ Hz), 384.5 (d) ($^{1}J_{Rh-Te} = 93$ Hz), 218.1 (d) ($^{1}J_{Rh-Te} = 98$ Hz).

9. *fac*-$[Mn(CO)_3(L^1)]CF_3SO_3$. The compounds $[Mn(CO)_5Cl]$ (0.05 g, 0.19 mmol) and $AgCF_3SO_3$ (0.05 g, 0.19 mmol) were stirred together in acetone (40 cm^3) at 60 °C for 1 h. The reaction was monitored by IR spectroscopy to check formation of $[Mn(CO)_3(acetone)_3]^+$ was complete, and then the precipitated AgCl was filtered off. L^1 (0.1 g, 0.19 mmol) was added and the solution refluxed for 0.5 h and then stirred at room temperature for 18 h. The solution was concentrated to 2 cm^3 and diethyl ether added to precipitate an orange solid, which was dried in vacuo. Yield: 0.08 g, 57%. Anal. Calcd for $C_{12}H_{18}F_3MnO_6STe_3$: C, 18.4; H, 2.3. Found: C, 18.8; H, 2.7%. ES$^+$ MS: *m/z* 637, calcd for $C_{11}H_{18}O_3Mn^{130}Te_3$ 637. IR cm^{-1}

(acetone solution): 2014, 1936. ^{1}H NMR (CDCl$_3$): 2.9−3.2 (m) CH$_2$Te, 2.4, 2.36, 2.32, 2.26 (Me), 2.02 (m) CH$_2$. ^{13}C{^{1}H} (CDCl$_3$): 217−220 (br) CO, 30.8 CH$_2$, 10.8, 8.6 CH$_2$Te, −8.5−9.3 MeTe. ^{125}Te{^{1}H} (acetone-d_6): 119.7, 128.5, 168.5, 169.0, 170.0 (sh) ^{55}Mn (300 K, acetone-d_6): −1338 (w$_{1/2}$ 900 Hz), −1362 (w).

10. *fac*-[Mn(CO)$_3$(L^2)]CF$_3$SO$_3$ was made similarly to **9** using [Mn(CO)$_5$Br] (0.1 g, 0.35 mmol), AgCF$_3$SO$_3$ (0.1 g, 0.35 mmol), and L^2 (0.22 g, 0.35 mmol). The orange solid was isolated in 0.19 g, 59% yield. Anal. Calcd for C$_{22}$H$_{22}$F$_3$MnO$_6$STe$_3$: C, 28.8; H, 2.4. Found: C, 28.6; H, 2.2. ES$^+$ MS: *m*/*z* 761, calcd for C$_{21}$H$_{22}$O$_3$Mn^{130}Te$_3$ 761. IR cm^{-1} (acetone solution): 2017, 1940. ^{1}H NMR (CDCl$_3$): 7.7−7.3 (m) Ph, 2.9−3.6 (br) CH$_2$Te, 2.0 (br) CH$_2$. ^{13}C{^{1}H} (CDCl$_3$): 220−222 (br) CO, 137−130, 112.7 Ph, 30.8 CH$_2$, 2.0, 1.1 CH$_2$Te. ^{125}Te{^{1}H} (CH$_2$Cl$_2$/CDCl$_3$): 417.5, 400, 362, 132.5, 107. ^{55}Mn (acetone-d_6): −1218 (w$_{1/2}$ 1100 Hz), −1254 (2600 Hz).

11. *fac*-[Mo(CO)$_3$(L^1)]. [Mo(CO)$_6$] (0.2 g, 0.76 mmol) was refluxed in MeCN (50 cm^3) under argon for 16 h to give [Mo(CO)$_3$(MeCN)$_3$]. The ligand L^1 (0.42 g, 0.76 mmol) was added, and the mixture was stirred for a further 16 h, when an IR spectrum of the solution showed the absence of [Mo(CO)$_3$(MeCN)$_3$]. The solvent was removed in vacuo and the residue extracted with CH$_2$Cl$_2$ (20 cm^3) and filtered through Celite. Concentration of the filtrate to 2 cm^3 and addition of diethyl ether gave a brown solid, which was washed with diethyl ether and dried in vacuo. Yield: 0.28 g, 56%. Anal. Calcd for C$_{11}$H$_{18}$MoO$_3$Te$_3$: C, 19.5; H, 2.7. Found: C, 19.6; H, 2.7%. IR cm^{-1} (CH$_2$Cl$_2$ solution): 1926, 1827. ^{1}H NMR (CDCl$_3$): 2.6 (m) CH$_2$Te, 2.1 (m) CH$_2$, 1.83 (s), 1.85 (s), 1.86 (s), 1.87 (s) Me.

12. [PtCl(L^1)]PF$_6$. PtCl$_2$ (0.15 g, 0.56 mmol) was dissolved in refluxing MeCN (30 cm^3) to produce a yellow solution. TlPF$_6$ (0.2 g, 0.56 mmol) and L^1 (0.28 g, 0.56 mmol) were added, and the mixture was stirred at room temperature for 16 h. The white TlCl was filtered off, the orange solution was concentrated to small volume, and diethyl ether (10 cm^3) was added slowly to precipitate an orange solid, which was collected and dried in vacuo. Yield: 0.41 g, 84%. The complex decomposes slowly in solution, but could be quickly recrystallized by dissolution in MeCN, filtering, and reprecipitation with diethyl ether. Anal. Calcd for C$_8$H$_{18}$ClF$_6$PPtTe$_3$: C, 11.0; H, 2.1. Found: C, 11.3; H, 1.6. ES$^+$ MS: *m*/*z* 729, calcd for C$_8$H$_{18}$^{35}Cl^{195}Pt^{130}Te$_3$ 734. ^{1}H NMR (CD$_3$CN): 2.1−2.2 (m) CH$_2$, 2.31 (s), 2.26 (s), 2.27 (s) Me, 2.4−3.0 (m) CH$_2$Te. ^{195}Pt{^{1}H} NMR (CD$_3$CN): −3770, −3825. ^{125}Te{^{1}H} NMR (CD$_3$CN): 183.5 ($^{1}J_{\mathrm{Te-Pt}}$ = 296 Hz), 194 ($^{1}J_{\mathrm{Te-Pt}}$ = 308 Hz), 355.5 ($^{1}J_{\mathrm{Te-Pt}}$ = 1400 Hz), 355 ($^{1}J_{\mathrm{Te-Pt}}$ = 1550 Hz).

13. [PtCl(L^2)]PF$_6$ was made similarly to **12** from PtCl$_2$ (0.1 g, 0.36 mmol), TlPF$_6$ (0.13 g, 0.36 mmol), and Te((CH$_2$)$_3$TePh)$_2$ (0.24 g, 0.36 mmol). Yield: 0.23 g, 64%. Anal. Calcd for C$_{18}$H$_{22}$ClF$_6$PPtTe$_3$: C, 21.7; H, 2.2. Found: C, 21.9; H, 2.3. ES$^+$ MS: *m*/*z* 852, calcd for C$_{18}$H$_{22}$^{35}Cl^{195}Pt^{130}Te$_3$ 858. ^{1}H NMR (CD$_3$CN): 2.3−3.2 (m) CH$_2$, 7.3−8.0 (m) Ph. ^{195}Pt NMR (CD$_3$CN): −3833, −3898. ^{125}Te (CD$_3$CN): 374 ($^{1}J_{\mathrm{Te-Pt}}$ = 1225 Hz), 373 ($^{1}J_{\mathrm{Te-Pt}}$ = 1200 Hz), 415.5 ($^{1}J_{\mathrm{Te-Pt}}$ = 485 Hz), 433 ($^{1}J_{\mathrm{Te-Pt}}$ = 486 Hz).

14. [RhCl$_3$(L^2)]. To a solution of RhCl$_3$·3H$_2$O (0.1 g, 0.41 mmol) in ethanol (20 cm^3) was added the ligand L^2 (0.25 g, 0.41 mmol) in ethanol (10 cm^3) and the mixture stirred at room temperature for 16 h. The product precipitated during this time as an orange-brown powder, which was washed with ethanol and dried in vacuo. Yield: 0.245 g, 72%. Anal. Calcd for C$_{18}$H$_{22}$Cl$_3$RhTe$_3$: C, 24.0; H, 2.45. Found: C, 24.3; H, 2.3. ES$^+$ MS (MeCN): *m*/*z* 838, calcd for C$_{18}$H$_{22}$^{35}Cl$_3$Rh^{130}Te$_3$ 836.

X-ray Crystal Structure of [Rh(η^5-C$_5$Me$_5$)(L^2)](PF$_6$)$_2$·MeOH. Orange rhomboid crystals were obtained from a methanol solution of the complex by vapor diffusion of diethyl ether. Crystallographic parameters are presented in Table 2. Data collection used an Enraf Nonius Kappa CCD diffractometer operating at 50 kV, 60 mA, with images collected at 1 deg intervals with 10 s exposure. The data were corrected by SORTAV,[13] and the structure was solved using heavy atom methods and refined by iterative cycles of full-matrix least-squares refinement.[14,15] During refinement one solvent MeOH molecule was identified in the asymmetric unit. All non-H atoms were refined anisotropically, and H atoms were included in fixed, calculated positions, except for the hydroxyl H atom of the MeOH, which was not located and was therefore omitted from the final structure factor calculation. Some of the F atoms of the PF$_6$$^-$ anions show slightly high thermal parameters, indicative of some disorder; however attempts to split their occupancies were not successful.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Rh(η^5-C$_5$Me$_5$)(L^2)]$^{2+}$

atom	atom	distance
Rh(1)	Te(1)	2.6177(7)
Rh(1)	Te(2)	2.6016(7)
Rh(1)	Te(3)	2.6015(7)
Te(1)	C(1)	2.118(7)
Te(1)	C(7)	2.152(7)
Te(2)	C(9)	2.155(7)
Te(2)	C(10)	2.155(7)
Te(3)	C(12)	2.145(7)
Te(3)	C(13)	2.110(6)
Rh−C in η^5-C$_5$Me$_5$		2.207(6)−2.236(7)

atom	atom	atom	angle
Te(1)	Rh(1)	Te(2)	91.87(2)
Te(1)	Rh(1)	Te(3)	92.56(2)
Te(2)	Rh(1)	Te(3)	89.70(2)

Table 2. Crystallographic Parameters for [Rh(η^5-C$_5$Me$_5$){(PhTe(CH$_2$)$_3$)$_2$Te}](PF$_6$)$_2$·MeOH

formula	C$_{29}$H$_{41}$F$_{12}$OP$_2$RhTe$_3$
M	1181.28
cryst syst	monoclinic
space group	$P2_1/c$
a/Å	14.5440(2)
b/Å	15.4506(2)
c/Å	16.5224(3)
β/deg	103.5441(9)
U/Å^3	3609.55(9)
Z	4
T/K	150
μ(Mo Kα)/cm^{-1}	30.24
total no. of reflns measured	27472 (R_{int} = 0.055)
no. of unique obsd reflns	7628
no. of obsd reflns with [$I > 3\sigma(I)$]	5149
R	0.037
R_{w}	0.045

Results and Discussion

Tritelluroethers. The tripodal ligands MeC(CH$_2$TeR)$_3$ (R = Me or Ph) contain only one Te environment and are made in "one-pot" reactions from (excess) RTeLi and MeC(CH$_2$Br)$_3$ in tetrahydrofuran.[3,4] However the linear tritelluroethers Te(CH$_2$CH$_2$CH$_2$TeR)$_2$ require sequential introduction of the central −CH$_2$TeCH$_2$− and terminal RTeCH$_2$− groups and illustrate the problems outlined in the Introduction. The triselenoether Se(CH$_2$CH$_2$CH$_2$SeMe)$_2$ is readily made by the routes

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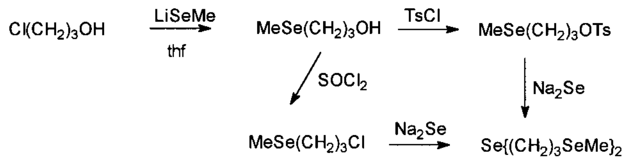
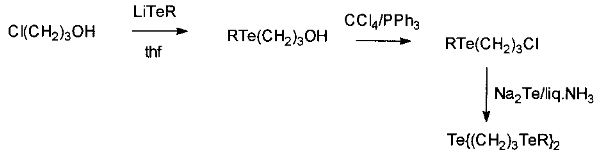
Scheme 1



Scheme 2



shown in Scheme 1,[11] and some years ago the same routes were explored to prepare $Te(CH_2CH_2CH_2TeMe)_2$.[3] These were unsuccessful: reaction of $MeTe(CH_2)_3OTs$ with Na_2Te in alcohol or thf resulted rapid deposition of elemental tellurium and formation of Me_2Te_2 (identified by ^{125}Te NMR). The reaction of $Te(CH_2CH_2CH_2OTs)_2$ with LiTeMe in thf similarly failed.[3] Attempts to prepare $MeTe(CH_2)_3Cl$ from the corresponding alcohol by reaction with $SOCl_2$ or $MeTe(CH_2)_3Br$ using PBr_3 failed due to halogenation at tellurium as well as replacement of the hydroxyl function. The new, successful route depends on the chlorination of $RTe(CH_2)_3OH$ with PPh_3/CCl_4[16] to $RTe(CH_2)_3Cl$, which then reacts with Na_2Te in liquid ammonia to give $Te(CH_2CH_2CH_2TeR)_2$ (Scheme 2). After purification by flash column chromatography, the tritelluroethers were obtained as orange oils in good yield. In contrast to the thio- and selenoether analogues, but like $RTe(CH_2)_3TeR$,[3] the new tritelluroethers are moderately air-sensitive and convert into insoluble white oily telluroxide materials on exposure to air. The new ligands showed parent ions with the correct isotope patterns in the EI^+ mass spectra, and their structures were confirmed by a combination of ^1H, $^{13}C\{^1H\}$, and ^{125}Te NMR (Experimental Section). The ^{125}Te chemical shifts are very characterstic of the substituents, and changes as remote as the γ-carbon are reflected in the shifts.[17] Reaction with excess MeI quaternized all three tellurium centers in each ligand to form $MeITe(CH_2CH_2CH_2TeMeRI)_2$, identified by analysis and by the large high-frequency shifts in the ^{125}Te NMR spectra.[3]

A series of complexes of both ligands was prepared, the metal systems being chosen to permit direct comparison with literature complexes of $MeC(CH_2TeR)_3$ or $Se(CH_2CH_2CH_2SeMe)_2$ (complexes of $Se(CH_2CH_2CH_2SePh)_2$ have not been reported[1]).

$[Rh(\eta^5\text{-}C_5Me_5)(L)][PF_6]_2$. The reaction of $RhCl_3\cdot 3H_2O$ with L^2 in EtOH gave $[RhCl_3(L^2)]$, but unfortunately, like $[RhCl_3\{MeC(CH_2TeMe)_3\}]$,[18] this complex proved to be poorly soluble in organic solvents and unsuitable for NMR studies. However the reaction of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$, $TlPF_6$, and either L^1 or L^2 gave good yields of orange $[(\eta^5\text{-}C_5Me_5)Rh(L)](PF_6)_2$, which were readily soluble in chlorocarbons. Since $[(\eta^5\text{-}C_5Me_5)Rh(L)](PF_6)_2$ (L = $MeC(CH_2SeMe)_3$, $MeC(CH_2TeMe)_3$, and $MeC(CH_2TePh)_3$) have been characterized recently,[8] these C_5Me_5 derivatives are ideal substrates for comparison of the ligand properties. Orange crystals of $[Rh(\eta^5\text{-}C_5Me_5)(L^2)](PF_6)_2\cdot MeOH$ were obtained by vapor diffusion of diethyl ether into a methanol solution of the complex. The structure shows (Figure 1, Table 1) the cation adopting a pseudo-octahedral geometry with L^2 functioning as a facially coordinated tridentate ligand and adopting the DL form, with one Ph group pointing toward the C_5Me_5 ring and the other pointing away. The Rh−Te and Rh−C distances are comparable with those in related complexes.[8] This arrangement is further stabilized by an interaction between H(18) on C(14) and the centroid of the other phenyl ring, H(18)···centroid = 2.54 Å. This results in the two phenyl rings on the termini of the tritelluroether lying at approximately 90° to each other. For a *fac*-coordinated tridentate L (L = L^1 or L^2), three invertomers are possible by symmetry (Scheme 3), *meso-1*, *meso-2*, and DL forms for each of the two orientations of the lone pair on the central Te, although it is possible that some may not be present in significant amounts. The effect of the different orientations of the central Te free lone pair may not be sufficient to cause resolvable differences in the NMR shifts, and in *fac*-octahedral complexes of $Se(CH_2CH_2CH_2SeMe)_2$ only three invertomers were observed.[11] Since pyramidal inversion is a high-energy process in most metal-coordinated telluroethers, the individual invertomers are expected to be observable in the NMR

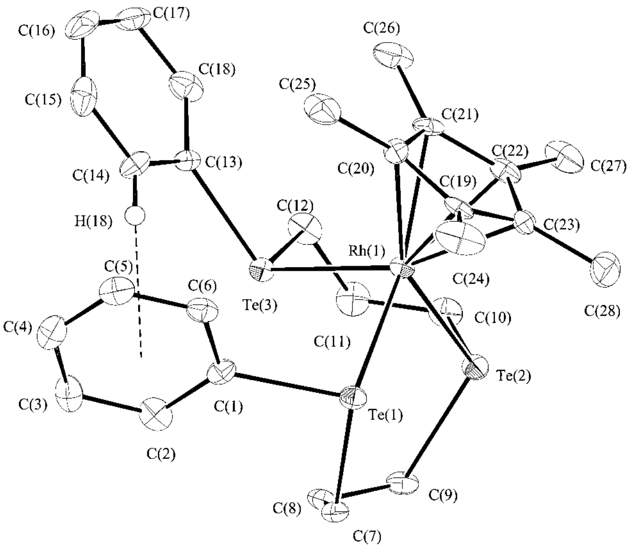
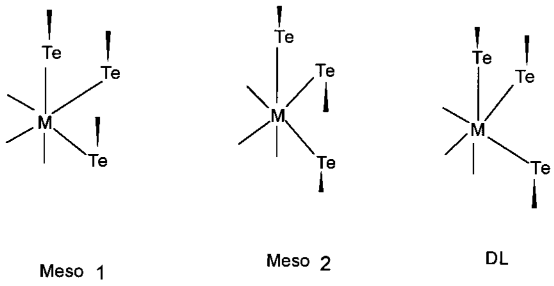


Figure 1. View of the structure of $[Rh(\eta^5\text{-}C_5Me_5)(L^2)]^{2+}$ with numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. The dashed line illustrates the weak interaction between H(18) and the centroid of the phenyl ring involving C(1)−C(6).

Scheme 3



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spectra. The complexity of the ^{1}H and ^{13}C NMR spectra means that assignment of resonances to individual invertomers is often not possible, but usually the number of invertomers present in significant amounts can be deduced. For $[(\eta^5\text{-}C_5Me_5)Rh(L^1)]^{2+}$ the ^{1}H NMR data show three δ(TeMe) doublets ($^3J_{Rh-H}$ 6 Hz) of approximately equal intensity and a fourth much weaker doublet, which is consistent with one *meso* and the DL as major forms and a second *meso* as the minor component. The $^{13}C\{^1H\}$ and ^{125}Te NMR data (Experimental Section) are consistent with this interpretation. For $[(\eta^5\text{-}C_5Me_5)Rh(L^2)](PF_6)_2$ the spectra are simpler, consistent with one major invertomer with equivalent PhTe− groups, almost certainly the *meso-1* form, and two minor doublets presumably due to the DL invertomer. Steric effects should make the bulky Ph groups avoid the $Rh(\eta^5\text{-}C_5Me_5)$ moiety, destabilizing the other invertomers. However, in the solid state the close contact between a C−H from one phenyl ring and the centroid of the other phenyl ring serves to stabilize the DL form; see above.

$[Mo(CO)_3(L)]$. Substituted group 6 carbonyls are often chosen as metal substrates upon which to explore the coordination properties of new ligands. The reaction of $[Mo(CO)_3(MeCN)_3]$[19] with L^1 in MeCN gave brown $[Mo(CO)_3(L^1)]$, but all attempts to isolate the corresponding complex of L^2 failed. The $[Mo(CO)_3(L^1)]$ was identified as the expected *fac* isomer from the presence of two ν(CO) vibrations (CH_2Cl_2 solution 1926, 1827 cm^{-1}) in the IR spectrum (theory $A_1 + E$), which can be compared with the corresponding modes in *fac*-$[Mo(CO)_3\{MeC(CH_2TeMe)_3\}]$ (1930, 1820 cm^{-1}).[10] Previous studies showed that $[M(CO)_3\{MeC(CH_2EMe)_3\}]$ (M = Cr, Mo, or W; E = S, Se, or Te) were unstable in solution, decomposing to $[M(CO)_4(\eta^2\text{-}MeC(CH_2EMe)_3\}]$ and other products, and the instability is greater with $[Mo(CO)_3(L^1)]$. Although we obtained a ^{1}H NMR spectrum that showed the presence of several invertomers, attempts to obtain ^{125}Te or ^{95}Mo NMR data failed even at low temperature due to this decomposition.

$[Mn(CO)_3(L)](CF_3SO_3)$. In view of the instability of the molybdenum complexes, we turned our attention to the more stable *fac*-$[Mn(CO)_3(\text{ligand})]^+$, for which examples with ligand = $MeC(CH_2TeMe)_3$, $MeC(CH_2TePh)_3$, $Se(CH_2CH_2CH_2SeMe)_2$, and $S(CH_2CH_2SMe)_2$ have been characterized recently.[4] The orange $[Mn(CO)_3(L)](CF_3SO_3)$ containing L^1 or L^2 were made in good yield from $[Mn(CO)_3(Me_2CO)_3](CF_3SO_3)$ in acetone. The cations were confirmed as *fac* isomers from the presence of two ν(CO) stretches in their solution IR spectra (for L^1 2014, 1936, L^2 2017,1940 cm^{-1}). These values may be compared with corresponding data on $[Mn(CO)_3(\text{ligand})]^+$ where ligand = $Se(CH_2CH_2CH_2SeMe)$ 2029, 1945 cm^{-1}, $MeC(CH_2TeMe)_3$ 2023, 1947 cm^{-1}, $MeC(CH_2TePh)_3$ 2028, 1959 cm^{-1}, and $S(CH_2CH_2SMe)_2$ 2047, 1968 cm^{-1}.[4] The shift of the two ν(CO) modes to low-frequency $S(CH_2CH_2SMe)_2 \rightarrow Se(CH_2CH_2CH_2SeMe)_2 \rightarrow MeC(CH_2TeMe)_3 \rightarrow L^2 \rightarrow L^1$ is evidence for the increased ligand → Mn donation observed as group 16 is descended[20] and suggests that L^1 and L^2 are similar, possibly even slightly better σ-donors than the $MeC(CH_2TeR)_3$. For a facially coordinated linear tridentate, the possible invertomers (Scheme 3) are not detectable in the IR data, but are easily observed in the NMR spectra. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra are complex and consistent with the presence of several invertomers, but the number of isomers is best established from the ^{55}Mn and ^{125}Te NMR spectra, which are much clearer. The ^{55}Mn NMR spectrum of $[Mn(CO)_3(L^1)]^+$ shows a strong resonance at δ −1338 and a weaker feature at −1362 (ratio ca. 10:1), and there are corresponding features at 119.7, 128.5 (major), (CH_2TeCH_2) 168.5, 169.0 (major), and 170.0 (TeMe) in the ^{125}Te NMR spectrum, which indicate that two invertomers are present, the DL (minor) and one *meso* (major), almost certainly *meso-1*, since *meso-2* where the −TeR are close to the CO groups is likely to be less favored. For the $[Mn(CO)_3(L^2)]^+$ two invertomers are also present [$\delta(^{55}Mn)$ −1218, −1254; $\delta(^{125}Te)$ 417.5, 400, 362 (PhTe), 132.5, 107 (CH_2TeCH_2)] but in approximately equal amounts, again tentatively assigned as DL and *meso-1*. We can also compare the ^{55}Mn NMR shifts with those in the complexes of $Se(CH_2CH_2CH_2SeMe)_2$ (−560), $MeC(CH_2TeMe)_3$ (−1509), and $MeC(CH_2TePh)_3$ (−1320). The low-frequency shifts in the telluroether complexes are again evidence of high electron density on the metal.[20]

$[PtCl(L)]PF_6$. The reaction of either tritelluroether with $PtCl_2$ in MeCN gave very poorly soluble brown solids which were unsuited to NMR study, but in the presence of 1 equiv of $TlPF_6$, the products were orange $[PtCl(L)]PF_6$. Both complexes show multiplet peaks with the correct isotope structure in the ES$^+$ mass spectra consistent with $[PtCl(L)]^+$. The ^{195}Pt NMR spectra of both complexes contain two broad resonances in the range δ −3600 to −4000, which can be compared with ca. −3000 to − 3300 for $Pt^{II}Cl_2Te_2$ and ca. −4700 to −5000 for $Pt^{II}Te_4$ donor sets.[7,21,22] Hence the present complexes are readily identified as containing planar $Pt^{II}Te_3Cl$ entities. The broad lines and the absence of ^{125}Te couplings are attributable to the onset of pyramidal inversion processes and are also observed in $[Pt(\text{ditelluroether})_2]^{2+}$ complexes,[22] where the high *trans* effect of *trans*-RTe−Pt−TeR arrangements lowers the inversion barrier. The ^{125}Te NMR spectra are sharper and show clear ^{195}Pt−^{125}Te couplings with two RTe resonances in each complex attributable to two *meso* arrangements at the planar Pt(II) center. The ^{125}Te NMR spectrum of $[PtCl(L^1)]^+$ shows some other very weak resonances which may be due to the DL form, but these were too weak to observe any ^{195}Pt coupling, and alternatively may be impurities. On standing for some hours, CH_2Cl_2 solutions of both complexes darken and now exhibit ^{195}Pt resonances with $\delta < -5000$ and ^{125}Te resonances without any ^{195}Pt couplings. We have not characterized these products, but it is likely they result from C−Te bond fission.

Conclusions. The spectroscopic data described above show that like $MeC(CH_2TeR)_3$ the linear tritelluroethers are strong σ-donors toward metal carbonyl fragments. The ligands also form complexes with medium oxidation state metals such as Rh(III) or Pt(II), although in the platinum case decomposition occurs in solution over

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several hours. The new tritelluroethers do not have the same steric limitations of the tripodal type and should support a wider range of metal center geometries. The synthetic route developed to $RTe(CH_2)_3Cl$ is expected to be sufficiently versatile to allow the preparation of tetradentate and macrocyclic telluroethers, and this is currently under investigation.

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Supporting Information Available: X-ray crystallographic files in CIF and PDF format. The material is available free of charge via the Internet at http://pubs.acs.org.

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