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Reactivity of $(p\text{-MeOC}_6H_4)_2TeO$ toward $t\text{-Bu}_2Si(OH)_2$. Synthesis of a 12-Membered Tellurasiloxane Ring, *cyclo*-$[(p\text{-MeOC}_6H_4)_2TeOSi\,t\text{-Bu}_2O]_3$

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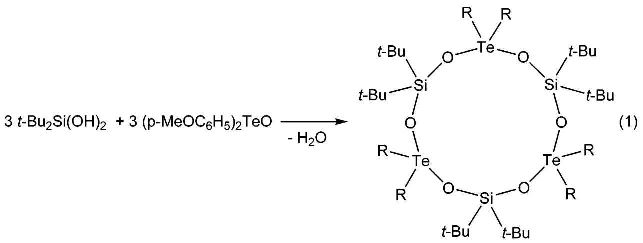
Summary: Condensation of $t\text{-Bu}_2Si(OH)_2$ *with* $(p\text{-MeOC}_6H_4)_2TeO$ *in a Si/Te ratio of 1:1.2 exclusively produced the 12-membered tellurasiloxane ring cyclo-*$[(p\text{-MeOC}_6H_4)_2TeOSi\,t\text{-Bu}_2O]_3$ *(**1**), whose molecular structure was determined by X-ray crystallography. At larger Si/Te ratios, the open-chain tellurasiloxanes* $HOt\text{-Bu}_2SiOR_2TeOSit\text{-Bu}_2OH$ *(**2**,* $R = p\text{-MeOC}_6H_4$*) and* $HOt\text{-Bu}_2SiOR_2TeOSit\text{-Bu}_2OR_2TeOSit\text{-Bu}_2OH$ *(**3**,* $R = p\text{-MeOC}_6H_4$*) were identified in solution by* ^{29}Si *and* ^{125}Te *NMR spectroscopy along with **1** and unreacted* $t\text{-Bu}_2Si(OH)_2$*. The analogous reaction of* $Ph_2Si(OH)_2$ *with* $(p\text{-MeOC}_6H_4)_2TeO$ *did not provide tellurasiloxanes, but led to the formation of the known siloxanes rings cyclo-*$(Ph_2SiO)_3$ *and cyclo-*$(Ph_2SiO)_4$*.*

Although the first diorganotellurium oxides R_2TeO (R = alkyl, aryl) were prepared more than 90 years ago,[1] only recently has attention been paid to their structure and reactivity. While diorganotellurium oxides, such as R_2TeO, having polar Te−O double bonds (R = Ph, C_6F_5, $p\text{-MeC}_6H_4$, $p\text{-MeOC}_6H_4$), are monomers in chloroform,[2] the structures in the solid state are more diverse. For instance, Ph_2TeO[3] and $(C_6F_5)_2TeO$[4] are asymmetric dimers with elongated Te−O double bonds and secondary Te···O intermolecular contacts, whereas $(p\text{-MeOC}_6H_4)_2TeO$ forms a 1D polymer with symmetric Te−O single bonds.[2] Diorganotellurium oxides have found applications as "oxygen" transfer reagents in organic[5] and organometallic synthesis.[6] Diorganotellurium oxides are Lewis bases and undergo condensation reactions to give tetraorganoditelluroxanes with proton acids, such as carboxylic acids,[7] HNO_3,[8] HO_3SCF_3, and HO_2PPh_2[9] Diorganotellurium oxides show potential for the preparation of tellurastannoxanes and related species featuring Te−O−Sn bonds, as well as for the fixation of carbon dioxide.[10]

Metallasiloxanes, compounds containing M−O−Si linkages (M includes metals as well as nonmetals), have attracted considerable attention in recent years owing to applications in material science and catalysis.[11] Although studies on metallasiloxanes have been extensive for most elements of the periodic table, there are very few reports on tellurasiloxanes.[12] As part of our interest in the chemistry of telluroxanes we have now investigated the reactivity of diorganotellurium oxides toward organosilanols. The condensation reaction of $t\text{-Bu}_2Si(OH)_2$ with 1.2 equiv of $(p\text{-MeOC}_6H_4)_2TeO$ provided the 12-membered tellurasiloxane ring *cyclo*-$[(p\text{-MeOC}_6H_4)_2TeOSi\,t\text{-Bu}_2O]_3$ (**1**) as colorless crystalline material in quantitative yield (eq 1).



1

R = p-MeOC$_6$H$_5$

The molecular structure of **1** has been established by X-ray crystallography and is shown in Figure 1. Selected bond parameters are collected in the caption of the figure. The geometry of the Te atoms of **1** can be described as distorted trigonal bipyramidal when taking into account the stereochemically active lone pair of Te.[2] The axial O coordination is rather symmetric, as the Te−O bond lengths (2.051(3)−2.064(3) Å) differ only marginally. No secondary Te···O intermolecular contacts are observed. Therefore, the coordination sphere of **1** resembles that of the parent $(p\text{-MeOC}_6H_5)_2TeO$, but differs substantially from those of related tetraorganoditelluroxanes[7−9] and tellurastannoxanes,[10] whose structures reveal a rather

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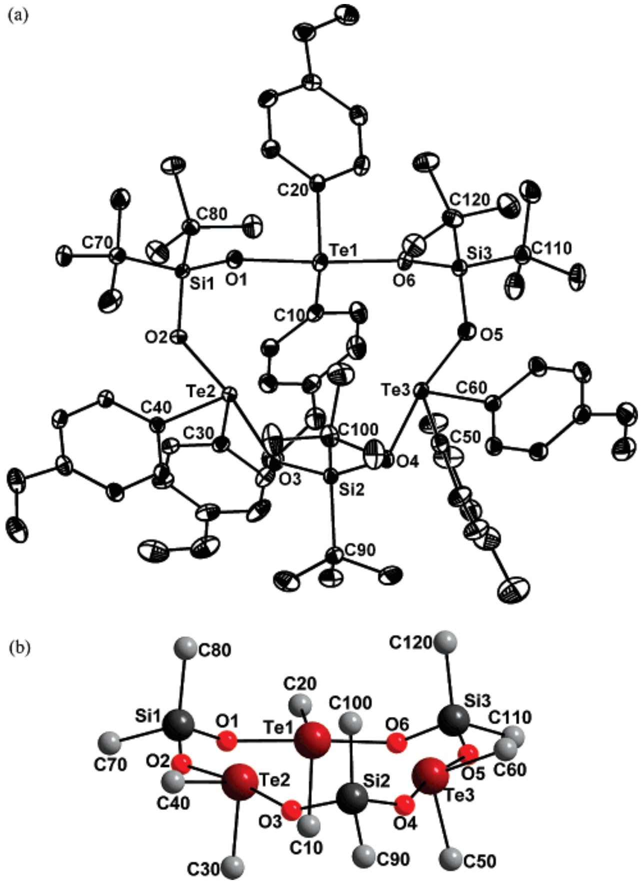

Figure 1. (a) Molecule of $(p\text{-}MeOC_6H_4)_2TeOSi\textit{t}\text{-}Bu_2O)_3$ (**1**) showing 30% probability displacement ellipsoids and the atom numbering. Selected bond parameters [Å, deg]: Si−O 1.617(4)−1.630(2), Te−O 2.051(3)−2.064(3), Si−O−Te 134.80(12)−141.70(13). (b) Ring conformation of **1** (only α-carbon atoms are shown for clarity) with the large deviation from the ideal $Te_3Si_3O_6$ plane being 0.46 Å for Si1. Selected torsion angles [deg]: Te1−O1−Si1−O2−64.35(24), O1−Si1−O2−Te2 57.77(22), Si1−O2−Te2−O3−159.67(51), O2−Te2−O3−Si2 170.02(50), Te2−O3−Si2−O4−60.71(24), O3−Si2−O4−Te3 53.82(25), Si2−O4−Te3−O5 177.20(45), O4−Te3−O5−Si3 174.29(45), Te3−O5−Si3−O6−54.56(24), O5−Si3−O6−Te1 69.63(21), Si3−O6−Te1−O1 166.05(56), O6−Te1−O1−Si1−173.95(54).

asymmetric axial O coordination and a number of secondary Te···O intra- and intermolecular contacts. The conformation of the inorganic 12-membered $Te_3Si_3O_6$ ring deviates from planarity, with the largest deviation of 0.46 Å being observed for Si1. Related torsion angles are collected in the caption of Figure 1. It is worth noting that the formation of 12-membered metallasiloxane rings is rare, while six- and eight-membered ring systems are more common.[11] We are aware of only one other 12-membered metallasiloxane ring derived from *t*-$Bu_2Si(OH)_2$, namely, *cyclo*-[(O)(Cl)VOSi*t*-$Bu_2O]_3$.[13] In $CDCl_3$ solution, the tellurasiloxane ring *cyclo*-[(*p*-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$ (**1**) is characterized by ^{29}Si and ^{125}Te NMR chemical shifts of δ −20.2 and 921.5, respectively.

In an effort to obtain insight into the formation of **1**, the reaction between *t*-$Bu_2Si(OH)_2$ and (*p*-$MeOC_6H_4)_2TeO$ was monitored by ^{29}Si and ^{125}Te NMR spectroscopy. While the reaction was quantitative at a Si/Te ratio of 1:1.2, increasing amounts of *t*-$Bu_2Si(OH)_2$ give varying mixtures of *cyclo*-[(*p*-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$ (**1**) and the open-chain tellurasiloxanes HO*t*-Bu_2SiOR_2TeOSi*t*-Bu_2OH (**2**, $\delta(^{29}Si)$ −13.5, $\delta(^{125}Te)$ 957.2, R = *p*-$MeOC_6H_4$) and HO*t*-Bu_2SiOR_2TeOSi*t*-Bu_2OR_2-TeOSi*t*-Bu_2OH (**3**, $\delta(^{29}Si)$ −13.6, −18.4 (2:1), $\delta(^{125}Te)$ 940.0 R = *p*-$MeOC_6H_4$). At Si/Te ratios of 2:1 and 4:1, the molar distribution of **1**, **2**, **3**, and unreacted *t*-$Bu_2Si(OH)_2$ ($\delta(^{29}Si)$ −6.5) was 5, 66, 18, and 11% and 8, 47, 26, and 19%, respectively. The assignment of the NMR signals is based on the relative integral intensities at the varying Si/Te ratios and the fact that bridging TeO−Si−OTe units ($\delta(^{29}Si)$ −18.4, −20.2) and terminal TeO−Si−OH units ($\delta(^{29}Si)$ −13.5, −13.6) can be clearly distinguished. At a Si/Te ratio of 2:1, the ESI-MS spectrum (positive mode, cone voltage 30 V) of a diluted solution in MeCN (1:100) reveals four mass clusters with relative intensities greater than 10% based on the highest peak that were unambiguously assigned to the cations $[R_2TeOH]^+$ (361.01), [*t*-$Bu_2SiOTeR_2OH]^+$ (519.12), $[R_2TeOR_2TeOH]^+$ (717.01), and [*t*-$Bu_2SiOR_2TeOR_2TeOH]^+$ (875.12), respectively (R = *p*-$MeOC_6H_4$). While two of these cations confirm the presence of Si−O−Te linkages, no quantitative information can be obtained about neutral species in solution. Attempts to isolate **2** and **3** by fractional crystallization and column chromatography failed. The equimolar reaction of $Ph_2Si(OH)_2$ with (*p*-$MeOC_6H_4)_2$-TeO under similar conditions did not afford tellurasiloxanes, but proceeds with condensation of the silanol groups to give a mixture (ratio 46:54%) of the known siloxane rings *cyclo*-$(Ph_2SiO)_3$ ($\delta(^{29}Si)$ −33.4) and *cyclo*-$(Ph_2SiO)_4$ ($\delta(^{29}Si)$ −42.3), which have been unambiguously identified by their ^{29}Si NMR chemical shifts.[14]

Experimental Section

Synthesis of [(*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O]$_3$ (1). A solution of (*p*-$MeOC_6H_4)_2TeO$[2] (292 mg, 0.82 mmol) and (*t*-Bu)$_2$Si(OH)$_2$[15] (120 mg, 0.68 mmol) in toluene (30 mL) was heated at reflux for 12 h in a Dean-Stark apparatus. The solvent was removed in a vacuum, and the solid residue was dissolved in ether (10 mL) and filtered. Slow evaporation of the solvent afforded colorless crystals of **1** (341 mg, 0.22 mmol, 97%; mp 230−235 °C).

^1H NMR ($CDCl_3$): δ 8.03, (d, 12H; *p*-$O_mMeC_6H_4$), 6.78 (d, 12 H; *p*-$O_oMeC_6H_4$), 3.76 (s, 18 H; OCH_3), 0.93 (s, 54 H; CH_3). ^{13}C NMR ($CDCl_3$): δ 161.2 (*p*-$O_iMeC_6H_4$), 133.8 (*p*-$O_mMeC_6H_4$), 130.6 (*p*-$O_pMeC_6H_4$), 114.0 (*p*-$O_oMeC_6H_4$), 55.1 (OCH_3), 29.1 (CH_3), 21.6 (C_qCH_3). ^{29}Si NMR ($CDCl_3$): δ −20.2. ^{125}Te-NMR ($CDCl_3$): δ 921.5. Anal. Calcd for $C_{66}H_{96}O_{12}Si_3Te_3$ (1548.52): C, 51.19; H, 6.25. Found: C, 50.89; H, 5.86.

Crystallography. Single crystals were grown by slow evaporation of a ether/CH_2Cl_2 solution of [(*p*-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$ (**1**). Crystal data and structure solution: $C_{66}H_{96}O_{12}Si_3Te_3$, M_r = 1548.56, monoclinic, $P2_1/n$, a = 14.079(3) Å, b = 22.641(5) Å, c = 22.189(5) Å, β = 93.219(5)°, V = 7062(3) Å^3, Z = 4, D_x = 1.456 Mg/m^3, $F(000)$ = 3144, μ = 1.338 mm^{-1}, T = 173 K. Intensity data were collected on a Bruker SMART 1000 CCD diffractometer fitted with Mo Kα radiation (graphite crystal monochromator, λ = 0.71073 Å) to a maximum of θ_{max} = 30.540° via ω scans (completeness 99.4% to θ_{max}). Data were reduced and corrected for absorption using the programs SAINT and SADABS.[16] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX

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2002.[17] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model (including free rotation about C−C) and were refined isotropically. $R_1 = 0.0409$ for 15 197 [$I > 2\sigma(I)$] and $wR_2 = 0.1102$ for 21 497 independent reflections. GooF = 1.047. The max. and min. residual electron densities were 1.742 and −0.762 e Å^{-3}. The figure was prepared using the DIAMOND program.[18]

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-634720. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-(0)12 23-33 60 33; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: A CIF file of the crystallographic data (excluding structure factors) of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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