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The Reactivity of Diorganotellurium Oxides Towards Phenol and *o*-Nitrophenol. Hypervalent and Secondary Bonding of Four Different Product Classes

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The reaction of the diorganotellurium oxides $\mathrm{R_2TeO}$ (R = Ph, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{Me_2NC_6H_4}$) with phenol and *o*-nitrophenol produces diorganotellurium hydroxy phenolates, $\mathrm{R_2Te(OH)OPh}$ (**1**, R = Ph; **2**, R = p-$\mathrm{MeOC_6H_4}$; **3**, R = p-$\mathrm{Me_2NC_6H_4}$), diorganotellurium bis(phenolates) $\mathrm{R_2Te(OPh)_2}$ (**4**, R = Ph; **5**, R = p-$\mathrm{MeOC_6H_4}$; **6**, R = p-$\mathrm{Me_2NC_6H_4}$), tetraorganoditelluroxane bis(*o*-nitrophenolates), $\mathrm{(R'O)R_2TeOTeR_2(OR')}$ (**7**, R = p-$\mathrm{MeOC_6H_4}$; **8**, R = p-$\mathrm{Me_2NC_6H_4}$; R′ = *o*-$\mathrm{NO_2C_6H_4}$), and a hexaphenyltritelluroxane bis(*o*-nitrophenolate) $\mathrm{(R'O)Ph_2TeOTePh_2OTePh_2(OR')}$ (**9**, R′ = *o*-$\mathrm{NO_2C_6H_4}$), respectively. The redistribution reactions of $\mathrm{R_2Te(OPh)_2}$ (**4**, R = Ph; **5**, R = p-$\mathrm{MeOC_6H_4}$; **6**, R = p-$\mathrm{Me_2NC_6H_4}$) with the corresponding diorganotellurium oxides $\mathrm{R_2TeO}$ and diorganotellurium dichlorides $\mathrm{R_2TeCl_2}$ (R = Ph, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{Me_2NC_6H_4}$) give rise to the formation of moisture sensitive tetraorganoditelluroxane bis(phenolates) $\mathrm{(PhO)R_2TeOTeR_2(OPh)}$ (**10**, R = Ph; **11**, R = p-$\mathrm{MeOC_6H_4}$; **12**, R = p-$\mathrm{Me_2NC_6H_4}$) and diorganotellurium chloro phenolates, $\mathrm{R_2Te(Cl)OPh}$ (**13**, R = Ph; **14**, R = p-$\mathrm{MeOC_6H_4}$; **15**, R = p-$\mathrm{Me_2NC_6H_4}$), respectively. The reaction of the diorganotellurium oxides $\mathrm{R_2TeO}$ with the corresponding diorganotellurium dichlorides $\mathrm{R_2TeCl_2}$ (R = Ph, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{Me_2NC_6H_4}$) affords tetraorganoditelluroxane dichlorides $\mathrm{ClR_2TeOTeR_2Cl}$ (**16**, R = Ph; **17**, R = p-$\mathrm{MeOC_6H_4}$; **18**, R = p-$\mathrm{Me_2NC_6H_4}$) as air-stable solid materials. The reactivity of **1**–**18** can be rationalized by the kinetic lability of the Te–O and Te–Cl bonds. Compounds **1**–**18** have been characterized by solution and solid-state ^{125}Te NMR spectroscopy and **2**, **4**, **6**, **7**, **9**, **17**, and **18** have also been analyzed by X-ray crystallography.

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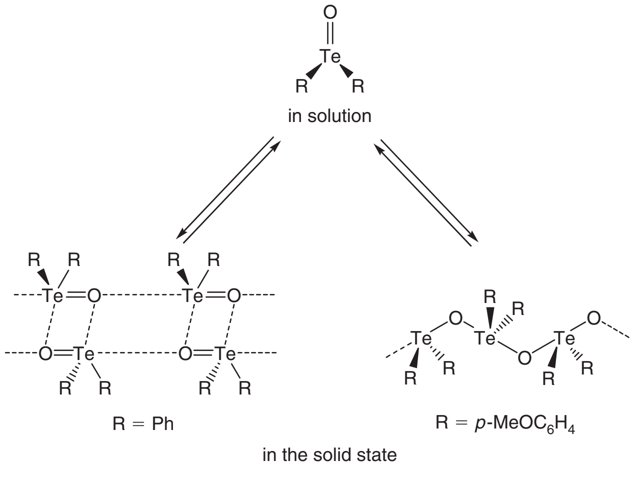
Introduction

Although the first diorganotellurium oxides, $\mathrm{R_2TeO}$ (R = alkyl, aryl), were described by Lederer more than 90 years ago,[1] for a long time little attention was directed to the structure and reactivity of this compound class, presumably because of the common misconception that tellurium chemistry closely resembles selenium chemistry. In solution, diorganotellurium oxides, such as $\mathrm{Ph_2TeO}$ and (p-$\mathrm{MeOC_6H_4)_2TeO}$, are only very slightly associated and comprise mostly monomers that have polar Te=O double bonds.[2] However, in the solid-state diorganotellurium oxides aggregate and show surprisingly diverse structures, as opposed to their lighter group 16 congeners. For instance, crystalline $\mathrm{Ph_2TeO}$ consists of two conformers with slightly elongated Te=O double bonds, which are connected by short secondary Te···O bonds, which gives rise to asymmetric dimers (Scheme 1).[3] The closely related (p-$\mathrm{MeOC_6H_4)_2TeO}$ contains a one-dimensional polymer with two Te–O single bonds in the solid-state and lacks any secondary interactions (Scheme 1).[2]



Scheme 1.

Recently, we have demonstrated that diorganotellurium oxides, such as (p-$\mathrm{MeOC_6H_4)_2TeO}$, show potential for the preparation of binary element oxides and for applications in the fixation of carbon dioxide.[4] In the present work, we report on the reaction of the diorganotellurium oxides $\mathrm{R_2TeO}$ (R = Ph, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{Me_2NC_6H_4}$) with phenol and *o*-nitrophenol, which provides access to four different compound classes, namely diorganotellurium hydroxy phenolates, diorganotellurium bis(phenolates), and tetraorganoditelluroxane and hexaorganotritelluroxanes bis(*o*-nitrophenolates). The reactivity of the Te=O double bond sharply contrasts that

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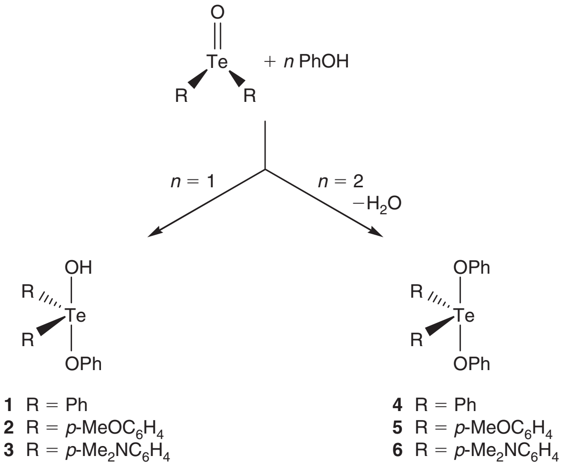


Scheme 2.

of most light p-block element oxides that have polar E–O double bonds (e.g., Ph_3PO, Ph_3AsO, Ph_2SO, Ph_2SeO), which form hydrogen-bonded complexes with phenol and related compounds.[5] A few diorganotellurium dialcoholates, such as $Ph_2Te(OMe)_2$, had been prepared previously by metathesis reactions, however, their characterization remained incomplete at the time.[6] During the course of this work, Srivastava et al. reported on tetramethylditelluroxane bis(*o*,*p*,*o*′-trinitrophenolate), which was fully characterized by X-ray crystallography.[7]

Results and Discussion

Synthetic Aspects and Structural Characterization

The reaction of the diorganotellurium oxides, R_2TeO (R = Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$), with one and two equivalents of phenol, PhOH, in refluxing toluene produced diorganotellurium hydroxy phenolates $R_2Te(OH)OPh$ (**1**, R = Ph; **2**, R = *p*-$MeOC_6H_4$; **3**, R = *p*-$Me_2NC_6H_4$) and diorganotellurium bis(phenolates) $R_2Te(OPh)_2$ (**4**, R = Ph; **5**, R = *p*-$MeOC_6H_4$; **6**, R = *p*-$Me_2NC_6H_4$), respectively, as colourless crystalline or microcrystalline compounds in high yields (Scheme 2).

The molecular structures of (*p*-$MeOC_6H_4)_2Te(OH)OPh$ (**2**), $Ph_2Te(OPh)_2$ (**4**), and (*p*-$Me_2NC_6H_4)_2Te(OPh)_2$ (**6**) are shown in Figs 1–3. Selected crystal and refinement data are collected in Table 1 and selected bond parameters are listed in the captions of the figures. Bearing in mind the sterically active lone pair, the spatial arrangement around the Te atoms is best described as distorted trigonal bipyramidal. Consistent with Bent's rule, the equatorial positions are occupied by two C atoms and the lone pair, whereas the more electronegative O atoms are situated in the axial positions. In compounds **4** and **6**, the Te atoms lie across crystallographic centres of inversion. As often observed for hypervalent main group compounds with trigonal bipyramidal structures,[8] the axial Te–O bond lengths of **2** (1.980(4), 2.209(4) Å) are somewhat different, whereas those of **4** (2.074(2) Å) and **6** (2.111(2) Å) are equal owing to the centrosymmetry. The Te–O bond lengths of **2**, **4**, and **6** compare well with those found for the (*p*-$MeOC_6H_4)_2TeO$ polymer (2.025(2) and 2.100(2) Å).[2] It has previously been proposed that π-electron delocalization might be operative in organotellurium compounds that contain *p*-dimethylaminophenyl groups and that besides an aromatic resonance structure (**A**), a second quinoid resonance structure (**B**) may contribute to the description of the electron distribution (Scheme 3).[9]

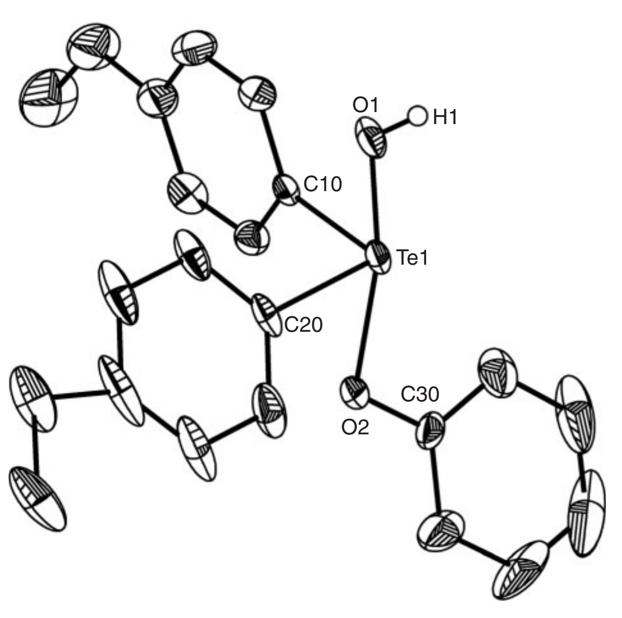


Fig. 1. Molecular structure of (*p*-$MeOC_6H_4)_2Te(OPh)OH$ (**2**) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = x, 0.5 - y, -0.5 + z$. Selected bond parameters [Å, °]: Te1–O1 1.980(4), Te1–C20 2.102(6), Te1–C10 2.113(5), Te1–O2 2.209(4), O1–H1 0.69(8), H1···O2a 2.05(8), O1···O2a 2.733(6), O1–Te1–C20 87.5(2), O1–Te1–C10 89.3(2), C20–Te1–C10 96.9(2), O1–Te1–O2 168.6(2), C20–Te1–O2 82.6(2), C10–Te1–O2 86.1(2), O1–H1–O2a 175(8).

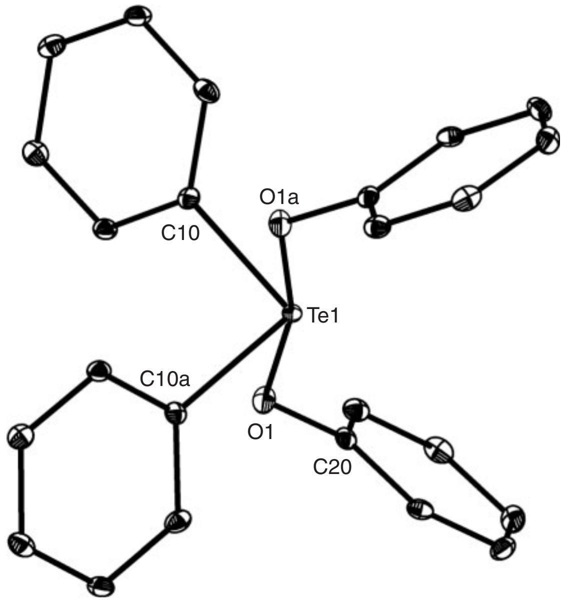


Fig. 2. Molecular structure of $Ph_2Te(OPh)_2$ (**4**) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = -x, y, 1.5 - z$. Selected bond parameters [Å, °]: Te1–O1 2.074(2), Te1–C10 2.106(4), C10–C15 1.373(5), C10–C11 1.385(5), C15–C14 1.380(5), C14–C13 1.382(5), C13–C12 1.379(6), C12–C11 1.376(5), O1–Te1–O1a 166.0(2), O1–Te1–C10a 84.9(1), O1–Te1–C10 86.0(1), C10–Te1–C10a 98.2(2).

In an effort to evaluate if quinoid π-electron delocalization is operative in **6**, the quinoid character *Q* has been calculated from the C–C bond lengths and compared with that of **4**.[10] For $Ph_2Te(OPh)_2$ (**4**) *Q* is 0.003 Å, which indicates

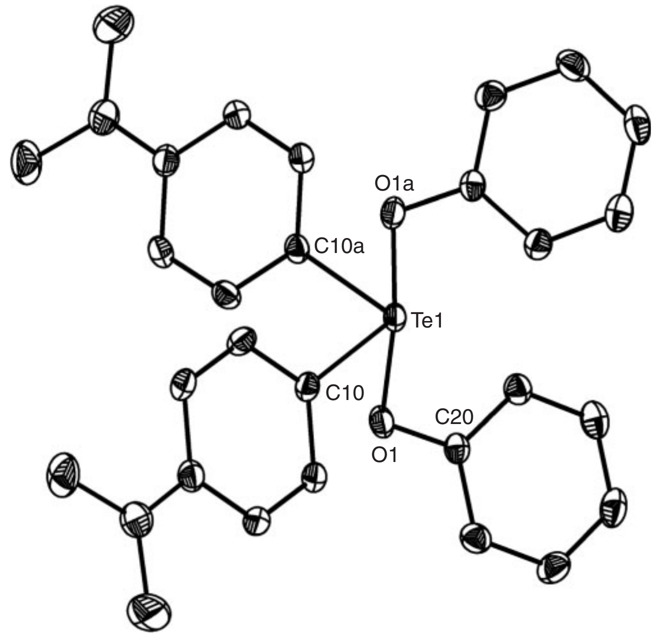


Fig. 3. Molecular structure of $(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{Te(OPh)}_2$ (**6**) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = 1 - x$, $0.5 - y$, z. Selected bond parameters [Å, °]: Te1–C10 2.096(3), Te1–O1 2.111(2), C13–C12 1.402(4), C13–C14 1.407(5), C10–C11 1.388(4), C10–C15 1.387(4), C12–C11 1.381(4), C14–C15 1.379(4), C13–N1 1.355(3), C10–Te1–C10a 95.0(2), C10–Te1–O1 86.6(1), C10–Te1–O1a 89.2(1), O1–Te1–O1a 173.8(1).

almost no contribution of the resonance structure B. For $(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{Te(OPh)}_2$ (**6**) the parameter Q is 0.016 Å, which is approximately half the value observed for $p\text{-H}_2\text{NC}_6\text{H}_4\text{NO}_2$ (0.032 Å). The idea of a bipolar resonance structure contribution is also supported by the C13–N1 bond length of 1.355(3) Å, which is significantly shorter than the expected value ($d(\text{C sp}^2\text{–N sp}^3) = 1.44$–$1.45$ Å). However, the Te1–C10 bond length of **6** (2.096(3) Å) is only 0.010 Å shorter than that of **4** (2.106(4) Å), which points to a disruption of the π-electron delocalization and to a poor or no involvement of the Te atom. Like the $(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ polymer,[2] the solid-state structures of **2**, **4**, and **6** lack any secondary Te–O interactions. In the crystal lattice, $(p\text{-MeOC}_6\text{H}_4)_2\text{Te(OH)OPh}$ (**2**) is associated by hydrogen bonding, whereby the phenolate group of an adjacent molecule acts as the hydrogen acceptor. The donor acceptor O1···O2a distance of 2.733(6) Å is indicative of a weak hydrogen bridge (symmetry code: $a = x$, $0.5 - y$, $-0.5 + z$).[11] The infrared (IR) spectra (KBr pellets) of the diorganotellurium hydroxo phenolates $\text{R}_2\text{Te(OH)OPh}$ exhibit bands at 3410 (**1**, R = Ph), 3388 (**2**, $p\text{-MeOC}_6\text{H}_4$), and 3414 cm^{-1} (**3**, $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$) that are assigned to OH stretching vibrations. The position of these bands is consistent with weak hydrogen bonding. Compounds **1**–**6** have been characterized by ^{125}Te MAS NMR spectroscopy. All compounds give rise to a single resonance between δ_{iso} 930 and 1184. Notably, the variation of the organic substituents in $\text{R}_2\text{Te(OH)OPh}$ and $\text{R}_2\text{Te(OPh)}_2$ (R = Ph: δ_{iso} 1046 (**1**) and 1111(**4**); $\text{R} = p\text{-MeOC}_6\text{H}_4$: δ_{iso} 991 (**2**) and 930 (**5**); $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$: δ_{iso} 1028 (**3**) and 1184 (**6**)) seems to have a larger effect on the ^{125}Te MAS NMR chemical shift than the number of phenolate groups. Owing to the rather large chemical shift anisotropy, the centre bands are accompanied by spinning sidebands, which have been analyzed using the Herzfeld Berger approach.[12] For all compounds except **5**, whose signal was too broad, the three independent tensor components have been obtained. The absolute anisotropy of **1**–**6** varies between ζ 292 and 619, whereas the asymmetry ranges from η 0.30 to 0.80. Compounds **1**–**6** are reasonably soluble in moderately polar solvents, such as toluene and chloroform. The ^{125}Te NMR spectra (CDCl_3) reveal sharp resonances for the diorganotellurium hydroxo phenolates $\text{R}_2\text{Te(OH)OPh}$ at δ 1035.8 (**1**, R = Ph), 1038.5 (**2**, $\text{R} = p\text{-MeOC}_6\text{H}_4$), and 1056.0 (**3**, $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$) and for the diorganotellurium bis(phenolates) $\text{R}_2\text{Te(OPh)}_2$ at δ 1067.0 (**4**, R = Ph), 1074.6 (**5**, $\text{R} = p\text{-MeOC}_6\text{H}_4$), and 1102.8 (**6**, $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$), which are low-field shifted compared with the ^{125}Te NMR chemical shifts of the corresponding diorganotellurium dichlorides Ph_2TeCl_2 (δ 919.7), $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ (δ 933.1), and $(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{TeCl}_2$ (δ 960.9).[13]

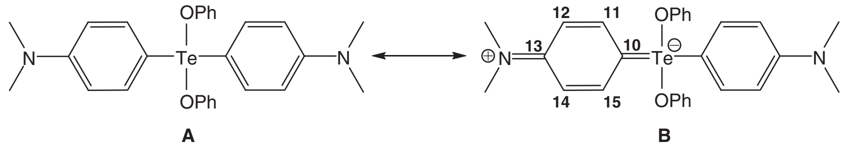
The reaction of the diorganotellurium oxides, R_2TeO (R = Ph, $p\text{-MeOC}_6\text{H}_4$, $p\text{-Me}_2\text{NC}_6\text{H}_4$), with o-nitrophenol in refluxing toluene proceeds with condensation and produces the tetraorganoditelluroxane bis(o-nitrophenolates) $(\text{R}'\text{O})\text{R}_2\text{TeOTeR}_2(\text{OR}')$ (**7**, $\text{R} = p\text{-MeOC}_6\text{H}_4$; **8**, $\text{R} = p\text{-Me}_2\text{NC}_6\text{H}_4$; $\text{R}' = o\text{-NO}_2\text{C}_6\text{H}_4$) and the hexaphenyltritelluroxane bis(o-nitrophenolate) $(\text{R}'\text{O})\text{Ph}_2\text{TeOTePh}_2\text{OTePh}_2(\text{OR}')$ (**9**, $\text{R}' = o\text{-NO}_2\text{C}_6\text{H}_4$) as yellow and orange microcrystalline solids in very good yield (Scheme 4). The yields of **7** and **8** are best when the ratio of the o-nitrophenol and diorganotellurium oxides R_2TeO ($\text{R} = p\text{-MeOC}_6\text{H}_4$, $p\text{-Me}_2\text{NC}_6\text{H}_4$) is 1:2. At a ratio of 1:1 the yield of **8** is substantially lower and a second unaccounted product is also obtained, which could not be purified. In case of **7** only a mixture of inseparable products is obtained.

Regardless of the stoichimetric ratio the reaction of diphenyltellurium oxide, Ph_2TeO, with o-nitrophenol gives rise to the formation of hexaphenyltritelluroxane bis(o-nitrophenolate) $(\text{R}'\text{O})\text{Ph}_2\text{TeOTePh}_2\text{OTePh}_2(\text{OR}')$ (**9**, $\text{R}' = o\text{-NO}_2\text{C}_6\text{H}_4$) that was isolated in good yields (Scheme 4).

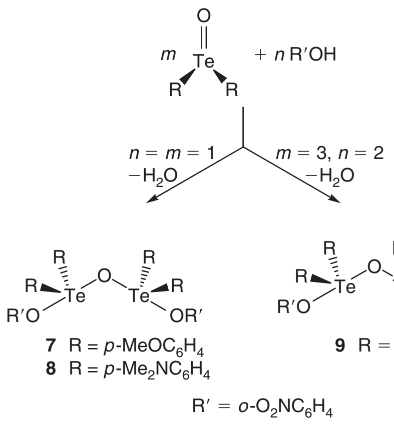
The formation of tetraorganoditelluroxanes and hexaorganotritelluroxanes rather than diorganotellurium hydroxy o-nitrophenolate or diorganotellurium bis(o-nitrophenolates) is tentatively explained by the coordination strength, which is greater for the phenolate ion than the o-nitrophenolate ion owing to the more effective delocalization of the negative charge across the aromatic π-system. The molecular and crystal structures of $(\text{R}'\text{O})\text{R}_2\text{TeOTeR}_2(\text{OR}')$ (**7**, $\text{R} = p\text{-MeOC}_6\text{H}_4$; $\text{R}' = o\text{-NO}_2\text{C}_6\text{H}_4$) and $(\text{R}'\text{O})\text{Ph}_2\text{TeOTePh}_2\text{OTePh}_2(\text{OR}')$ (**9**, $\text{R}' = o\text{-NO}_2\text{C}_6\text{H}_4$) are shown in Figs 4–7. Selected crystal and refinement data are collected in Table 1 and selected bond parameters are listed in the caption of the figures. Like in compounds **2**, **4**, and **6**, the spatial arrangement (first coordination sphere) around the Te atoms of **7** and **9** is distorted trigonal bipyramidal with the expected occupancy of the ligand atoms. However, unlike the mononuclear compounds, the axial distortion of dinuclear species **7** is more pronounced, with the Te1–O1 and Te2–O1 bond lengths of the oxygen bridge (2.018(2) and 2.024(2) Å) being somewhat shorter than the Te1–O4 and Te2–O2 bond lengths for the o-nitrophenolate coordination (2.236(2) and 2.244(2) Å). However, the mean Te–O distance of the o-nitrophenolate anions to the Te atoms of **7** (av. 2.240 (6) Å) is still shorter than those of related tetraorganoditelluroxanes that contain other oxygen anions, e.g., $(\text{RO})\text{Me}_2\text{TeOTeMe}_2(\text{OR})$ (av. 2.365(3) Å; $\text{R} = o,p,o'$-trinitrophenyl),[7] $(\text{F}_3\text{CCO}_2)\text{Ph}_2\text{TeOTePh}_2(\text{O}_2\text{CCF}_3)\cdot 0.5\text{H}_2\text{O}$ (av. 2.352(10) Å),[14] $(\text{Ph}_2\text{PO}_2)\text{R}_2\text{TeOTeR}_2(\text{O}_2\text{PPh}_2)\cdot 2\text{Ph}_2\text{PO}_2\text{H}$ (2.440(2) Å; $\text{R} = p\text{-MeOC}_6\text{H}_4$),[15] $(\text{NO}_3)\text{Ph}_2\text{TeOTePh}_2$

Table 1. Crystal data and structure refinement for 2, 4, 6, 7, 9, 17, and 18

Parameter	**2**	**4**	**6**	**7**	**9**	**17**	**18**
Formula	$C_{20}H_{20}O_4Te$	$C_{24}H_{20}O_2Te$	$C_{28}H_{30}N_2O_2Te$	$C_{40}H_{36}N_2O_{11}Te_2 \cdot CH_2Cl_2$	$C_{48}H_{38}N_2O_8Te_3$	$C_{56}H_{56}Cl_4O_{10}Te_4 \cdot C_6H_5O$	$C_{32}H_{40}Cl_2N_4OTe_2$
Formula weight [g mol^{-1}]	451.96	468.00	554.14	1060.83	1153.60	1634.32	822.78
Crystal system	Monoclinic	Monoclinic	Tetragonal	Triclinic	Monoclinic	Triclinic	Monoclinic
Crystal size [mm^3]	0.19 × 0.21 × 0.28	0.02 × 0.08 × 0.31	0.13 × 0.11 × 0.04	0.04 × 0.16 × 0.23	0.04 × 0.20 × 0.33	0.04 × 0.09 × 0.27	0.06 × 0.08 × 0.18
Space group	$P2_1/c$	$C2/c$	$I4/a$	$P-1$	$P2_1/n$	$P-1$	$C2/c$
a [Å]	17.962(5)	18.379(5)	19.3793(16)	13.107(2)	14.711(3)	10.580(4)	22.943(8)
b [Å]	10.737(3)	5.691(5)	19.3793(16)	13.311(2)	12.595(3)	12.807(5)	14.385(8)
c [Å]	9.540(3)	18.181(5)	13.495(2)	13.797(2)	24.300(5)	13.104(5)	10.053(4)
α [°]	90	90	90	88.658(3)	90	110.154(7)	90
β [°]	99.238(6)	107.416(5)	90	76.251(3)	101.287(5)	109.153(7)	100.973(13)
γ [°]	90	90	90	62.010(3)	90	96.127(8)	90
V [Å^3]	1816.1(9)	1814.5(17)	5068.0(10)	2053.9(5)	4415.2(17)	1525.4(9)	3257(2)
Z	4	4	8	2	4	1	4
D_{calcd} [Mg m^{-3}]	1.653	1.713	1.453	1.715	1.735	1.779	1.678
T [K]	173	173	173	173	173	173	173
μ [mm^{-1}]	1.659	1.656	1.200	1.613	2.025	2.128	1.987
$F(000)$	896	928	2240	1048	2240	797	1624
θ range [°]	1.2 to 25.0	2.3 to 30.6	1.8 to 30.6	1.5 to 30.5	1.0 to 30.5	0.9 to 30.6	1.7 to 30.2
Index ranges	$-21 \le h \le 21$	$-23 \le h \le 26$	$-27 \le h \le 26$	$-18 \le h \le 13$	$-21 \le h \le 19$	$-15 \le h \le 11$	$-32 \le h \le 32$
	$-12 \le k \le 11$	$-8 \le k \le 7$	$-25 \le k \le 27$	$-18 \le k \le 18$	$-17 \le k \le 17$	$-18 \le k \le 11$	$-20 \le k \le 19$
	$-11 \le l \le 9$	$-25 \le l \le 25$	$-19 \le l \le 19$	$-19 \le l \le 19$	$-34 \le l \le 34$	$-18 \le l \le 18$	$-12 \le l \le 14$
No. of reflns collcd	7930	9805	31127	25622	53036	12578	18659
Completeness to $\theta_{\max}$ [%]	99.9	98.8	99.8	96.8	99.7	91.0	99.0
No. of indep reflns/R_{int}	3196	2771	3878	12172	13445	8551	4783
No. of reflns obsd with ($I > 2\sigma(I)$)	2507	2420	2729	8907	10196	5766	3264
No. refined params	248	123	150	541	550	370	186
GooF (F^2)	1.105	1.072	1.039	1.079	1.123	0.946	0.942
R_1 (F) ($I > 2\sigma(I)$)	0.0404	0.0439	0.0391	0.0360	0.0319	0.0377	0.0417
wR_2 (F^2) (all data)	0.0922	0.0914	0.1049	0.0881	0.0833	0.0853	0.0920
$(\Delta/\sigma)_{\max}$	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Largest diff peak/hole [e Å^{-3}]	1.311/−0.978	1.807/−3.284	1.121/−0.672	1.181/−0.855	1.213/−0.819	1.523/−1.225	2.011/−0.898



Scheme 3.



Scheme 4.

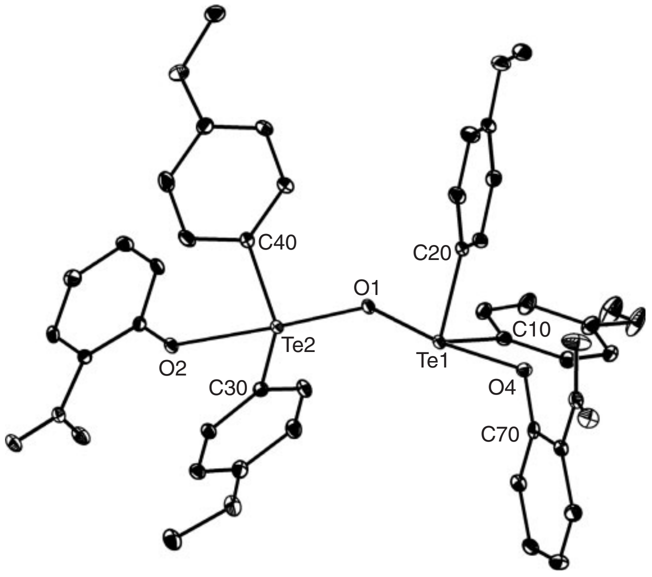


Fig. 4. Molecular structure of $(R'O)R_2TeOTeR_2(OR')$ (**7**, $R = p$-$MeOC_6H_4$, $R' = o$-$O_2NC_6H_4$) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1–O1 2.018(2), Te1–C20 2.111(3), Te1–C10 2.131(3), Te1–O4 2.236(2), Te2–O1 2.024(2), Te2–C40 2.117(3), Te2–C30 2.128(3), Te2–O2 2.244(2), O1–Te1–C20 91.5(1), O1–Te1–C10 89.5(1), C20–Te1–C10 95.2(1), O1–Te1–O4 173.0(1), C20–Te1–O4 82.5(1), C10–Te1–O4 87.4(1), O1–Te2–C40 88.0(1), O1–Te2–C30 92.6(1), C40–Te2–C30 97.0(1), O1–Te2–O2 171.4(1), C40–Te2–O2 86.0(1), C30–Te2–O2 82.0(1), Te1–O1–Te2 115.7(1).

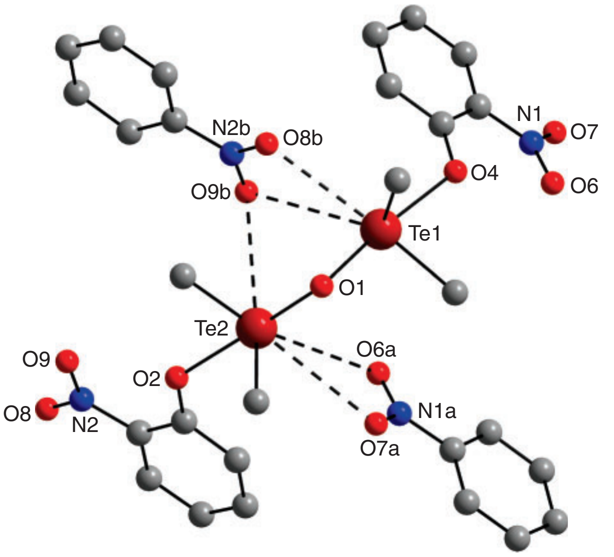


Fig. 5. Perspective view of $(R'O)R_2TeOTeR_2(OR')$ (**7**, $R = p$-$MeOC_6H_4$, $R' = o$-$O_2NC_6H_4$) showing the supramolecular association of individual molecules by secondary Te···O interactions. Symmetry operation used to generate equivalent atoms: $a = 1 - x$, $1 - y$, $-z$, $b = 1 - x$, $2 - y$, $-z$. Selected bond parameters [Å]: Te1···O8b 3.078(5), Te1···O9b 3.414(6), Te2···O6a 3.671(6), Te2···O7a 3.341(5), Te2···O9b 3.303(9).

$(NO_3)Ph_2Te(OH)NO_3$ (av. Te–O: 2.452(3) Å),[16] and $(F_3CSO_3)R_2TeOTeR_2(O_3SCF_3)$ (av. 2.619(6) Å; $R = p$-$MeOC_6H_4$).[15] The molecular structure of hexaorganotritelluroxane **9** and the ligand occupancies around the Te atoms resembles that of **7**. The axial distortion is more pronounced at the terminal Te atoms (Te2–O1 1.963(2) Å/Te2–O3 2.310(2) Å, Te3–O2 1.945(2) Å/Te3–O4 2.397(2) Å) than at the central Te atom (Te1–O1 2.082(2) Å/Te1–O2 2.102(2) Å). Besides the primary coordination sphere, the crystal structures of **7** and **9** reveal several secondary Te···O interactions (Figs 5 and 7) that are shorter or slightly longer than the sum of the van der Waals radii (3.58 Å). For the tetraorganoditelluroxane **7** these contacts are a result of the intermolecular coordination of two adjacent nitro groups that increase the coordination number of Te1 and Te2 by 2 and 3 secondary contacts, respectively. In hexaorganotritelluroxane **9** the secondary interactions from the coordination of two nitro groups and one phenolate group increase the coordination number of Te2 and Te3 by 2 and of Te1 by 3. Attempts were also made to characterize compounds **7**–**9** by ^{125}Te MAS NMR spectroscopy; however, a reasonable spectrum was only obtained for **9**, which shows three signals of equal intensity at δ_{iso} 1060, 1137, and 1176. The large chemical shift anisotropy was also investigated by an Herzfeld Berger analysis.[12] The absolute anisotropies of the three signals being ζ 332, 366, and 373 are very similar, whereas the asymmetry (η 0.00) of the central tellurium (δ_{iso} 1060) is significantly lower than the outer Te atoms (η 0.70 and 0.90). In $CDCl_3$ solution, the tetraorganoditelluroxanes **7** and **8** give rise to broad ^{125}Te NMR resonances at δ 1098.3 and 1117.0, whereas the hexaorganotritelluroxane **9** shows only one broad signal at δ 1095.3. The single broad ^{125}Te NMR signal for **9** is indicative of a dynamic process that compromises the configurational stability of the Te atoms in solution.

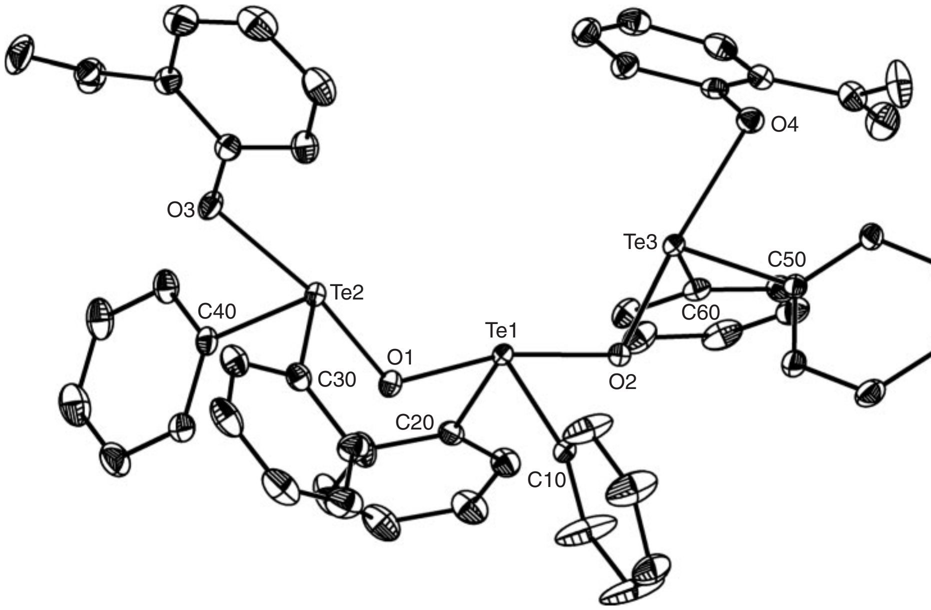


Fig. 6. Molecular structure of $(R'O)Ph_2TeOTePh_2OTePh_2(OR')$ (**9**, $R' = o\text{-}O_2NC_6H_4$) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1–O1 2.082(2), Te1–O2 2.102(2), Te1–C10 2.114(3), Te1–C20 2.133(3), Te2–O1 1.963(2), Te2–C40 2.113(3), Te2–C30 2.129(3), Te2–O3 2.310(2), Te3–O2 1.945(2), Te3–C60 2.117(3), Te3–C50 2.126(3), Te3–O4 2.397(2), O1–Te1–O2 167.5(1), O1–Te1–C10 86.2(1), O2–Te1–C10 84.9(1), O1–Te1–C20 87.2(1), O2–Te1–C20 85.8(1), C10–Te1–C20 100.4(1), O1–Te2–C40 90.6(1), O1–Te2–C30 88.8(1), C40–Te2–C30 96.4(1), O1–Te2–O3 171.3(1), C40–Te2–O3 82.3(1), C30–Te2–O3 86.9(1), O2–Te3–C60 91.6(1), O2–Te3–C50 91.0(1), C60–Te3–C50 96.9(1), O2–Te3–O4 172.6(1), C60–Te3–O4 81.5(1), C50–Te3–O4 87.1(1), Te3–O2–Te1 119.8(1), Te2–O1–Te1 123.1(1).

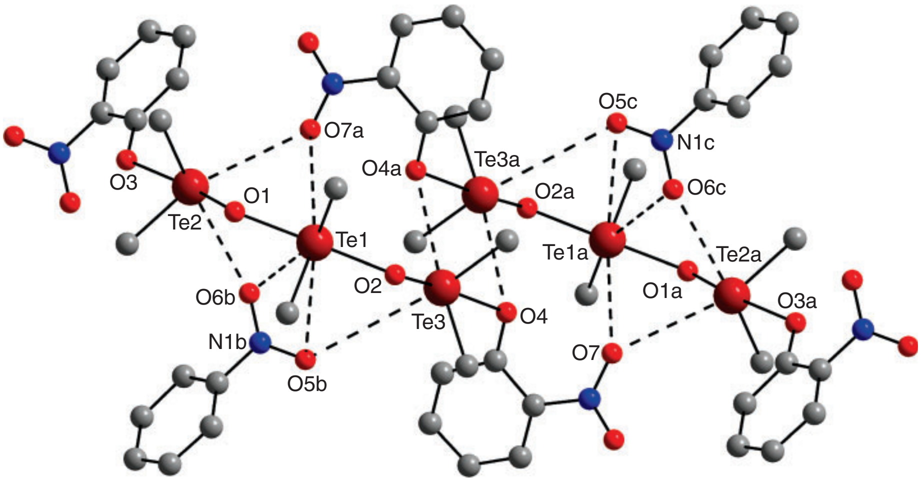
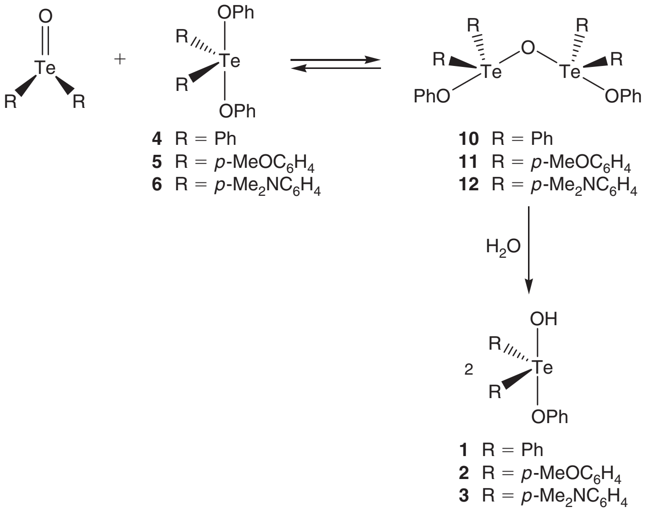


Fig. 7. Perspective view of $(R'O)Ph_2TeOTePh_2OTePh_2(OR')$ (**9**, $R' = o\text{-}O_2NC_6H_4$) showing the supramolecular association of individual molecules by secondary Te···O interactions. Symmetry operation used to generate equivalent atoms: $a = 1-x,\ 1-y,\ 1-z$, $b = -x,\ 1-y,\ 1-z$. Selected bond parameters [Å]: Te2···O7a 3.358(6), Te2···O6b 3.153(8), Te1···O6b 3.197(4), Te1···O5b 3.449(4), Te1···O7a 3.592(5), Te3···O4a 3.168(6), Te3···O5b 3.792(8).

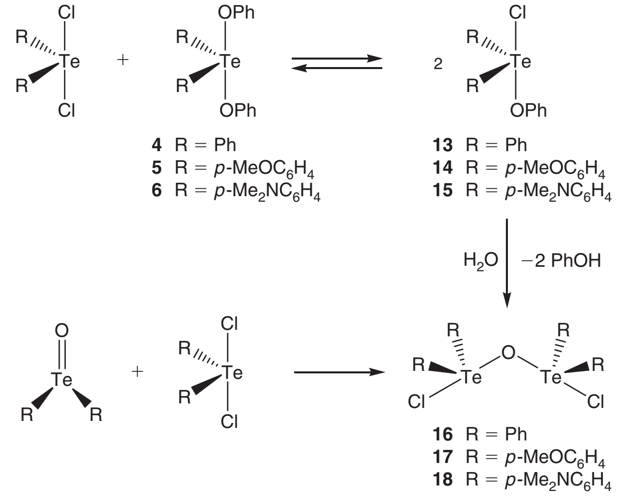
The number of ^{13}C NMR resonances of **9** is indicative of only one phenyl group (see Experimental section).

Insertion and Redistribution Reactions

The equimolar reaction of the diorganotellurium oxides R_2TeO ($R = Ph$, $p\text{-}MeOC_6H_4$, $p\text{-}Me_2NC_6H_4$) with diorganotellurium bis(phenolates) $R_2Te(OPh)_2$ (**4**, $R = Ph$; **5**, $R = p\text{-}MeOC_6H_4$; **6**, $R = p\text{-}Me_2NC_6H_4$) in $CDCl_3$ at 50°C under rigorous exclusion of moisture provided colourless solutions that were investigated by ^{125}Te NMR spectroscopy. The detected ^{125}Te signals at δ 1055.6, 1062.8, and 1082.0, have been assigned to the tetraorganoditelluroxanes $(PhO)R_2TeOTeR_2(OPh)$ (**10**, $R = Ph$; **11**, $R = p\text{-}MeOC_6H_4$; **12**, $R = p\text{-}Me_2NC_6H_4$) (Scheme 5). Removal of the solvent afforded moisture sensitive oils, whose reaction with water from the air upon standing furnished solid diorganotellurium hydroxy phenolates $R_2Te(OH)OPh$ (**1**, $R = Ph$; **2**, $R = p\text{-}MeOC_6H_4$; **3**, $R = p\text{-}Me_2NC_6H_4$) in nearly quantitative yields (Scheme 5).



Scheme 5.



Scheme 6.

The equimolar reaction of diorganotellurium dichlorides R_2TeCl_2 (R = Ph, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$) with diorganotellurium bis(phenolates) $R_2Te(OPh)_2$ (**4**, R = Ph; **5**, R = p-$MeOC_6H_4$; **6**, R = p-$Me_2NC_6H_4$) in $CDCl_3$ at room temperature for 1 h under rigorous exclusion from moisture produced equilibrium mixtures of the starting compounds and the diorganotellurium chloro phenolates $R_2Te(Cl)OPh$ (**13**, R = Ph; **14**, R = p-$MeOC_6H_4$; **15**, R = p-$Me_2NC_6H_4$) (Scheme 6). The ^{125}Te NMR spectra ($CDCl_3$) of the three equilibrium mixtures reveal signals at δ 919.7 (integral 15%; Ph_2TeCl_2), 1048.6 (integral 70%; **13**), and 1067.0 (integral 15%; **4**), at δ 933.1 (integral 15%; (p-$MeOC_6H_4)_2TeCl_2$), 1060.3 (integral 70%; **14**), and 1074.6 (integral 15%; **5**), as well as at δ 960.9 (integral 15%; (p-$Me_2NC_6H_4)_2TeCl_2$), 1091.1 (integral 70%; **15**), and 1102.8 (integral 15%; **6**). Longer reaction times had no influence on the integral ratios. In all cases, the removal of the solvent leaves a colourless sensitive oil, whose reaction with moist air gives rise to the formation of solid tetraorganotelluroxane dichlorides $ClR_2TeOTeR_2Cl$ (**16**, R = Ph; **17**, R = p-$MeOC_6H_4$; **18**, R = p-$Me_2NC_6H_4$) and phenol (Scheme 6). A more rational synthesis of the tetraorganotelluroxane dichlorides **16**–**18** involves the redistribution of equimolar amounts of diorganotellurium oxides R_2TeO (R = Ph, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$) and the corresponding diorganotellurium dichlorides R_2TeCl_2 (Scheme 6). Compounds **16**–**18** were obtained as microcrystalline solids. It is worth mentioning that several tetraorganotelluroxane dichlorides have been obtained previously by the incomplete hydrolysis of diaryltellurium dihalides, however, their characterization remained incomplete at that time.[17]

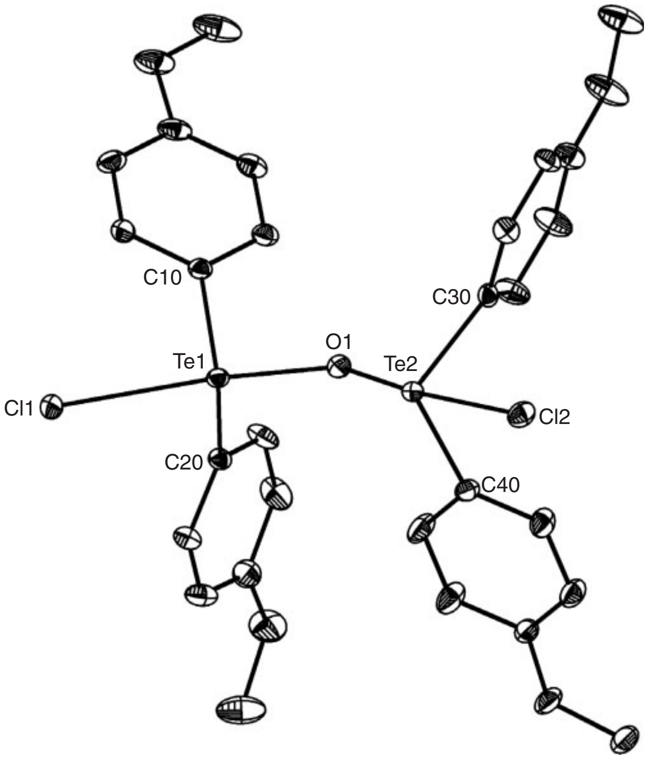


Fig. 8. Molecular structure of $ClR_2TeOTeR_2Cl$ (**17**, R = p-$MeOC_6H_4$) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1–O1 1.975(3), Te1–C20 2.098(4), Te1–C10 2.108(4), Te1–Cl1 2.736(1), Te2–O1 1.995(3), Te2–C30 2.082(4), Te2–C40 2.111(4), Te2–Cl2 2.720(1), O1–Te1–C20 89.0(1), O1–Te1–C10 90.7(1), C20–Te1–C10 96.2(2), O1–Te1–Cl1 175.5(1), C20–Te1–Cl1 87.4(1), C10–Te1–Cl1 92.3(1), O1–Te2–C30 87.5(1), O1–Te2–C40 90.7(1), C30–Te2–C40 99.1(2), O1–Te2–Cl2 175.0(1), C30–Te2–Cl2 87.6(1), C40–Te2–Cl2 90.7(1), Te1–O1–Te2 121.0(1).

The molecular and crystal structures of $ClR_2TeOTeR_2Cl$ (**17**, R = p-$MeOC_6H_4$; **18**, R = p-$Me_2NC_6H_4$) are shown in Figs 8–10. Compound **17** cocrystallizes with a molecule of phenol, which fills a void in the crystal lattice. Selected crystal and refinement data are collected in Table 1 and selected bond parameters are listed in the captions of the figures. The Te atoms also show trigonal bipyramidal geometries with a marked distortion of the axial ligands.[7] Thus, the average Te–Cl bond length of **17** and **18** being 2.722(1) is slightly longer than that observed for Ph_2TeCl_2 (2.506(3) Å).[18] The average Te–O bond length of 1.980(2) Å is slightly shorter than the 'standard' Te–O single bond of **4** (2.074(2) Å) and of $[(p\text{-}MeOC_6H_4)_2TeO]_n$ (2.063(2) Å).[2] The Te–O–Te angle of **17** is 121.0(1), and is comparable with those of **7** (115.7(1)°), **9** (119.8(1)°), (123.1(1)°), and other tetraorganoditelluroxanes.[13–15] The Te–O–Te angle of **18** is 131.8(2)° and appears to be very large for no obvious reason. Since the O1 atom of **18** is situated on a

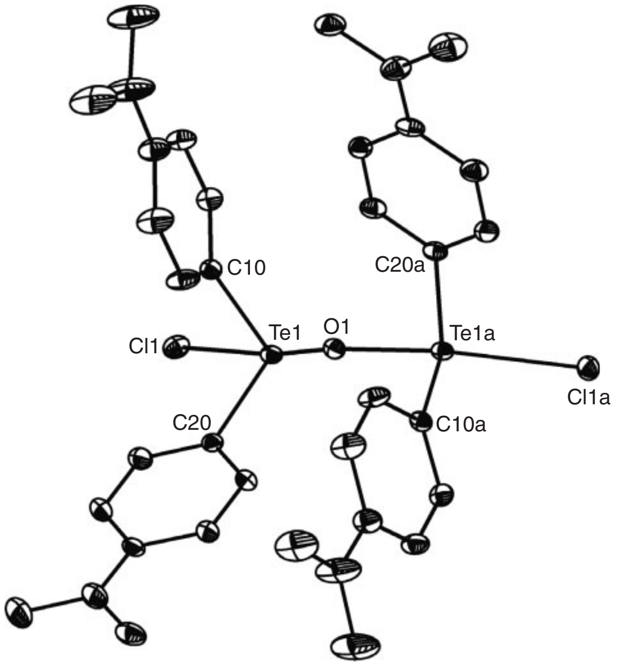


Fig. 9. Molecular structure of $ClR_2TeOTeR_2Cl$ (**18**, R = *p*-$Me_2NC_6H_4$) showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = 1 - x, y, 0.5 - z$. Selected bond parameters [Å, °]: Te1–O1 1.970(2), Te1–C10 2.093(4), Te1–C20 2.124(4), Te1–Cl1 2.716(1), O1–Te1–C10 85.2(1), O1–Te1–C20 88.9(1), C10–Te1–C20 96.0(1), O1–Te1–Cl1 172.8(1), C10–Te1–Cl1 87.7(1), C20–Te1–Cl1 93.0(1), Te1–O1–Te1a 131.8(2).

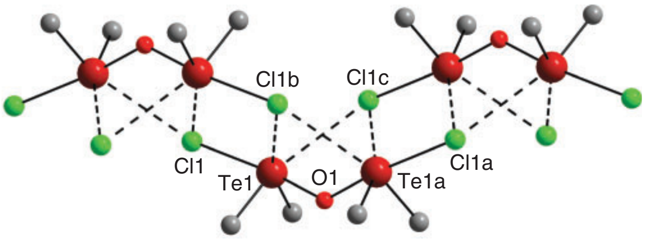


Fig. 10. Perspective view on $ClR_2TeOTeR_2Cl$ (**18**, R = *p*-$Me_2NC_6H_4$) showing the supramolecular association of individual molecules by secondary Te···Cl interactions. Symmetry operation used to generate equivalent atoms: $b = 1 - x,\ 1 - y,\ 1 - z$, $c = x,\ 1 - y,\ -0.5 + z$. Selected bond parameters [Å]: Te1···Cl1b 3.789(5), Te1···Cl1c 3.618(13).

crystallographic centre of inversion the related angle should be interpreted with caution. Compound **17** and **18** are associated by secondary Te···Cl interactions that link individual molecules and gives rise to an infinite coordination polymer in the crystal lattice. In this way the solid-state structures of **17** and **18** differ from that of $IR_2TeOTeR_2I$ (R = *p*-$MeOC_6H_4$), which adopts a dimeric structure.[19]

The supramolecular motifs of **17** and **18** are very similar for both compounds and are shown for **18** in Fig. 10. The secondary Te···Cl of 3.789(5) and 3.618(13) Å increase the coordination number of the Te atom by 2. The tetraorganotelluroxanes $ClR_2TeOTeR_2Cl$ (**16**, R = Ph; **17**, R = *p*-$MeOC_6H_4$; **18**, R = *p*-$Me_2NC_6H_4$) were characterized by ^{125}Te MAS NMR spectroscopy. The spectra exhibit a single centre band at δ_{iso} 1149, 1154, and 1153, which are high-field shifted by comparison with their parent compounds Ph_2TeCl_2 (δ_{iso} 900.0), (*p*-$MeOC_6H_4)_2TeCl_2$ (δ_{iso} 979.4/1001.7), (*p*-$Me_2NC_6H_4)_2TeCl_2$ (δ_{iso} 969.0),[13] Ph_2TeO (δ_{iso} 1133/1103), (*p*-$MeOC_6H_4)_2TeO$ (δ_{iso} 903),[2] and (*p*-$Me_2NC_6H_4)_2TeO$ (δ_{iso} 857.5),[20] respectively. The ^{125}Te MAS NMR of **16** and **18** were suitable for a Herzfeld Berger tensor analysis.[12] The absolute anisotropies of ζ 277 and 344 and the asymmetries η 0.45 and 0.25 are comparable with those of the starting materials.[13] Compounds **16**–**18** are rather poorly soluble in most organic solvents, a fact that may be attributable to the strong supramolecular association by secondary contacts. The ^{125}Te NMR spectra ($CDCl_3$) of **17** and **18** reveal one signal at δ 1092.9 and 1072.0, whereas no signal could be obtained for **16** because of the poor solubility.

Conclusion

The reactivity of diorganotellurium oxides towards phenol and *o*-nitrophenol is surprisingly diverse and affords diorganotellurium hydroxy phenolates, diorganotellurium bis(phenolates), tetraorganoditelluroxane bis(*o*-nitrophenolates), and hexaorganotritelluroxane bis(*o*-nitrophenolates) depending on the stoichiometry and the reaction conditions applied (Schemes 2 and 4). In contrast, other main group element oxides, such as Ph_3PO, Ph_3AsO, Ph_2SO, and Ph_2SeO, which have polar E–O double bonds form hydrogen bonded complexes with phenols and related compounds.[5] The behaviour of monomeric *p*-$(MeOC_6H_4)_2TeO$ to crystallize from solution as a polymer (Scheme 1) is reminiscent of aqueous formaldehyde solutions, which deposit polymeric paraformaldehyde upon standing. Similarly, the condensation reactions of diorganotellurium oxides with phenol resemble the acetalization of ketones with alcohols (Scheme 2). The reactivity of the diorganotellurium bis(phenolates) in redistribution reactions with diorganotellurium oxides and diorganotellurium dichlorides can be rationalized by the kinetic lability of the Te–O and Te–Cl bonds under laboratory conditions (Schemes 5 and 6). We are currently seeking to combine the reactivity of diorganotellurium oxides towards phenols and with the ability to absorb carbon dioxide.[4] The goal of this research is the synthesis of a single source precursor that may be able to liberate diphenyl carbonate (DPC) upon heating.

Experimental

General

The diorganotellurium oxides R_2TeO (R = Ph,[2] *p*-$MeOC_6H_4$,[3] *p*-$Me_2NC_6H_4$[20]) have been prepared according to literature procedures. The ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded using a Jeol GX 270 and a Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^{1}H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te CP MAS NMR spectra were obtained at 126.26 MHz using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 30 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain signal-to-noise ratios adequate for the tensor analyses. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced against Me_2Te using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2/685.5). The tensor analyses were performed using DMFit 2002[21] and are based on relative intensities of the spinning sidebands. Definitions δ_{iso} (ppm) $= -\sigma_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) $= \sigma_{33} - \sigma_{iso}$, and $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$ where

σ_{11}, σ_{22}, and σ_{33} (ppm) are the principal tensor components of the shielding anisotropy (SA), and are sorted as follows $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$. Microanalyses were obtained from a Vario EL elemental analyzer.

*Synthesis of Diorganotellurium Hydroxy Phenolates **1–3***

A mixture of the appropriate R_2TeO (0.30 g for R = Ph, 0.36 g for R = p-$MeOC_6H_4$, 0.38 g for R = p-$Me_2NC_6H_4$, 1.00 mmol) and phenol (0.096 g, 1.0 mmol) was dissolved in toluene (50 mL) and stirred for 12 h. The solvent was removed under vacuum to ~25 mL and the remaining clear solution was cooled to 4°C. Within 24 h colourless crystals formed that were collected by filtration.

*Compound **1***: 0.33 g, 0.84 mmol, 84% yield, mp 124–128°C (softening at 121°C). δ_H ($CDCl_3$) 7.98 (d, 4H, Te_oPh), 7.45 (m, 6H, Te_mPh/Te_pPh), 7.17 (t, 2H, O_mPh), 6.78 (t, 1H, O_pPh), 6.59 (d, 2H, O_oPh). δ_C ($CDCl_3$) 161.4 (O_iPh), 137.7 (Te_iPh), 132.4 (Te_oPh), 130.7 (Te_pPh), 129.4 (Te_mPh), 129.3 (O_mPh), 120.4 (O_oPh), 118.3 (O_pPh). δ_{Te} ($CDCl_3$) 1035.8. ^{125}Te CP MAS NMR δ_{iso}: 1046, ζ: 372, η: 0.50 (σ_{11}: −1325, σ_{22}: −1139, σ_{33}: −674). ν_{max} (KBr)/cm^{-1} ν(OH) 3410. (Found: C 55.33, H 3.88. Calc. for $C_{18}H_{16}O_2Te$ (391.92): C 55.16, H 4.11%.)

*Compound **2***: 0.31 g, 0.69 mmol, 69% yield, mp 141–146°C (softening at 132°C). δ_H ($CDCl_3$) 7.82 (d, 4H, p-$Te_oC_6H_4OMe$), 7.10 (t, 2H, O_mPh), 6.91 (d, 4H, p-$Te_mC_6H_4OMe$), 6.72 (t, 1H, O_pPh), 6.52 (d, 2H, O_oPh), 3.80 (s, 6H, OMe). δ_C ($CDCl_3$) 161.9 (O_iPh), 161.5 (p-$Te_pC_6H_4OMe$), 133.8 (p-$Te_oC_6H_4OMe$), 129.3 (O_mPh), 128.1 (p-$Te_iC_6H_4OMe$), 120.2 (O_oPh), 118.0 (O_pPh), 114.8 (p-$Te_mC_6H_4OMe$), 55.3 (OMe). δ_{Te} ($CDCl_3$) 1038.5. ^{125}Te CP MAS NMR δ_{iso}: 991, ζ: 292, η: 0.80 (σ_{11}: −1254, σ_{22}: −1020, σ_{33}: −699). ν_{max} (KBr)/cm^{-1} ν(OH) 3388. (Found: C 53.47, H 4.26. Calc. for $C_{20}H_{20}O_4Te$ (451.97): C 53.15, H 4.46%.)

*Compound **3***: 0.38 g, 0.79 mmol, 79% yield, mp 155–158°C (softening at 139°C). δ_H ($CDCl_3$) 7.75 (d, 4H, p-$Te_oC_6H_4NMe_2$), 7.09 (t, 2H, O_mPh), 6.75–6.57 (m, 5H, p-$Te_mC_6H_4NMe_2$/O_pPh), 6.55 (d, 2H, O_oPh), 2.98 (s, 12H, NMe_2). δ_C ($CDCl_3$) 162.4 (O_iPh), 151.7 (p-$Te_pC_6H_4NMe_2$), 133.3 (p-$Te_oC_6H_4NMe_2$), 129.1 (O_mPh), 122.5 (p-$Te_iC_6H_4NMe_2$), 120.1 (O_oPh), 117.3 (O_pPh), 112.4 (p-$Te_mC_6H_4NMe_2$), 40.0 (NMe_2). δ_{Te} ($CDCl_3$) 1056.0. ^{125}Te CP MAS NMR δ_{iso}: 1028, ζ: −355, η: 0.80 (σ_{11}: −708, σ_{22}: −992, σ_{33}: −1383). ν_{max} (KBr)/cm^{-1} ν(OH) 3414. (Found: C 55.58, H 5.34, N 5.50. Calc. for $C_{22}H_{26}N_2O_2Te$ (478.05): C 55.27, H 5.48, N 5.86%.)

*Synthesis of Diorganotellurium Bis(phenolates) **4–6***

A mixture of the appropriate R_2TeO (0.30 g for R = Ph, 0.36 g for R = p-$MeOC_6H_4$, 0.38 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) and phenol (0.20 g, 2.1 mmol) was dissolved in toluene (80 mL) and heated under reflux in a Dean Stark apparatus for 12 h. The solvent was removed under vacuum to ~25 mL and the remaining clear solution was cooled to 4°C. Within 24 h colourless crystals formed that were collected by filtration.

*Compound **4***: 0.44 g, 0.94 mmol, 94% yield, mp 144–145°C. δ_H ($CDCl_3$) 8.26 (m, 4H, Te_oPh), 7.56 (m, 6H, Te_mPh/Te_pPh), 7.24 (m, 4H, O_mPh), 6.90 (t, 2H, O_pPh), 6.82 (d, 4H, O_oPh). δ_C ($CDCl_3$) 160.2 (O_iPh), 136.3 (Te_iPh), 132.8 (Te_oPh), 131.3 (Te_pPh), 129.8 (Te_mPh), 129.4 (O_mPh), 120.5 (O_oPh), 120.1 (O_pPh). δ_{Te} ($CDCl_3$) 1067.0. ^{125}Te CP MAS NMR δ_{iso}: 1111, ζ: −381, η: 0.50 (σ_{11}: −826, σ_{22}: −1016, σ_{33}: −1492). (Found: C 61.47, H 4.27. Calc. for $C_{24}H_{20}O_2Te$ (468.01): C 61.59, H 4.31%.)

*Compound **5***: 0.48 g, 0.91 mmol, 91% yield, mp 194–196°C. δ_H ($CDCl_3$) 8.09 (d, 4H, p-$Te_oC_6H_4OMe$), 7.17 (m, 4H, O_mPh), 7.04 (d, 4H, p-$Te_mC_6H_4OMe$), 6.83 (t, 2H, O_pPh), 6.73 (d, 4H, O_oPh), 3.83 (s, 6H, OMe). δ_C ($CDCl_3$) 162.0 (O_iPh), 160.4 (p-$Te_pC_6H_4OMe$), 134.3 (p-$Te_oC_6H_4OMe$), 129.6 (O_mPh), 126.8 (p-$Te_iC_6H_4OMe$), 120.5 (O_oPh), 119.9 (O_pPh), 115.3 (p-$Te_mC_6H_4OMe$), 55.4 (OMe). δ_{Te} ($CDCl_3$) 1074.6. ^{125}Te CP MAS NMR δ_{iso}: 930 (broad). (Found: C 59.34, H 4.66. Calc. for $C_{26}H_{24}O_4Te$ (528.07): C 59.14, H 4.58%.)

*Compound **6***: 0.49 g, 0.88 mmol, 88% yield, mp 175–178°C (turns red). δ_H ($CDCl_3$) 7.99 (d, 4H, p-$Te_oC_6H_4NMe_2$), 7.18 (m, 4H, O_mPh), 6.78 (m, 10H, p-$Te_mC_6H_4NMe_2$/O_oPh/O_pPh), 3.00 (s, 12H, NMe_2). δ_C ($CDCl_3$) 160.9 (O_iPh), 151.9 (p-$Te_pC_6H_4NMe_2$), 133.7 (p-$Te_oC_6H_4NMe_2$), 129.4 (O_mPh), 121.0 (p-$Te_iC_6H_4NMe_2$), 120.6 (O_oPh), 119.4 (O_pPh), 112.7 (p-$T_mC_6H_4NMe_2$), 40.0 (NMe_2). δ_{Te} ($CDCl_3$) 1102.8. ^{125}Te CP MAS NMR δ_{iso}: 1184, ζ: −619, η: 0.30 (σ_{11}: −782, σ_{22}: −967, σ_{33}: −1803). (Found: C 60.61, H 5.22, N 5.02. Calc. for $C_{28}H_{30}N_2O_2Te$ (554.15): C 60.69, H 5.46, N 5.06%.)

*Synthesis of Tetraorganoditelluroxane Bis(*o*-nitrophenolates) **7** and **8***

A mixture of the appropriate R_2TeO (0.35 g for R = p-$MeOC_6H_4$, 0.39 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) and o-nitrophenol (0.28 g, 2.0 mmol) was dissolved in toluene (80 mL) and heated under reflux in a Dean Stark apparatus for 12 h. The solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2/diethyl ether. Within 48 h yellow (**7**) or orange (**8**) crystals formed that were collected by filtration.

*Compound **7***: 0.45 g, 0.46 mmol, 92% yield, mp 116–118°C. δ_H ($CDCl_3$) 7.81 (d, 2H, o-$O_mC_6H_4N_oO_2$), 7.71 (d, 8H, p-$Te_oC_6H_4OMe$), 7.18 (t, 2H, o-$O_mC_6H_4N_pO_2$), 6.89 (d, 8H, p-$Te_mC_6H_4OMe$), 6.63 (t, 2H, o-$O_pC_6H_4NO_2$), 6.43 (d, 2H, o-$O_oC_6H_4N_mO_2$), 3.80 (s, 12H, OMe). δ_C ($CDCl_3$) 161.7 (p-$Te_pC_6H_4OMe$), 158.1 (o-$O_iC_6H_4NO_2$), 139.7 (o-$O_oC_6H_4N_iO_2$), 134.9 (o-$O_mC_6H_4N_pO_2$), 133.9 (p-$Te_oC_6H_4OMe$), 128.2 (p-$Te_iC_6H_4OMe$), 125.7 (o-$O_mC_6H_4N_oO_2$), 123.9 (o-$O_pC_6H_4NO_2$), 116.9 (o-$O_oC_6H_4N_mO_2$), 115.0 (p-$Te_mC_6H_4OMe$), 55.4 (OMe). δ_{Te} ($CDCl_3$) 1098.3. (Found: C 49.01, H 3.63, N 2.80. Calc. for $C_{40}H_{36}N_2O_{11}Te_2$ (975.92): C 49.23, H 3.72, N 2.87%.)

*Compound **8***: 0.46 g, 0.45 mmol, 90% yield, mp 119–124°C. δ_H ($CDCl_3$) 7.80 (d, 2H, o-$O_mC_6H_4N_oO_2$), 7.67 (d, 8H, p-$Te_oC_6H_4NMe_2$), 7.13 (t, 2H, o-$O_mC_6H_4N_pO_2$), 6.64 (d, 8H, p-$Te_mC_6H_4NMe_2$), 6.56 (t, 2H, o-$O_pC_6H_4NO_2$), 6.42 (d, 2H, o-$O_oC_6H_4N_mO_2$), 2.99 (s, 24H, NMe_2). δ_C ($CDCl_3$) 159.0 (o-$O_iC_6H_4NO_2$), 151.6 (p-$Te_pC_6H_4NMe_2$), 140.01 (o-$O_oC_6H_4N_iO_2$), 134.1 (o-$O_mC_6H_4N_pO_2$), 133.6 (p-$Te_oC_6H_4NMe_2$), 125.6 (o-$O_mC_6H_4N_oO_2$), 124.2 (o-$O_pC_6H_4NO_2$), 122.1 (p-$Te_iC_6H_4NMe_2$), 115.6 (o-$O_oC_6H_4N_mO_2$), 112.4 (p-$Te_mC_6H_4NMe_2$), 40.0 (NMe_2). δ_{Te} ($CDCl_3$) 1117.0. (Found: C 51.75, H 4.55, N 8.01. Calc. for $C_{44}H_{48}N_6O_7Te_2$ (1028.09): C 51.40, H 4.71, N 8.17%.)

*Synthesis of Hexaorganotritelluroxanes Bis(*o*-nitrophenolates) **9***

A mixture of Ph_2TeO (0.30 g, 1.0 mmol) and o-nitrophenol (0.15 g, 1.1 mmol) was dissolved in toluene (80 mL) and heated under reflux in a Dean Stark apparatus for 12 h. The solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2/diethyl ether. Within 48 h yellow microcrystals (**9**) formed that were collected by filtration.

*Compound **9***: 0.30 g, 0.26 mmol, 78% yield, mp 129–134°C. δ_H ($CDCl_3$) 7.81 (d, 2H, $o\text{-}O_mC_6H_4N_oO_2$), 7.73 (d, 12H, Te_oPh), 7.37 (m, 18H, Te_mPh/Te_pPh), 7.12 (t, 2H, $o\text{-}O_mC_6H_4N_pO_2$), 6.58 (t, 2H, $o\text{-}O_pC_6H_4NO_2$), 6.32 (d, 2H, $o\text{-}O_oC_6H_4N_mO_2$). δ_C ($CDCl_3$) 159.3 ($o\text{-}O_iC_6H_4NO_2$), 140.7 ($o\text{-}O_oC_6H_4N_iO_2$), 138.1 (Te_iPh), 134.3 ($o\text{-}O_mC_6H_4N_pO_2$), 132.1 (Te_oPh), 130.8 (Te_pPh), 129.4 (Te_mPh), 125.8 ($o\text{-}O_mC_6H_4N_oO_2$), 124.8 ($o\text{-}O_pC_6H_4NO_2$), 115.7 ($o\text{-}O_oC_6H_4N_mO_2$). δ_{Te} ($CDCl_3$) 1095.3 (broad). ^{125}Te CP MAS NMR δ_{iso}: 1060, ζ: 332, η: 0.00 (σ_{11}: −1227, σ_{22}: −1227, σ_{33}: −728) 35%, δ_{iso}: 1137, ζ: 366, η: 0.70 (σ_{11}: −1448, σ_{22}: −1192, σ_{33}: −771) 34%, δ_{iso}: 1176, ζ: 373, η: 0.90 (σ_{11}: −1530, σ_{22}: −1195, σ_{33}: −803) 31%. (Found: C 49.99, H 3.14, N 2.40. Calc. for $C_{48}H_{38}N_2O_8Te_3$ (1153.62): C 49.97, H 3.32, N 2.43%.)

*Redistribution Reaction of R_2TeO and $R_2Te(OPh)_2$. Preparation of Tetraorganoditelluroxane Bis(phenolates) **10–12***

A mixture of the appropriate R_2TeO (0.30 g for R = Ph, 0.36 g for R = p-$MeOC_6H_4$, 0.38 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) and $R_2Te(OPh)_2$ (0.47 g for R = Ph, 0.53 g for R = p-$MeOC_6H_4$, 0.54 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) was dissolved in $CHCl_3$ (50 mL) under a dry argon atmosphere and heated at 50°C for 1 h. The solvent was removed under vacuum to form a brown oil.

*Compound **10***: δ_{Te} ($CDCl_3$) 1055.6.

*Compound **11***: δ_{Te} ($CDCl_3$) 1062.8.

*Compound **12***: δ_{Te} ($CDCl_3$) 1082.0.

*Redistribution Reaction of R_2TeCl_2 and $R_2Te(OPh)_2$. Preparation of Tetraorganoditelluroxane Dichlorides **13–15***

A mixture of the appropriate R_2TeCl_2 (0.35 g for R = Ph, 0.41 g for R = p-$MeOC_6H_4$, 0.44 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) and $R_2Te(OPh)_2$ (0.47 g for R = Ph, 0.53 g for R = p-$MeOC_6H_4$, 0.54 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) was dissolved in $CDCl_3$ (6 mL) under a dry argon atmosphere and heated to 50°C for 1 h.

*Compound **13***: δ_{Te} ($CDCl_3$) 1048.6.

*Compound **14***: δ_{Te} ($CDCl_3$) 1060.3.

*Compound **15***: δ_{Te} ($CDCl_3$) 1091.1.

*Synthesis of Tetraorganoditelluroxane Dichlorides **16–18***

The diorganotellurium oxide R_2TeO (0.30 g for R = Ph, 0.36 g for R = p-$MeOC_6H_4$, 0.38 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) and R_2TeCl_2 (0.35 g for R = Ph, 0.41 g for R = p-$MeOC_6H_4$, 0.44 g for R = p-$Me_2NC_6H_4$, 1.0 mmol) were dissolved separately in $CHCl_3$ (25 mL) and combined. After a short time white microcrystals formed that were collected by filtration.

*Compound **16***: 0.61 g, 0.94 mmol, 94% yield, mp 232–237°C. δ_H ($CDCl_3$) 7.81 (d, 8H, Te_oPh), 7.36 (m, 12H, Te_mPh/Te_pPh). ^{125}Te CP MAS NMR δ_{iso}: 1149, ζ: −277, η: 0.45 (σ_{11}: −948, σ_{22}: −1073, σ_{33}: −1426). (Found: C 44.06, H 2.73. Calc. for $C_{24}H_{20}Cl_2OTe_2$ (650.52): C 44.31, H 3.10%.)

*Compound **17***: 0.59 g, 0.75 mmol, 75% yield, mp 198–200°C. δ_H ($CDCl_3$) 7.74 (d, 8H, $p\text{-}Te_oC_6H_4OMe$), 6.81 (d, 8H, $p\text{-}Te_mC_6H_4OMe$), 3.75 (s, 12H, OMe). δ_C ($CDCl_3$) 161.3 ($p\text{-}Te_pC_6H_4OMe$), 134.7 ($p\text{-}Te_oC_6H_4OMe$), 128.3 ($p\text{-}Te_iC_6H_4OMe$), 114.7 ($p\text{-}Te_mC_6H_4OMe$), 55.1 (OMe). δ_{Te} ($CDCl_3$) 1092.9. ^{125}Te CP MAS NMR δ_{iso}: 1154, ζ: −344, η: 0.45 (σ_{11}: −905, σ_{22}: −1059, σ_{33}: −1498). (Found: C 43.45, H 3.43. Calc. for $C_{28}H_{28}Cl_2O_5Te_2$ (770.62): C 43.64, H 3.66%.)

*Compound **18***: 0.68 g, 0.83 mmol, 83% yield, mp 213–216°C (dec.). δ_H ($CDCl_3$) 7.78 (d, 8H, $p\text{-}Te_oC_6H_4NMe_2$), 6.61 (d, 8H, $p\text{-}Te_mC_6H_4NMe_2$), 2.95 (s, 24H, NMe_2). δ_C ($CDCl_3$) 152.0 ($p\text{-}Te_pC_6H_4NMe_2$), 133.9 ($p\text{-}Te_oC_6H_4NMe_2$), 121.3 ($p\text{-}Te_iC_6H_4NMe_2$), 112.5 ($p\text{-}Te_oC_6H_4NMe_2$), 40.2 (NMe_2). δ_{Te} ($CDCl_3$) 1072.0. ^{125}Te CP MAS NMR δ_{iso}: 1153, ζ: −324, η: 0.25 (σ_{11}: −950, σ_{22}: −1031, σ_{33}: −1477). (Found: C 46.32, H 4.51, N 6.72. Calc. for $C_{32}H_{40}Cl_2N_4OTe_2$ (822.79): C 46.71, H 4.90, N 6.81%.)

Crystallography

Single crystals suitable for X-ray crystallography were grown from toluene (**2**, **4**, **6**), CH_2Cl_2/diethyl ether (**7**, **9**), and $CHCl_3$ (**17**, **18**). Intensity data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs *SAINT* and *SADABS*.[22] The structures were solved by direct methods and difference Fourier synthesis using *SHELXS-97* implemented in the program *WinGX 2002*.[23] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Disorder was resolved for O4 and C26 of **2** and C16 of **7**, which were refined over two positions with an occupancy ratio of 0.60:0.40 and over three positions with an occupancy ratio of 0.33:0.33:0.33, respectively. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Figures were created using *DIAMOND*.[24] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 676121 (**2**), 676122 (**4**), 676123 (**6**), 676124 (**7**), 676125 (**9**), 676126 (**17**) and 676127 (**18**). 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; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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