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Rhenium(I) Tellurolate, Telluroether and Bidentate-Telluroether Complexes: Crystal Structures of $Re(CO)_3Br(PhTe(CH_2)_3TePh)$, $PhTeRe(CO)_5$, $Re_2(\mu\text{-}SePh)_2(CO)_8$ and $[(PhTeMe)Re(CO)_5][BF_4]$

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The monomeric rhenium(I) complex with bidentate telluroether ligand $Re(CO)_3Br(PhTe(CH_2)_3TePh)$ (**1**) was accessible via reaction of the $PhTe(CH_2)_3TePh$ with $Re(CO)_5Br$. This chelate complex crystallized in triclinic space group $P\bar{1}$ with $a = 9.390(5)$ Å, $b = 10.961(3)$ Å, $c = 11.849(4)$ Å $\alpha = 63.30(3)^\circ$, $\beta = 87.49(4)^\circ$, $\gamma = 69.31(4)^\circ$, $V = 1009.5(7)$ Å^3, $Z = 2$, $R = 0.033$, and $R_w = 0.034$. Reaction of $Re(CO)_5Cl$ with NaTePh yielded the Re(I) species $PhTeRe(CO)_5$ (**2**). This complex crystallized in triclinic space group $P\bar{1}$ with $a = 7.085(1)$ Å, $b = 9.203(1)$ Å, $c = 11.341(1)$ Å, $\alpha = 107.24(1)^\circ$, $\beta = 100.56(1)^\circ$, $\gamma = 96.47(1)^\circ$, $V = 683.2(2)$ Å^3, $Z = 2$, $R = 0.027$, $R_w = 0.022$. Reaction of $PhTeRe(CO)_5$ and $(PhSe)_2$ in THF at 65 °C yielded a product that was confirmed crystallographically to be the known species $Re_2(\mu\text{-}SePh)_2(CO)_8$ (**3**), in which two phenylselenolate ligands bridge the two Re(I). Compound **3** crystallized in monoclinic space group $P2_1/n$ with $a = 7.210(2)$ Å, $b = 18.862(6)$ Å, $c = 9.083(3)$ Å, $\beta = 107.48(3)^\circ$, $V = 1178.2(7)$ Å^3, $Z = 2$, $R = 0.046$, and $R_w = 0.051$. Methylation of $PhTeRe(CO)_5$ with $[Me_3O][BF_4]$ afforded Re(I) product $[(PhTeMe)Re(CO)_5][BF_4]$ (**4**). This monodentate telluroether species crystallized in monoclinic space group $P2_1/n$ with $a = 8.405(1)$ Å, $b = 13.438(3)$ Å, $c = 15.560(2)$ Å, $\beta = 92.59(1)^\circ$, $V = 1755.5(5)$ Å^3, $Z = 4$, $R = 0.035$, and $R_w = 0.035$.

INTRODUCTION

Complexes containing tellurolate and telluroether ligands[1] were synthesized by tellurolysis via reaction of metal alkyls and tellurol,[2] by insertion of tellurium into a metal-carbon bond,[3] by nucleophilic attack of a metal hydride on diorganylditellurides,[4] and by oxidative addition of diorganylditellurides to metal complexes.[5] A typical procedure is to treat transition-metal halides with [cation][TeR] ligands, even though conventional metathesis reactions commonly result in formation of diorganylditelluride and metal fragment.[2] According to the literature, the coordination chemistry of transition metals with multidentate telluroethers/telluroether is much neglected,[1,6] and in particular little is reported about the reactivity of metal tellurolates.[2,7]

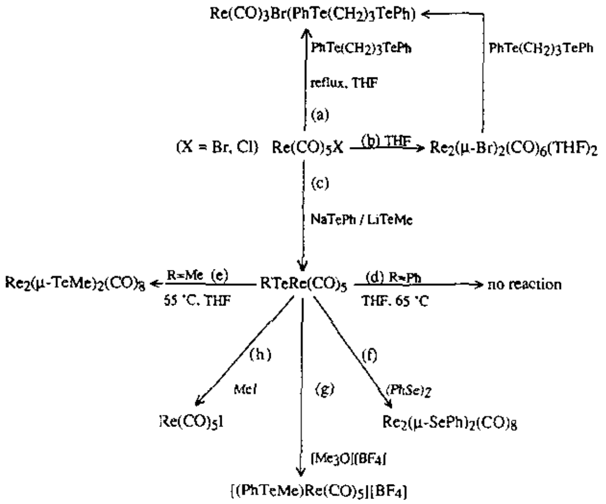
We recently demonstrated an exceptional mode of coordination in $MeTe(CH_2)_3TeMe$/RTeTeR and prepared polymeric coordination complexes $[Ag((MeTe(CH_2)_3TeMe)_{1/2})_4]_n[BF_4]_n$, $[Cu(\mu\text{-}Cl)(\mu\text{-}MeTeTeMe)_{1/2}]_n$, and diorganylditelluride-multiply-bridged $[Ag_2(NCCH_3)_4(\mu\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$.[8] To extend the range of transition-metal telluroethers and tellurolates, we used facile synthetic routes to prepare bidentate telluroether-, tellurolate-, and monodentate telluroether-rhenium(I) species; reactivity experiments provided insight into comparison of bond strengths of Re-Se and Re-Te.

RESULTS AND DISCUSSION

Monomeric transition-metal complex $Re(CO)_3Br(PhTe(CH_2)_3TePh)$ **1** containing bidentate telluroether was synthesized in high yield by reaction of $Re(CO)_5Br$ with chelate ligand $PhTe(CH_2)_3TePh$ in THF at 65 °C (Scheme Ia).[9] This colorless, air-sensitive matelial is slightly soluble in polar organic solvents. Compound **1** can also be prepared from reaction of $Re_2(\mu\text{-}Br)_2(CO)_6(THF)_2$ with $PhTe(CH_2)_3TePh$ in stoichiometric proportions via bridge splitting in THF at ambient temperature (Scheme Ib).[10]

The structure of $Re(CO)_3Br(PhTe(CH_2)_3TePh)$ was confirmed by X-ray diffraction measurements on a single crystal. The infrared spectrum of compound **1** shows bands in the carbonyl stretching region at 2027 vs, 1942 s, and 1904s cm^{-1} in THF. This pattern is well documented for a facial tricarbonyl complex in THF at ambient temperature containing an unsymmetrical bonding environment around the rhenium(I) atom.[10,11] In ^{1}H NMR spectra, a methylene multiplet (-Te-CH$_2$-, 3.00-3.27 (m) ppm, overlapping sets of triplets) also indicated a six-membered ring $\mathrm{ReTe_2C_3}$ possessing conformational isomers (boat-configuration (*meso, dl*) ⇔ chair-configuration (*meso, dl*)) in $\mathrm{CD_2Cl_2}$ solution at ambient temperature (structural isomerism was observed in solution for the chalcogenether complexes).[6]

Scheme I



The conventional metathetical reaction between $\mathrm{Re(CO)_5Cl}$ and NaTePh, achieved by dropwise addition of $\mathrm{NaBH_4}$ in ethanol to $\mathrm{(PhTe)_2}$ in ethanol at 0 °C,[10] in ethanol at ambient temperature provides a straightforward route to rhenium(I)-tellurolate $\mathrm{PhTeRe(CO)_5}$ **2** with a high yield (Scheme Ic). Rhenium(I)-tellurolate $\mathrm{PhTeRe(CO)_5}$ is an orange solid that is stable indefinitely when stored under nitrogen at room temperature or when heated in THF at 65 °C for 1 h (Scheme Id). By contrast, the analogous $\mathrm{MeTeRe(CO)_5}$ is stable for prolonged periods (four days) in the solid state in the absence of air at ambient temperature. In THF solution $\mathrm{MeTeRe(CO)_5}$ was converted into $\mathrm{Re_2(CO)_8(\mu\text{-}TeMe)_2}$ in one hour at 65 °C (Scheme Ie) or overnight at ambient temperature.[13] $\mathrm{PhTe(CH_2)_3TePh}$ and $\mathrm{(PhTe)_2}$ ligands catalyzed the formation of $\mathrm{Re_2(\mu\text{-}TePh)_2(CO)_8}$ on heating $\mathrm{PhTeRe(CO)_5}$ and $\mathrm{PhTe(CH_2)_3TePh}$ or $\mathrm{(TePh)_2}$ individually in THF at 65 °C.

Examination of the reactivity of this rhenium(I)-tellurolate species indicates that the reaction of $\mathrm{PhTeRe(CO)_5}$ with $\mathrm{(PhSe)_2}$ totally removed the tellurolate ligand and yielded a dimer $\mathrm{Re_2(CO)_8(\mu\text{-}SePh)_2}$ **3** bridged by only phenylselenolates with formation of diphenylditelluride as judged by the color, ^{1}H NMR spectra, and the structure of a single crystal (Scheme If).[10,14]

Nucleophilic reaction of $\mathrm{PhTeRe(CO)_5}$ with hard alkylating reagent $\mathrm{[Me_3O][BF_4]}$ in equimolar proportions in acetonitrile at ambient temperature for 3 min yielded monodentate telluroether rhenium(I) derivative $\mathrm{[(PhTeMe)Re(CO)_5][BF_4]}$ **4** (Scheme Ig). ^{1}H NMR spectra of $\mathrm{[(PhTeMe)Re(CO)_5][BF_4]}$ at room temperature become even more straightforward to confirm methylation of tellurium. The hydrogen ($\mathrm{TeCH_3}$) nuclei couple to ^{125}Te (I = 1/2, 6.99%) producing one set of satellites (2.73 (s) ppm, $J_{^{1}\mathrm{H\text{-}C\text{-}}^{125}\mathrm{Te}} = 24$ Hz) that provide valuable structural information.[9] In contrast to the reaction of $\mathrm{[Me_3O][BF_4]}$ and $\mathrm{PhTeRe(CO)_5}$, the reaction of $\mathrm{PhTeRe(CO)_5}$ with MeI produces the well known $\mathrm{Re(CO)_5I}$ (ν_{CO} (cm^{-1}) (hexane) 2146 w, 2093 w, 2038 s, 1990 m) and PhTeMe (^{1}H NMR ($\mathrm{CD_3CN}$): δ 2.63 (s) ($\mathrm{CH_3}$), 7.20-7.79 (m) ppm ($\mathrm{C_6H_5}$)) (Scheme Ih).[15]

Structure of $\mathrm{Re(CO)_3Br(PhTe(CH_2)_3TePh)}$

As depicted in Fig. 1, compound **1** has one bidentate telluroether chain chelated to a Re(I) center. The Te(1)-Re-Te(2) angle is 89.42(4)° so to produce distorted octahedral coordination around the metal. The Re-Te distances average 2.761(2) Å in compound **1**, smaller than another Re-Te distance 2.773(1) Å in $\mathrm{[(PhTeMe)Re(CO)_5][BF_4]}$. The Re-C bond of length 1.920(9) Å (average of Re-C(2) and Re-C(3)) is longer than the Re-C(1) bond of length 1.902(10) Å. The most remarkable feature of compound **1** is the stereochemistry of the chelating telluroether chain. The chelate ring on rhenium adopts a boat-like conformation with two phenyl rings lying on the same side of the chelating chain and Re-Te(1)-C(4) bond angle 107.6(3)°, Re-Te(2)-C(6) 107.3(3)°, Te(1)-C(4)-C(5) 117.6(6)°, Te(2)-C(6)-C(5) 118.1(6)°. A top view of compound **1** shows the Br atom to be significantly tilted toward two tellurium atoms (Te(1)-Re-Br 83.37(4)° and Te(2)-Re-Br 85.19(6)°) and indicates a

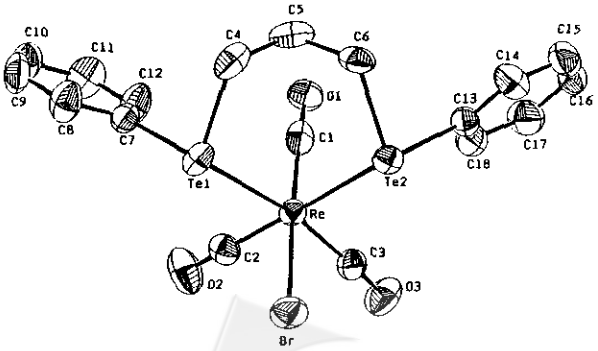


Fig. 1. ORTEP drawing and labeling scheme of $\mathrm{Re(CO)_3Br(PhTe(CH_2)_3TePh)}$ with thermal ellipsoids drawn at the 50% probability level.

meso conformation in the solid state.

Structure of PhTeRe(CO)$_5$

Compound **2** has an almost regular octahedral coordination geometry (Fig. 2). The Re-Te bond of length 2.813(1) Å in compound **2** is larger than the terminal Re-Te bond of length 2.773(1) Å in compound **4**, 2.761(2) Å (average) in compound **1**, and also longer than the Re-TeH bond of length 2.743(1) Å in Cp*Re(H)(CO)$_2$(TeH).[16a] The Re-Te-C(6) bond angle 101.6(2)° indicates a slightly distorted tetrahedral disposition of electron pairs about the tellurium atom. Re-C distances of two distinct kinds are seen. The larger distance 1.993(9) Å (average) is typical of Re-C bonds for carbonyls trans to π-acceptor carbonyl ligands. The smaller Re-C(3) distance (1.920(8) Å) is observed for carbonyl trans to σ-bonding phenyltellurolate ligand.

Structure of Re$_2$(μ-SePh)$_2$(CO)$_8$

The core geometry of compound **3** is best described as a Re$_2$Se$_2$ planar rhombus with two phenyl groups adopting a trans configuration in the solid state (Fig. 3). The molecule is symmetrical due to a crystallographically imposed inversion center. Four terminally bonded carbonyl groups and bridging selenolates define the distorted octahedral geometry of each rhenium atom, leading to an acute angle Se-Re-Se′ 83.37(4)°. An interesting aspect of this structure is that the selenium atom adopts a severely distorted tetrahedral arrangement of three bonding pairs and one lone pair of electrons because of the sharp bridge angle Re-Se-Re′ 96.63(4)°.[16b] The Re-Se distance (average 2.680(1) Å) compares well with the Re-Se distance 2.604(4) Å in the rhenium(I) dimer Re$_2$(CO)$_6$(μ-Br)$_2$(μ-Se$_2$Ph$_2$).[16c]

Structure of [(PhTeMe)Re(CO)$_5$]$^+$

The structure of the compound **4** unit in its BF$_4^-$ salt is shown in Fig. 4. The compound crystallizes as discrete cations of [(PhTeMe)Re(CO)$_5$]$^+$ and anions BF$_4^-$. In crystals of this monodentate telluroether complex, the coordination geometry around the rhenium(I) center is a distorted octahedron. The length 2.773(1) Å of the Re-Te bond in com-

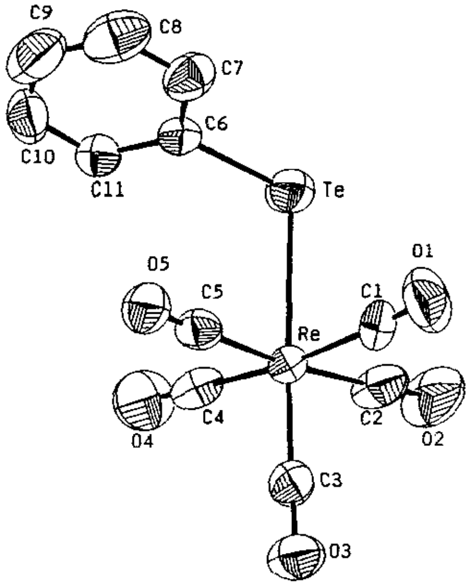


Fig. 2. ORTEP drawing and labeling scheme of PhTeRe(CO)$_5$ with thermal ellipsoids drawn at the 50% probability level.

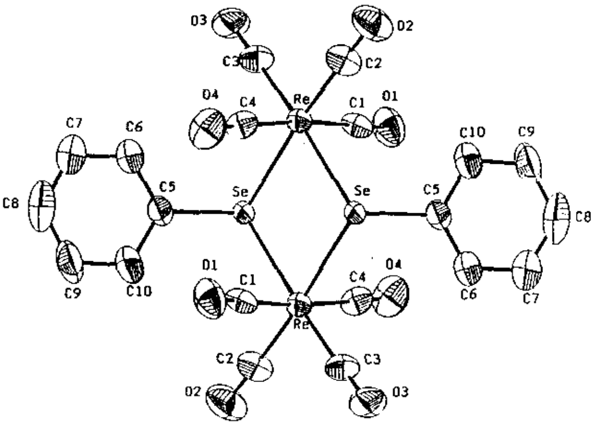


Fig. 3. ORTEP drawing and labeling scheme of Re$_2$(μ-SePh)$_2$(CO)$_8$ with thermal ellipsoids drawn at the 50% probability level.

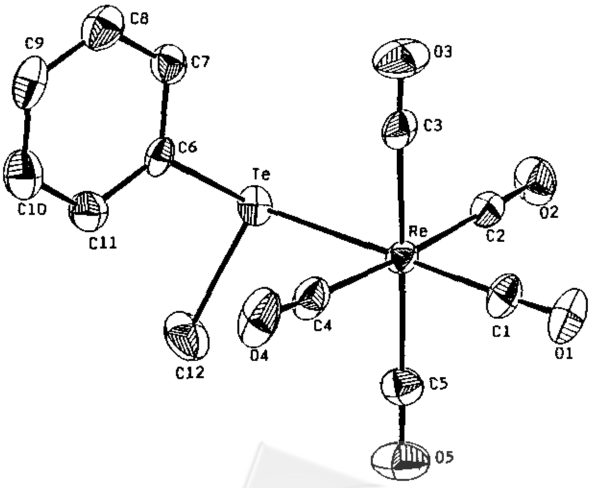


Fig. 4. ORTEP drawing and labeling scheme of [(PhTeMe)Re(CO)$_5$]$^+$ with thermal ellipsoids drawn at the 50% probability level.

pound **4** is comparable to that of another Re-Te distance 2.760(4) Å of structurally characterized, corresponding neutral rhenium-telluroether derivative $Re_2(\mu\text{-}Br)_2(CO)_6$-(PhTeTePh).[17] The C(6)-Te-C(12) bond angle 96.4(4)° indicates a greatly distorted tetrahedral disposition of electron pairs about the tellurium atom. The Te-C(Ph) bonds of length 2.126(9) Å in compound **4** parallel the Te-C(Ph) bond of length 2.132(7) Å in compound **2**, 2.139(9) Å in compound **1** and corresponds to the sum of radii 2.10 Å of Te (1.37 Å) and sp^2 C (0.73 Å).[18] The Re-C(1) bond length 1.926(10) Å for carbonyl trans to PhTeMe ligand is fortuitously similar to the Re-C bond length 1.920(9) Å (average) for carbonyls trans to chelating telluroether in compound **1**.

SUMMARY

We present an account of preparation and characterization of chelate-telluroether-, tellurolate- and monodentate-telluroether-rhenium(I) derivatives, including X-ray structures, and the reactivities of $PhTeRe(CO)_5$ toward $(PhSe)_2$, $(PhTe)_2$, $PhTe(CH_2)_3TePh$, $[Me_3O][BF_4]$, and MeI. Reactivity experiments provided insight into the comparison of bond strengths of Re-Se and Re-Te.

EXPERIMENTAL

Manipulations, transfer and reactions of samples were carried out under standard Schlenk techniques (N_2 atmosphere) and in a glovebox with a nitrogen atmosphere. Solvents were distilled under N_2 from appropriate drying agents (hexane and tetrahydrofuran (THF) from Na/benzophenone; ethanol from Mg/I_2; diethyl ether from calcium hydride; acetonitrile from CaH_2/P_2O_5) and then stored in dried, N_2-filled flasks over activated 4 Å molecular sieve. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were made via stainless-steel cannula under N_2 at positive pressure. The reagents rhenium pentacarbonyl bromide, tellurium powder, sodium borohydride, 1,3-dibromopropane, trimethyloxonium tetrafluroborate, diphenyldiselenide, methyl lithium, phenylmagnesium bromide (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) using sealed solution cells (0.1 mm) with KBr windows. NMR spectra were recorded on a Bruker AC 200 spectrometer; chemical shifts for ^{125}Te NMR spectra are relative to Me_2Te. Analyses of carbon, hydrogen were obtained with a CHN analyzer (Heraeus).

Preparation of $PhTe(CH_2)_3TePh$

To a solution of NaTePh, obtained by slow addition of $NaBH_4$ (76 mg, 2 mmol) to $(PhTe)_2$ (0.407 g, 1 mmol)[19] in ethanol at 0 °C, was added 1,3-dibromopropane (0.1 mL, 1 mmol) in ethanol (15 mL) at ambient temperature. The reaction mixture was stirred for 10 min and the color of the solution became light yellow. The solvent was removed under vacuum. Hexane (15 mL) and degassed H_2O (5 mL) were added individually and the top layer hexane solution was carefully transferred into another flask via cannula. The orange-yellow oily product $PhTe(CH_2)_3TePh$ (0.91 g, 98%) was obtained after removing hexane solvent under vacuum.[9] ^1H NMR (CD_3COCD_3): δ 2.94 (t), 2.26 (q), 7.76-7.14 (m) ppm. ^{13}C NMR (CD_3COCD_3): δ 33.98 (s) (satellite, $J_{^{13}C\text{-}C\text{-}^{125}Te} = 33.28$ Hz), 10.97 (s) (satellite, $J_{^{13}C\text{-}Te} = 108.19$ Hz), 137.90, 129.62, 127.71, 112.56 ppm.

Synthesis of $Re(CO)_3Br(PhTe(CH_2)_3TePh)$ 1

$Re(CO)_5Br$ (82 mg, 0.2 mmol) was loaded into a Schlenk flask (50 mL) and dissolved in THF (10 mL) at ambient temperature. Orange-yellow oily $PhTe(CH_2)_3TePh$ (91 mg, 0.2 mmol) was syringed into the mixture. The reaction mixture was stirred and refluxed for two hours, yielding a colorless solution. This solution, layered with hexane (4-fold portion), was then placed in a refrigerator (-10 °C) for three weeks. Colorless crystals (0.155 g, 97%) were obtained suitable for X-ray crystallography. IR ν_{CO} (THF) 1904 s, 1942 s, 2027 vs cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.00-3.27 (m) ($Te\text{-}CH_2$), 2.15-2.34 (m) ($Te\text{-}CH_2\text{-}CH_2\text{-}$), 7.28-8.00 (m) ppm ($C_6H_5$). ^{13}C NMR (CD_2Cl_2): δ 12.31, 12.46, 12.59, 15.07, 27.01 ($Te\text{-}CH_2\text{-}CH_2\text{-}$), 137.69, 137.14, 136.31, 130.78, 130.62, 130.39, 130.26, 129.72, 113.27, 111.73, 111.47 (C_6H_5), 187.9, 189.6 ppm (CO). Anal. Calc for $C_{18}H_{16}O_3BrTe_2Re$: C, 26.97; H, 2.01. Found: C, 27.11; H, 2.11.

Synthesis of $PhTeRe(CO)_5$ 2

A solution of NaTePh (0.5 mmol) in ethanol (15 mL) was added to $Re(CO)_5Cl$ (0.181 g, 0.5 mmol) at ambient temperature. The clear solution immediately turned orange. After stirring the resulting solution for 0.5 h, the solvent was removed under vacuum, and hexane (30 mL) was added to extract the product. Recrystallization by dissolving the product in a minimum amount of hexane and then cooling to -10 °C for two weeks afforded orange crystals of $PhTeRe(CO)_5$ (0.241 g, 91%).[20] IR ν_{CO} (THF) 2128 w, 2024 s, 1986 m cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.0-7.85 (m) ppm. ^{125}Te NMR (CD_3CN): δ -493.3 ppm. ^{13}C NMR (CD_3COCD_3): δ 182.30, 183.37 (CO), 142.25, 130.18, 129.21, 127.75 ppm (C_6H_5). Anal. Calcd for $C_{11}H_5O_5TeRe$: C, 24.88; H, 0.95. Found: C, 24.97; H, 1.09.

Reaction of PhTeRe(CO)$_5$ with Diphenyldiselenide

PhTeRe(CO)$_5$ (0.266 g, 0.5 mmol) and (PhSe)$_2$ (75 mg, 0.25 mmol) in THF (10 mL) were reacted at 65 °C for 2 h. The orange solution turned red-orange. The solvent was removed under vacuum. Hexane was added to dissolve the red-orange solid that was identified as diphenylditelluride by ^{1}H NMR spectra and X-ray crystallography,[14] leaving a light yellow solid. Recrystallization by dissolving the light-yellow solid in a minimum amount of THF, layering it with hexane, and keeping in the refrigerator at -10 °C for three weeks afforded light yellow crystals Re$_2$(μ-SePh)$_2$(CO)$_8$ **3** (0.19 g, 84%).[21] IR ν_{CO} (THF) 2087 w, 2013 s, 1990 m, 1952 m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 7.27-7.74 (m) ppm (C_6H_5). Anal. Calcd for $C_{20}H_{10}O_8Se_2Re_2$: C, 26.44; H, 1.11. Found: C, 25.87; H, 1.23.

Synthesis of [(PhTeMe)Re(CO)$_5$][BF$_4$] 4

PhTeRe(CO)$_5$ (0.266 g, 0.5 mmol) was loaded into a Schlenk flask (50 mL) with [Me$_3$O][BF$_4$] (74 mg, 0.5 mmol). Dried and degassed acetonitrile (10 mL) was added to give a light yellow solution. The reaction mixture was stirred at ambient temperature for 5 min. The reaction mixture was dried under vacuum, and THF was slowly added to precipitate the white solid. The mother liquor was removed via cannula. The residue was washed with THF several times and dried under vacuum. White solid [(PhTeMe)Re(CO)$_5$][BF$_4$] **4** (0.25 g) was isolated in 80% yield. Recrystallization of the product from a minimum volume of CH_3CN and THF, layering it with diethyl ether in four-fold proportion, and then cooling to -10 °C for three weeks afforded colorless crystals of [(PhTeMe)Re(CO)$_5$][BF$_4$] suitable for X-ray crystallography. IR ν_{CO} (THF) 2150 w, 2084 w, 2040 s, 1981 m cm^{-1}. ^{1}H NMR (CD_3CN): δ 2.73 (s) (satellite, $J_{^1H\text{-}C\text{-}^{125}Te}$ = 24 Hz), 7.30-7.76 (m) ppm (C_6H_5). ^{125}Te NMR (CD_3CN): δ 167.9 ppm. ^{13}C NMR (CD_3CN): δ 181.6, 176.3 (CO); 134.6, 131.5, 131.1, 111.8 ppm (C_6H_5). Anal. Calcd for $C_{12}H_8O_5BF_4TeRe$: C, 22.78; H, 1.28. Found: C, 23.28; H, 1.49.

Preparation of MeTeRe(CO)$_5$ and Re$_2$(μ-TeMe)$_2$(CO)$_8$

Into a Schlenk flask (50 mL) was charged Re(CO)$_5$Cl (0.181 g, 0.5 mmol) and a portion of LiTeMe in THF solution, prepared by addition of MeLi (0.32 mL, 1.6 M in diethyl ether, 0.5 mmol) to tellurium powder (0.064 g, 0.5 mmol) in THF at -90 to 15 °C. The reaction mixture was stirred for 0.5 h at ambient temperature. The THF solvent was removed under vacuum and the orange-red residue was extracted with hexane. Upon removal of hexane in vacuum, an orange-red solid MeTeRe(CO)$_5$ (0.206 g, 88%) was obtained. IR ν_{CO} (THF) 2127 w, 2070 w, 2020 s, 1985 m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 1.78 (s) ppm (satellite, $J_{^1H\text{-}C\text{-}^{125}Te}$ = 21.4 Hz). Neutral solid MeTeRe(CO)$_5$ is stable for prolonged periods (four days) in the absence of air at ambient temperature. In THF solution MeTeRe(CO)$_5$ transformed into yellow Re$_2$(μ-TeMe)$_2$(CO)$_8$ at 65 °C for 2 h. IR ν_{CO} (THF) 2074 m, 1996 s, 1985 sh, 1951 m cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 2.31 (s), 2.26 (s) ppm (CH_3). The spectral properties are consistent with formation of the Re$_2$(μ-TeMe)$_2$(CO)$_8$ dimer.[22]

Reactions of PhTeRe(CO)$_5$ and (PhTe)$_2$/PhTe(CH$_2$)$_3$TePh

Heating PhTeRe(CO)$_5$ (0.107 g, 0.2 mmol) and (PhTe)$_2$ (82 mg, 0.2 mmol) (or PhTe(CH$_2$)$_3$TePh, 91 mg, 0.2 mmol) THF solution for 1 h produced a red-brown solution. This solution was dried under vacuum, and hexane was slowly added to dissolve the (PhTe)$_2$. The hexane was removed and light orange solid Re$_2$(μ-TePh)$_2$(CO)$_8$ was dried under vacuum. The carbonyl-stretching bands at 2080 m, 2008 vs, 1989 s, 1952 m cm^{-1} (THF) were consistent with formation of Re$_2$(μ-TePh)$_2$(CO)$_8$. ^{1}H NMR (CD_3CN): δ 7.3-7.8 (m) ppm (C_6H_5).

Crystallography

Crystal data for compounds **1**, **2**, **3** and **4** are summarized in Table 1. The air-sensitive crystal Re(CO)$_3$Br(PhTe(CH$_2$)$_3$TePh) chosen for diffraction measurement ca. 0.05 × 0.35 × 0.45 mm (moderately air-sensitive crystal PhTeRe(CO)$_5$, crystal dimension 0.05 × 0.25 × 0.45 mm; air-stable crystal Re$_2$(μ-SePh)$_2$(CO)$_8$, crystal dimension 0.50 × 0.50 × 0.50 mm; moderately air-sensitive crystal [(PhTeMe)Re(CO)$_5$][BF$_4$], crystal size 0.03 × 0.28 × 0.35 mm) was mounted on a glass fiber and coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections (25 °C) (18.00° < 2θ < 33.16° for **1**; 18.74° < 2θ < 36.18° for **2**; 19.50° < 2θ < 38.28° for **3**; 19.84° < 2θ < 36.92° for **4**). Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated MoK$_\alpha$ radiation employing the θ/2θ scan mode; ψ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[23] Selected bond distances and angles are listed in Tables 2 and 3.

Table 1. Crystallographic Data for Compounds **1**, **2**, **3** and **4**

compound	**1**	**2**	**3**	**4**
chemical formula	$C_{18}H_{16}O_3BrTe_2Re$	$C_{11}H_5O_5TeRe$	$C_{20}H_{10}O_8Se_2Re_2$	$C_{12}H_8O_5BF_4TeRe$
formula mass/g	801.63	530.96	908.62	632.80
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
λ/Å (Mo, K_α)	0.7107	0.7107	0.7107	0.7107
a/Å	9.390(5)	7.085(1)	7.210(2)	8.405(1)
b/Å	10.961(3)	9.203(1)	18.862(6)	13.438(3)
c/Å	11.849(4)	11.341(1)	9.083(3)	15.560(2)
α/deg	63.30(3)	107.24(1)	90	90
β/deg	87.49(4)	100.56(1)	107.48(3)	92.59(1)
γ/deg	69.31(4)	96.47(1)	90	90
V/Å^3	1009.5(7)	683.2(2)	1178.2(7)	1755.5(5)
Z	2	2	2	4
$d_{(calcd)}$/g cm^{-3}	2.637	2.581	2.561	2.394
μ/cm^{-1}	109.2	111.2	135.1	87.1
F(000)	724	476	872	1152
no. of reflcs. ($I>2\sigma(I)$)	3540(3123)	2407(2139)	2694(2247)	3069(2415)
no. of parameters	227	164	146	218
R^a	0.033	0.027	0.046	0.035
R_w^{b}	0.034	0.022	0.051	0.035

[a] $R = \Sigma|(F_o-F_c)|/\Sigma F_o$

[b] $R_w = [\Sigma(\omega(F_o-F_c)^2/\Sigma\omega F_o^2]^{1/2}$

Table 2. Selected Bond Distances/Å and Angles/deg for (a) Compound **1** and (b) Compound **2**

(a) $Re(CO)_3Br(PhTe(CH_2)_3TePh)$			
Re-Te(1)	2.756(1)	Te(1)-C(4)	2.171(10)
Re-Te(2)	2.765(2)	Te(1)-C(7)	2.134(8)
Re-C(1)	1.902(10)	Te(2)-C(6)	2.172(8)
Re-C(2)	1.923(9)	Te(2)-C(13)	2.144(9)
Re-C(3)	1.916(8)	Re-Br	2.638(2)
Te(1)-Re-Te(2)	89.42(4)	Re-Te(1)-C(7)	106.18(24)
Te(1)-Re-Br	83.37(4)	Re-Te(2)-C(6)	107.3(3)
Te(2)-Re-Br	85.19(6)	Re-Te(2)-C(13)	107.43(23)
Te(1)-Re-C(1)	96.74(23)	Te(1)-C(4)-C(5)	117.6(6)
Te(1)-Re-C(2)	89.1(3)	Te(2)-C(6)-C(5)	118.1(6)
Te(1)-Re-C(3)	170.3(3)	C(4)-Te(1)-C(7)	92.9(3)
Re-Te(1)-C(4)	107.6(3)	C(6)-Te(2)-C(13)	92.4(3)
(b) $PhTeRe(CO)_5$			
Re-Te	2.813(1)	Re-C(5)	1.996(8)
Re-C(1)	1.999(9)	Re-C(3)	1.920(8)
Re-C(2)	1.997(8)	Te-C(6)	2.132(7)
Re-C(4)	1.980(9)		
Te-Re-C(1)	87.20(24)	Te-Re-C(4)	86.44(22)
Te-Re-C(2)	84.74(21)	Te-Re-C(5)	89.83(20)
Te-Re-C(3)	176.89(22)	Re-Te-C(6)	101.61(18)

Table 3. Selected Bond Distances/Å and Angles/deg for (a) Compound **3** and (b) Compound **4**

(a) $Re_2(\mu\text{-}SePh)_2(CO)_8$			
Re-Se	2.679(1)	Re-C(4)	1.965(12)
Re-Se′	2.681(1)	Re-C(2)	1.916(13)
Se-C(5)	1.988(12)	Re-C(3)	1.940(13)
Re-C(1)	1.975(12)		
Se-Re-Se′	83.37(4)	Se-Re-C(3)	93.6(4)
Re-Se-Re′	96.63(4)	Se-Re-C(4)	90.2(4)
Re-Se-C(5)	107.1(3)	Se′-Re-C(1)	90.4(3)
Re′-Se-C(5)	109.0(3)	Se′-Re-C(2)	93.2(4)
Se-Re-C(1)	85.7(3)	Se′-Re-C(3)	176.9(4)
Se-Re-C(2)	176.1(4)	Se′-Re-C(4)	85.9(3)
(b) $[(PhTeMe)Re(CO)_5][BF_4]$			
Re-Te	2.773(1)	Re-C(2)	2.008(9)
Te-C(6)	2.126(9)	Re-C(3)	2.008(9)
Te-C(12)	2.127(10)	Re-C(4)	2.007(10)
Re-C(1)	1.926(10)	Re-C(5)	2.004(9)
C(6)-Te-C(12)	96.4(4)	Te-Re-C(2)	87.8(3)
Re-Te-C(6)	100.52(24)	Te-Re-C(3)	89.2(3)
Re-Te-C(12)	103.3(4)	Te-Re-C(4)	89.0(3)
Te-Re-C(1)	179.2(3)	Te-Re-C(5)	90.2(3)

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Key Words

Rhenium(I)-tellurolate; -Telluroether.

SUPPLEMENTARY MATERIALS

Tables of crystallographic details, atomic coordinates, bond lengths and angles, and u(i, j) or U values for Re(CO)$_3$Br(PhTe(CH$_2$)$_3$TePh) (4 pages); (PhTeRe(CO)$_5$ (4 pages); Re$_2$(μ-SePh)$_2$(CO)$_8$ (4 pages); [(PhTeMe)Re(CO)$_5$]-[BF$_4$] (4 pages)) are available on request of G.-H. Lee, S.-M. Peng or W.-F. Liaw.

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