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Four Distinctively Different Decomposition Pathways of Metastable Supermesityltellurium(IV) Trichloride[†]

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Chlorination of bis(supermesityl)ditelluride RTeTeR (R = 2,4,6-*t*-$Bu_3C_6H_2$) with 3 equiv of sulfuryl chloride SO_2Cl_2 provided the intrinsically unstable supermesityltellurium(IV) trichloride $RTeCl_3$ (**1**) as bright yellow crystals. Severe repulsion between the equatorial Cl atom and one *tert*-butyl group in an ortho position in the supermesityl ligand is the reason for the extreme reactivity of **1**, which is in contrast to that of all previously known monoorganotellurium trihalides. In the solid state at room temperature, (the triclinic modification of) **1** reacts slowly under HCl elimination and intramolecular Te–C bond formation to give the bicyclic 5,7-di-*tert*-butyl-2-hydro-3,3-dimethylbenzo[*b*]tellurophene-1,1-dichloride (**2**), which was originally obtained as a colorless amorphous solid. On one occasion, when the solid-state reaction was allowed to occur under air conditions, compound **2** and a colorless crystalline byproduct, namely, *trans*-supermesityltellurium hydroxide dichloride (**3**), had formed, from which a few crystals were hand-selected. The formation of **3** has been tentatively rationalized by a solid-state hydrolysis of a second (monoclinic?) modification present in the bulk material of **1**. In diethyl ether, THF, or carbon disulfide, a redox equilibrium exists between yellow supermesityltellurium(IV) trichloride $RTeCl_3$ (**1**), deep blue supermesityltellurenyl(II) chloride RTeCl (**4**), and chlorine gas, which can be shifted to **4** when the reaction vessel is purged with argon to remove the chlorine gas. Compound **4** was also obtained by the reaction of RTeTeR (R = 2,4,6-*t*-$Bu_3C_6H_2$) with 1 equiv of SO_2Cl_2. When a solution of **1** was stored with an excess of SO_2Cl_2 for a prolonged amount of time, Te–C bond cleavage occurred and $[(Et_2OH)_2Te_2Cl_{10}]\cdot 2Et_2O$ (**5**) was formed. Compounds **1**–**5** have been characterized by X-ray crystallography.

Introduction

Monoorganotellurium trihalides $RTeX_3$ (R = alkyl and aryl; X = F, Cl, Br, I) are well-known and find applications as starting materials for a variety of different tellurium compounds.[1] The vast majority of these compounds are indefinitely stable and can be handled even in moist air for short periods of time. However, very few monoorganotellurium trihalides $RTeX_3$ containing bulky organic substituents have been described,[1] which prompted us to attempt the synthesis of the sterically encumbered supermesityltellurium(IV) trichloride (**1**). Surprisingly, this compound turned out to be intrinsically unstable due to repulsion of the inorganic moiety and the *tert*-butyl groups in an ortho position of the supermesityl ligand. Depending on the aggregate state and the absence or presence of water, four distinctively different

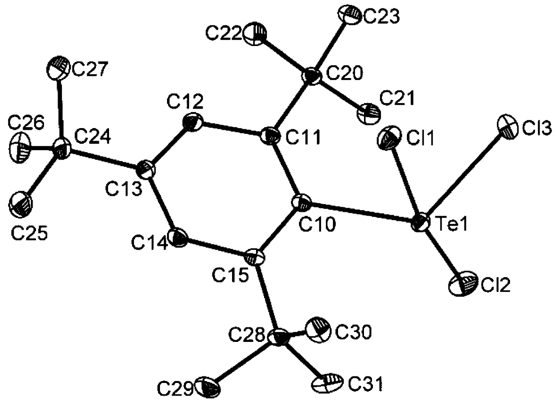

Figure 1. Molecular structure of **1** showing 30% probability displacement ellipsoids and the atom numbering system.

[†] This paper contains part of the Bachelor thesis of Stephan Heitz and part of the intended Ph.D. thesis of Malte Hesse.

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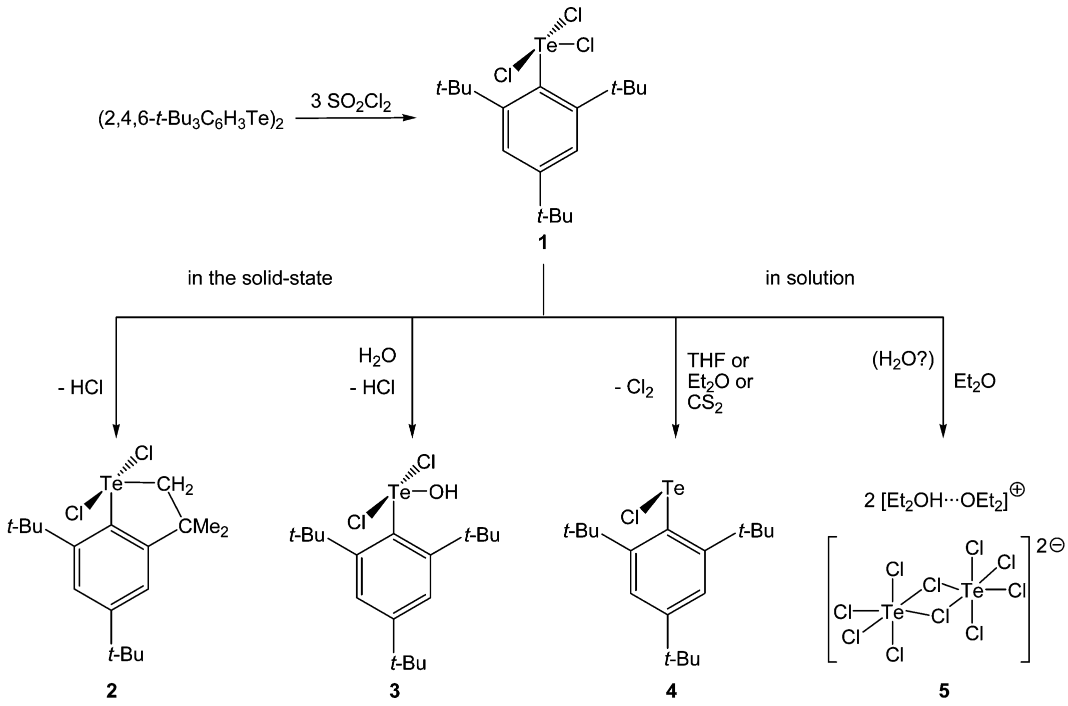
Scheme 1



decomposition pathways of **1** have been identified, which lead to the formation of the bicyclic 5,7-di-*tert*-butyl-2-hydro-3,3-dimethylbenzo[*b*]tellurophene-1,1-dichloride (**2**), *trans*-supermesityltellurium hydroxide dichloride (**3**), supermesityltellurenyl(II) chloride RTeCl (**4**), and the dodecachloroditellurate dianion $[(Et_2OH)_2Te_2Cl_{10}]\cdot 2Et_2O$ (**5**).

Results and Discussion

Bis(supermesityl)ditelluride, $(2,4,6\text{-}t\text{-}Bu_3C_6H_2Te)_2$, the starting material of this study, has been prepared previously by the reaction of supermesityl lithium with tellurium powder followed by air oxidation.[2] In the original report, supermesityl lithium was prepared by the transmetalation of supermesityl bromide with butyl lithium and isolated prior to reaction with tellurium to avoid the unwanted side reaction of the intermediate lithium tellanide with butyl bromide.[2] In an effort to circumvent the isolation of supermesityl lithium and the tedious removal of butyl bromide, we have prepared supermesityl lithium directly from supermesityl bromide and lithium granulate using 4,4′-di-*tert*-butylbiphenyl (5 mol %) as an electron-transfer catalyst.[3] The chlorination of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2Te)_2$ with 3 equiv of SO_2Cl_2 in THF, Et_2O, or CS_2 produced $2,4,6\text{-}t\text{-}Bu_3C_6H_2TeCl_3$ (**1**) in almost quantitative yields as a bright yellow crystalline solid (Scheme 1). Compound **1** is only sparingly soluble in most common organic solvents. The ^{125}Te NMR spectrum of **1** in $CDCl_3$ shows a resonance at δ 1791.0, which is substantially low-field-shifted when compared with the value of the parent $PhTeCl_3$ (δ 917 in benzene).[4]

The molecular structure of (triclinic) **1** established by X-ray crystallography is shown in Figure 1. Selected crystal data and selected bond parameters of **1** are collected in Tables 1 and 2. Like most organotellurium trichlorides, **1** resembles a distorted trigonal-bipyramidal geometry, in which the supermesityl group, one chlorine atom (Cl3), and the lone pair occupy the equatorial positions, whereas two chlorine atoms (Cl1, Cl2) are situated in the axial positions. The Te1−Cl3 bond length of 2.330(3) Å is significantly shorter than the Te1−Cl1 and Te1−Cl2 bond lengths of 2.504(2) and 2.484(2) Å. The slight deviation of the axial Te−Cl bond lengths can be attributed to a single-sided secondary Te1···Cl1a contact of 3.569(13) Å (symmetry code: $a = -x, -y, -z$), which links two individual molecules in the crystal lattice via a crystallographic center of inversion (Figure 2). In sharp contrast to all previously known monoorganotellurium trihalides, the Te1 atom of **1** is not coplanar with the phenyl ring, with the largest deviation from the ideal plane being 0.248 Å, which can be attributed to severe repulsion with the *tert*-butyl groups in an ortho position of the ligand. Additionally, repulsion of the equatorial Cl3 atom with one *tert*-butyl group causes the C11−C10−Te1 and C15−C10−Te1 angles of **3** to deviate from the putative 120° angle to 127.13(23)° and 109.12(22)°, respectively. These several distortions from ideal geometry are the reason for the high reactivity of **1** compared with other monorganotellurium trihalides.[1]

When solid (triclinic) **1** is kept under argon for several hours at room temperature, the bright yellow color gradually fades away and air-stable 5,7-di-*tert*-butyl-2-hydro-3,3-dimethylbenzo[b]tellurophene-1,1-dichloride (**2**) is formed as a colorless amorphous solid in high yields (Scheme 1). The formation of **2** can be rationalized by the intramolecular radical reaction of the equatorial Cl3 atom with one methyl

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Table 1. Crystal Data and Structure Refinement of **1**−**5**

	1	**2**·$^1/_2$EtOH	**3**	**4**	**5**
formula	$C_{18}H_{29}Cl_3Te$	$C_{38}H_{56}Cl_4OTe_2$	$C_{18}H_{29}ClTe$	$C_{18}H_{30}Cl_2OTe$	$C_{16}H_{42}Cl_{10}O_4Te_2$
fw, g mol^{-1}	479.36	925.83	408.46	460.92	908.20
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$C2/c$	$Fddd$
a, Å	10.1127(19)	10.536(2)	5.9188(12)	22.573(4)	8.763(5)
b, Å	10.224(2)	18.065(4)	15.599(3)	10.0611(17)	25.607(5)
c, Å	11.903(2)	11.779(3)	20.123(4)	19.194(3)	31.505(5)
α, deg	105.140(5)	90	90	90	90
β, deg	108.065(4)	114.308(5)	90	111.869(3)	90
γ, deg	107.293(4)	90	90	90	90
V, Å^3	1029.0(3)	2043.1(8)	1857.9(7)	4045.4(12)	7070(4)
Z	2	2	4	8	16
ρ_{calcd}, Mg m^{-3}	1.547	1.505	1.460	1.514	1.707
T, K	173	173	173	133	173
μ(Mo Kα), mm^{-1}	1.831	1.717	1.736	1.735	2.426
F(000)	480	928	824	1856	3552
θ range, deg	0.97−30.56	0.98−30.53	0.99−30.53	0.99−30.51	2.05−30.64
no. reflns collected	12 766	25 267	23 197	24 214	21 204
completeness to θ_{max}, %	96.8	98.3	99.9	99.2	99.0
no. indep reflns	6130	6137	5691	6135	2727
no. obsd reflns with ($I > 2\sigma(I)$)	5511	5388	4718	5323	2279
no. refined params	199	229	181	235	78
GOF (F^2)	1.015	1.048	1.081	1.050	1.393
$R_1(F)$ ($I > 2\sigma(I)$)	0.0422	0.0224	0.0324	0.0216	0.0542
$R_2(F^2)$ (all data)	0.1100	0.0621	0.0778	0.0565	0.0993
largest diff peak/hole, e Å^{-3}	3.011/−3.266 (near Te)	1.193/−0.411	1.105/−0.810	0.810/−0.609	1.309/−2.363 (near Te)

Table 2. Selected Bond Parameters (Å, deg) of **1**−**4**

	1 (X = Cl3)	**2** (X = C21)	**3** (X = O1)	**4**
Te1−Cl1	2.504(2)	2.584(8)	2.510(1)	2.384(1)
Te1−Cl2	2.484(2)	2.482(8)	2.476(1)	
Te1−X	2.330(3)	2.106(2)	1.993(2)	
Te1−C10	2.178(8)	2.103(2)	2.172(2)	2.134(3)
Cl1−Te1−C10	83.71(9)	88.66(4)	86.23(5)	93.41(8)
Cl2−Te1−C10	98.21(9)	92.36(4)	98.53(5)	
X-Te1−C10	116.82(9)	85.73(7)	113.38(6)	
Cl1−Te1−Cl2	168.96(3)	174.32(2)	166.25(3)	
Cl1−Te1−X	84.68(4)	86.31(6)	83.54(5)	
Cl2−Te1−X	84.76(4)	88.19(6)	82.73(5)	
C11−C10−Te1	127.13(23)	110.07(13)	127.34(10)	118.98(19)
C15−C10−Te1	109.12(22)	126.97(11)	109.67(10)	118.81(20)
C13−C10−Te1	157.58(16)	170.36(9)	161.96(7)	160.13(14)

group attached at the *tert*-butyl group in an ortho position of the ligand and proceeds with HCl elimination and formation of a new Te−C bond. The life span of **1** can be largely extended when the temperature is lower than 0 °C and/or the sample is kept under dynamic vacuum. The latter observation is tentatively explained by a catalytic effect of the HCl gas, which apparently accelerates the rate of conversion of **1** to **2**. Notably, the high reactivity of the supermesityl group toward intramolecular cyclization was observed earlier for supermesityl group 15 element dichlorides $RECl_2$ (E = P, As, Sb).[5] The bicyclic diorganotellurium dichloride **2** has poor solubility in most organic solvents. The ^{125}Te NMR spectrum of **2** shows a single resonance at δ 1106.9, which is consistent with values reported for other diorganotellurium dichlorides, such as Me_2TeCl_2 (δ 1218) and Et_2TeCl_2 (δ 1090).[4] The structural assignment of **2** was achieved by ^{13}C and ^{1}H NMR spectroscopy (Experimental Section) and X-ray crystallography. The molecular structure of **2** is shown in Figure 3. Selected crystal data and selected bond parameters of **1** are collected in Tables 1 and 2. The molecular structure features a distorted bipyramidal geometry with the expected ligand occupancies. Unlike in **1**, the Te1 atom and the phenyl ring of **2** are almost coplanar, with the largest deviation from the ideal plane being 0.036 Å. Apparently, the driving force for the intramolecular reaction of **1** giving **2** is the energy gain associated with the relief of distortion from coplanarity. In the crystal lattice, two molecules of **2** are associated via secondary Te1···Cl1a interactions of 3.358(1) Å (symmetry code: $a = -x, -y, -z$) at a crystallographic center of inversion.

When solid **1** was isolated for the first time and exposed to (moist) air, a small amount of a colorless single-crystalline byproduct was isolated in addition to the amorphous **2**, which was found to be *trans*-2,4,6-*t*-$Bu_3C_6H_2Te(OH)Cl_2$ (**3**) by X-ray analysis. Apparently, **3** has been formed as a result of a solid-state hydrolysis of a second unaccounted for (monoclinic?) modification of **1**, which proceeded while the crystal habit remained unchanged. The molecular structure of **3** is shown in Figure 4. Selected crystal data and selected bond parameters of **3** are collected in Tables 1 and 2. Like that of the parent **1**, the geometry of **3** resembles a distorted trigonal bipyramid, in which the organic ligand, the lone pair, and the hydroxyl group occupy the equatorial positions, whereas the Cl atoms are situated in the axial positions. The deviation of the Te1 atom of **3** from the ideal plane defined by the phenyl ring is 0.189 Å shorter than that in the starting

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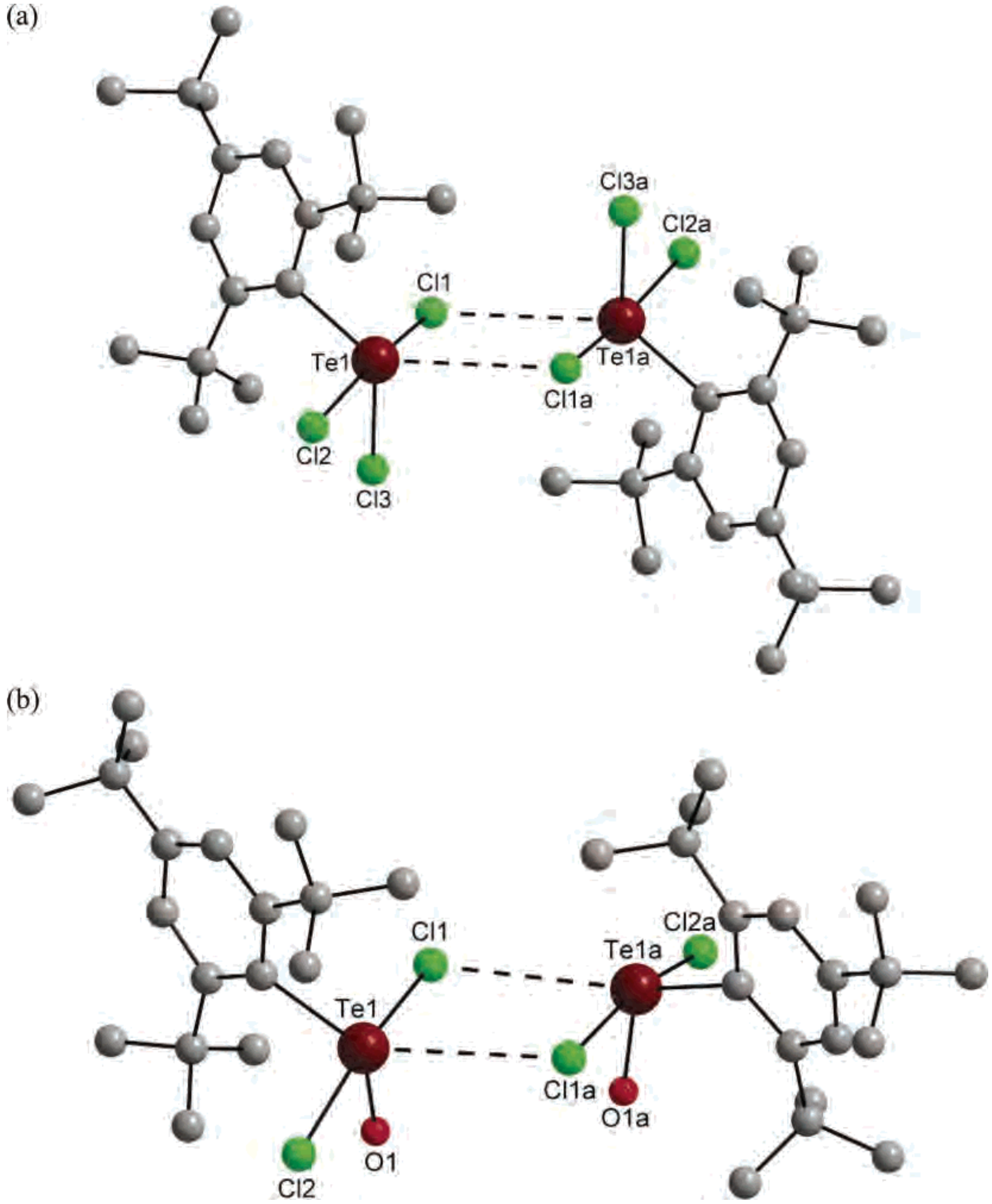

Figure 2. Supramolecular association of (a) **1** (symmetry code used to generate equivalent atoms: $a = x, y, z$) and (b) **3** (symmetry code used to generate equivalent atoms: $a = 2 - x, y, 0.5 - z$) in the solid state.

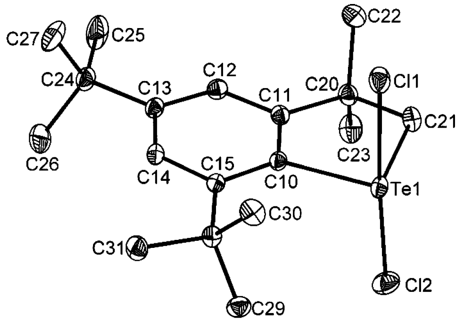

Figure 3. Molecular structure of **2** showing 30% probability displacement ellipsoids and the atom numbering system.

compound of **1**, which can be attributed to the fact that oxygen is smaller than chlorine, and therefore, the repulsion of the equatorial ligand and the *tert*-butyl group in an ortho position is substantially reduced. However, the strong repulsion of the equatorial ligand with one *tert*-butyl group is still evident by the deviation of the C11−C10−Te1 and C15−C10−Te1 angles of 127.34(10)° and 109.67(10)°, respectively, from the value of 120°. Like in the parent **1**, two individual molecules of **3** are associated via secondary Te···Cl interactions of 3.550(6) Å (symmetry code: $a = 2 - x, y, 0.5 - z$). However, differences between the supramolecular motif of **1** and **3** are observed in the relative orientation of the equatorial ligands (Cl3/Cl3a (**1**) and O1/O1a (**3**)), which are situated trans in the dimer of **1** and cis in the dimer of **3** (Figure 2). The observation of the cis configuration in the dimer of **3** and the fact that the crystal habit remained unchanged when **1** transformed into **3** provide strong evidence that a second (monoclinic?) modification of

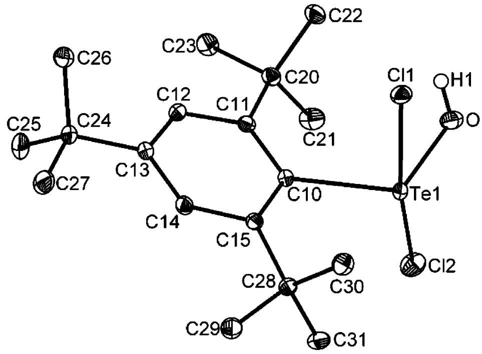

Figure 4. Molecular structure of **3** showing 30% probability displacement ellipsoids and the atom numbering system.

1 exists. It is worth noting that polymorphism is very common for organotellurium halides or presumably more frequently observed since it is often accompanied by indicative color changes.[6] Unfortunately, all attempts at preparing the elusive second modification of **1** for a second time failed. The phenomenon of "disappearing polymorphs" has been recognized, and a number of different explanations have been suggested to account for it.[7] Attempts to prepare **3** by the controlled hydrolysis of **1** in solution failed, and consequently, the spectroscopic characterization of **3** must remain incomplete at this point. According to Bent's rule,[8] *cis*-2,4,6-*t*-$Bu_3C_6H_2Te(OH)Cl_2$ would have been the anticipated isomer instead of *trans*-2,4,6-*t*-$Bu_3C_6H_2Te(OH)Cl_2$ (**3**). Density functional theory (DFT) calculations at the B3LYP/LanL2DZdp level of theory reveal that the related *trans*-PhTe(OH)Cl_2 is, by 7.48 kcal mol^{-1}, more stable than *cis*-PhTe(OH)Cl_2, which suggests that **3** is, indeed, not only the kinetically but also the thermodynamically favored isomer.

The reactivity of **1** in solution is entirely different from that in the solid state. When a Schlenk flask charged with a solution of **1** in THF, Et_2O, or CS_2 is purged with dry argon to remove chlorine gas, the color changes from bright yellow to deep blue and supermesityltellurenyl(II) chloride 2,4,6-*t*-$Bu_3C_6H_2TeCl$ (**4**) is formed quantitatively (Scheme 1). Solutions of **4** in donor solvents remain unchanged for several weeks when kept at −15 °C. From these solutions, solid **4** has been isolated as blue crystals in very high yields. Once isolated, the solubility of **4** is very poor, even in the same donor solvents, which is tentatively explained by the high lattice energy related to the supramolecular association of the individual molecules (see below). Compound **4** has also been prepared by the reaction of bis(supermesityl)ditelluride (2,4,6-*t*-$Bu_3C_6H_2Te)_2$ with 1 equiv of sulfuryl chloride SO_2Cl_2 in the same solvents. Apparently, in solution, a redox equilibrium exists in THF, Et_2O, and CS_2 that can be shifted from **4** to **1** and vice versa by removing chlorine with a purge of argon and by adding SO_2Cl_2, respectively. Attempts to prepare **4** from nondonor solvents proved unsuccessful. At temperatures higher than 15 °C, solutions of **4** in THF, Et_2O, and CS_2 slowly deposit an inhomogeneous precipitate, from which (2,4,6-*t*-$Bu_3C_6H_4Te)_2$ has been identified, whereas other species remain unaccounted for. Solid **4** can be stored unchanged for several days under inert conditions at 0 °C, although moisture seems to have little effect on the stability.

The successful isolation of **4** deserves a comment. Usually, organotellurenyl(II) pseudohalides RTeX (R = alkyl, aryl; X = pseudohalides) are intrinsically unstable compounds that undergo spontaneous disproportion and aggregation reactions. Most organotellurenyl(II) halides, such as PhTeX (X = Cl, Br,[9] I[10]) and β-NapTeI (Nap = napthalene),[11] prepared (in situ) either by the halogenation of RTeTeR or by the synproportion of RTeTeR with $RTeX_3$, rapidly form the corresponding diorganotellurium(IV) dihalides and elemental tellurium. On the other hand, MesTeI (Mes = mesityl)[12] spontaneously decomposes to give $MesTeI_3$, elemental tellurium, and the dinuclear complex $Mes_2TeTeMesI$.[13] Under appropriate conditions, monomeric PhTeI undergoes cyclization to form the tetranuclear compound $(PhTeI)_4$, whose four-membered ring structure has been confirmed by X-ray crystallography.[11,14] On the basis of their physical properties (color, melting point, solubility), the organotellurenyl(II) iodides RTeI (R = β-Nap,[15] *p*-MeC_6H_4, *p*-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$)[16] and organotellurenyl(II) bromides RTeBr (R = Ph, *p*-$MeOC_6H_4$, *p*-$C_6H_5C_6H_4$)[16] having rather small substituents may be assigned similar oligomeric or even polymeric structures having tetravalent Te atoms that reveal Te−Te bonds. Monomeric organotellurenyl(II) pseudohalides, RTeX (R = alkyl, aryl; X = pseudohalides), stable at room temperature can be obtained by electronic stabilization using inter-[14,17−20] and intramolecular[21−23] donor functions.

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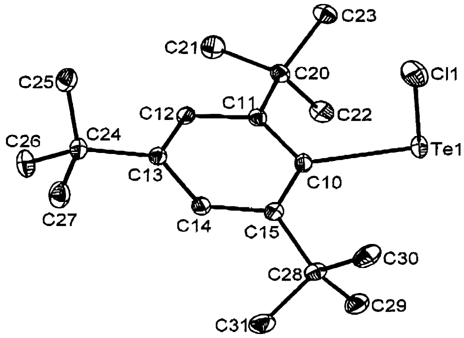

Figure 5. Molecular structure of **4** showing 30% probability displacement ellipsoids and the atom numbering system.

Kinetically stabilized monomeric organotellurenyl(II) bromides, iodides, and pseudohalides containing bulky organic substituents such as *o*-$C_6H_5C_6H_4TeX$,[24] 2,4,6-*i*-$Pr_3C_6H_2TeX$, 2,4,6-*t*-$Bu_3C_6H_2TeX$ (X = Br, I),[25] $(Me_3Si)_3CTeX$ (X = Br, I,[26] CN, SCN, SeCN, NCO, N_3),[27] and 2,4,6-$Ph_3C_6H_2TeI$[28] have also been described; however, to the best of our knowledge, only three iodides, 2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$-TeI,[23] 2,4,6-*t*-$Bu_3C_6H_2TeI$,[29] and $(PhMe_2Si)_3CTeI$,[30] as well as two azides, 2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3TeN_3$ and$(PhMe_2Si)_3CTeN_3$,[23] have been characterized by X-ray diffraction. Within these compounds, the large pseudohalides provide additional kinetic stabilization. Whereas kinetically stabilized organotellurenyl(II) fluorides, RTeF, are entirely unknown,[31] only one kinetically stabilized organotellurenyl(II) chloride, namely, $(Me_3Si)_3CTeCl$, has been claimed in the literature,[26] which, however, was not structurally characterized. The ^{125}Te NMR spectrum (CS_2, $CDCl_3$-capillary) of **4** reveals a signal at δ 1179.0, which is nearly identical to that reported for 2,4,6-*t*-$Bu_3C_6H_2TeI$ (δ 1162).[23]

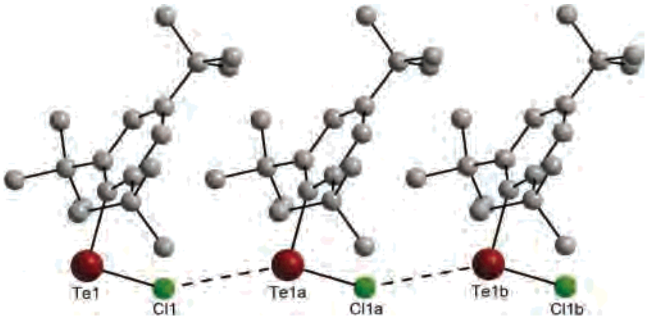

Figure 6. Supramolecular association of **4** (symmetry code used to generate equivalent atoms: $a = x + 1, y, z$).

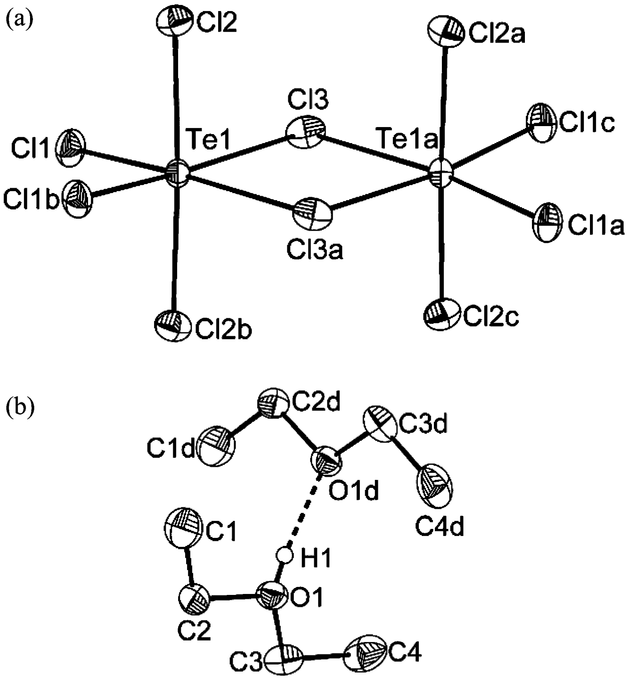

Figure 7. Molecular structure of **5** showing 30% probability displacement ellipsoids and the atom numbering system (symmetry code used to generate equivalent atoms: $a = 1.25 - x, 0.25 - y, z$; $b = 1.25 - x, y, 1.25 - z$; $d = 0.75 - x, -0.25 - y, z$.).

The molecular structure of **4** is shown in Figure 5. Selected crystal data and selected bond parameters of **4** are collected in Tables 1 and 2. The geometry of the Te1 atom of **4** is characterized by a small Cl1−Te1−C10 angle of 93.41(8)°, which agrees well with the corresponding angle reported for 2,4,6-*t*-$Bu_3C_6H_2TeI$ (95.75(8)°).[29] The Te1−Cl1 bond length of **4** of 2.384(1) Å lies approximately midway between the equatorial and axial Te−Cl bond lengths of **1**. Like that of 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$ (**1**), the Te1 atom of 2,4,6-*t*-$Bu_3C_6H_2$-TeCl (**4**) is, by 0.248 Å, displaced from the ideal plane defined by the phenyl ring. However, with the lack of an equatorial ligand, the C11−C10−Te1 and C15−C10−Te1 angles in **4** of 118.98(19)° and 118.81(20)°, respectively, are only slightly distorted as opposed to those of **1**. In the crystal lattice, individual molecules of **4** are linked via secondary Te1$\cdots$Cl1a bonds of 3.677(1) Å (symmetry code: $a = x + 1, y, z$), giving rise to a 1D-coordination polymer (Figure 6). The secondary Te$\cdots$Cl interactions are somewhat reminiscent of the secondary I$\cdots$Cl contacts in α- and *β*-ICl.[32] However, in contrast to the structures of α- and *β*-ICl also showing additional I$\cdots$I contacts, no secondary Te$\cdots$Te interactions are observed for **4**. The lattice energy associated with the formation of the 1D-coodination polymer may explain the low solubility of **4** in most organic solvents once it has been isolated.

When a Schlenk tube containing a solution of **1** in Et_2O was kept for several days at −15 °C in the presence of a slight excess of SO_2Cl_2, a yellow crystalline material was deposited, which on the basis of an X-ray diffraction analysis has been identified as $[Et_2OH]_2[Te_2Cl_{10}]\cdot 2Et_2O$ (**5**) (Scheme 1). The exact mechanism for the formation of **5** remains

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Table 3. Selected Bond Parameters (Å, deg) of **5**[a]

Te1−Cl1	2.386(6)	Te1−Cl2	2.495(1)
Te1−Cl3	2.804(7)	O1−H1	0.723(2)
H1···O1d	1.722(4)	O1···O1d	2.439(6)
Cl1−Te1−Cl1b	92.70(1)	Cl1−Te1−Cl2	89.83(1)
Cl1−Te1−Cl2b	88.40(1)	Cl1−Te1−Cl3	92.03(1)
Cl1−Te1−Cl3a	173.43(1)	Cl2−Te1−Cl2b	177.44(1)
Cl2−Te1−Cl3	87.06(1)	Cl2−Te1−Cl3a	94.86(1)
Te1−Cl3−Te1a	96.37(1)	Te1−Cl3a−Te1a	96.37(1)

[a] Symmetry codes: $a = 1.25 - x, 0.25 - y, z$; $b = 1.25 - x, y, 1.25 - z$; $d = 0.75 - x, -0.25 - y, z$.

unknown; however, a similar material, namely, $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$, featuring the same $[Te_2Cl_{10}]^{2-}$ anion has been recently isolated from the reaction of Ph_3P with $TeCl_4$ in the presence of air moisture.[33] Thus, one conceivable way to rationalize the formation of **5** involves the initial oxidative cleavage of the Te−C bond in **1** by SO_2Cl_2, affording the intermediate $TeCl_4$, which subsequently reacts with Et_2O, moisture, and chloride anions to produce **5**. The molecular structure of the $[Te_2Cl_{10}]^{2-}$ anion in **5** is very similar to that of $\{(Ph_3PO)_2H\}_2[Te_2Cl_{10}]$.[33] The $[Et_2O{-}H{\cdots}OEt_2]$ cation of **5** features a proton that is involved in a (disordered) asymmetric hydrogen bridge with two crystallographically related ether molecules and has been previously reported for a number of different counterions.[34] The hydrogen bond parameters (H1−O1 0.723(2) Å, H1···O1a 1.722(4) Å, O1···O1a 2.439(6) Å, O1−H1···O1a 171.66(2)°; symmetry code: $a = 0.75 - x, -0.25 - y, z$) are nearly identical to those reported in the literature and are consistent with medium-strength hydrogen bonding.[35]

Experimental Section

Tellurium powder, 4,4′-di-*tert*-butyldiphenyl, and sulfuryl chloride were commercially available and used as received, whereas 1-bromo-2,4,6-tri-*tert*-butylbenzene was prepared according to known routes.[36] NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and are referenced against Me_4Si. IR spectra were recorded with a 5 SXC Nicolet DTGS FT-IR spectrometer. Microanalyses were obtained from a Vario EL elemental analyzer.

Modified Synthesis of Bis(supermesityl)ditelluride.[2] A suspension of Li (2.5 g, 360 mmol) and 4,4′-di-*tert*-butylbiphenyl (1.0 g, 3.85 mmol) in THF (80 mL) was prepared and stirred until the solution turned green (approximately 1 h). Then, a solution of bromo-2,4,6-tri-*tert*-butylbenzene (25.0 g, 76.9 mmol) in THF (180 mL) was added dropwise. The addition was stopped when the color turned red and was continued when the color turned green again. The reaction mixture was transferred to a Schlenk tube charged with Te powder (11.7 g, 92.0 mmol) via cannula and stirred overnight. A vigorous steam of air was bubbled through the solution. Then, all volatile materials were removed in vacuo and the solid residue was extracted with hexane using a Dean Stark extractor. Approximately 10 mL of the solvent was removed. Bis(supermesityl)ditelluride crystallized as dark red microcrystalline solid (yield: 23.4 g, 31.5 mmol, 41%; mp 194−195 °C (dec) [lit. 192 °C (dec)].[11]

^{1}H NMR ($CDCl_3$): $\delta = 7.30$ (s, 4H, Ar), 1.40 (s, 36H, CH_3), 1.32 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 157.3$, 149.9, 121.5, 112.0 (Ar), 39.6 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$). $^{125}Te\{^1H\}$ NMR ($CDCl_3$): $\delta = 547.8$. Anal. Calcd for $C_{36}H_{58}Te_2$ (741.09): C 58.34; H 7.90. Found: C 58.38; H 7.87.

Synthesis of Supermesityltellurium Trichloride (1). To a solution of bis(supermesityl)ditelluride (2.00 g, 2.70 mmol) in ether (50 mL) was slowly added SO_2Cl_2 (1.02 g, 7.56 mmol) at 0 °C. The mixture was vigorous stirred for 1 h and then allowed to warm to room temperature. The solution was reduced to an approximate volume of 15 mL and cooled to −15 °C. **1** crystallized as a bright yellow crystalline solid (yield: 2.49 g, 5.18 mmol, 96%).

^{1}H NMR ($CDCl_3$): $\delta = 7.24$ (s, 2H; Ar), 1.31 (s, 9H, CH_3), 1.31 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 149.9$, 127.3, 123.1, 119.4 (Ar), 40.1 (1C; $C(CH_3)_3$, 35.3 (2C, $C(CH_3)_3$), 31.6 (3C, $C(CH_3)_3$), 31.0 (6C, $C(CH_3)_3$). $^{125}Te\{^1H\}$ NMR ($CDCl_3$): $\delta = 1791.0$. Anal. Calcd for $C_{18}H_{29}TeCl_3$ (479.38): C 45.03, H 6.11. Found: C 44.88, H 6.02.

Synthesis of 5,7-Di-*tert*-butyl-2-hydro-3,3-dimethylbenzo[*b*]-tellurophene-1,1-dichloride (2). Solid **1** (1.00 g, 2.09 mmol) was stored at room temperature under argon. After 14 days, the yellow color had faded and an amorphous solid had formed that was recystallized from ethanol. **2** crystallized as a colorless crystalline solid (yield: 890 mg, 2.01 mmol, 96%).

^{1}H NMR ($CDCl_3$): $\delta = 7.05$ (s, 2H, Ar), 1.58 (s, 2H, CH_2), 1.40 (s, 6H, $C(CH_3)_2$), 1.36 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 145.03$, 127.1, 123.3, 119.7 (Ar), 50.0 (CH_2), 40.2 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 31.0 ($C(CH_3)_3$), 30.6 ($C(CH_3)_2$), 20.1 ($C(CH_3)_2$). $^{125}Te\{^1H\}$ NMR ($CDCl_3$): $\delta = 1106.9$. Anal. Calcd for $C_{18}H_{28}Cl_2Te$ (442.92): C 48.81, H 6.37. Found: C 48.81, H 6.59.

When solid **1** was crystallized the first time and exposed to (moist) air, a small amount of a colorless single-crystalline solid, *trans*-2,4,6-*t*-$Bu_3C_6H_2Te(OH)Cl_2$ (**3**), was formed along with the main product of **2**. A single crystal was hand-selected for the X-ray diffraction analysis.

When a solution of **1** in ether was stored with a slight excess of SO_2Cl_2 for prolonged times at −15 °C, a yellow crystalline solid, $[Et_2OH]_2[Te_2Cl_{10}]\cdot 2Et_2O$ (**5**), deposited. A single crystal was hand-selected for the X-ray diffraction analysis.

Synthesis of Supermesityltellurenyl Chloride (4). To a solution of bis(supermesityl)ditelluride (500 mg, 0.67 mmol) in ether (30 mL) was slowly added SO_2Cl_2 (0.09 g, 0.67 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. Approximately 10 mL of solvent was removed and stored at −15 °C. **4** crystallized as a deep blue crystalline solid (yield: 462 mg, 1.13 mmol, 82%).

^{1}H NMR ($CS_2/CDCl_3$-cap.): $\delta = 7.7$ (s, 2H, Ar), 1.88 (s, 9H, CH_3), 1.56 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR ($CS_2/CDCl_3$-cap.): $\delta = 150.5$, 127.9, 122.9, 120.1 (Ar), 40.8 ($C(CH_3)_3$, 35.1 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$). $^{125}Te\{^1H\}$ NMR ($CS_2/CDCl_3$-cap.): $\delta = 1179.0$. Anal. Calcd for $C_{18}H_{29}ClTe$ (408.48): C 52.93, H 7.16. Found: C 52.52, H 7.50.

Crystallography. Intensity data of **1**−**5** were collected on a Bruker SMART 1000 CCD diffractometer, equipped with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and

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SADABS.[37] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[38] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-H atoms. Disorder of one *tert*-butyl group of **1** was resolved with split occupancies of 0.6 (C25, C26, and C27) and 0.4 (C25′, C26′, and C27′). Disorder was also resolved for the ethanol molecule present in the crystal lattice of **1**. The ethanol molecule lies on a crystallographic center of inversion. O1 and O1′ were resolved with a split occupancy of 0.25. Disorder for the inorganic moiety of **2** was resolved with split occupancies of 0.9 (Te1, Cl1, Cl2, O1, and H1) and 0.1 (Te1′, Cl1′, Cl2′, O1′, and H1′). The proton H1 of **5** is disordered on two crystallographically related positions and was refined with split occupancies of 0.5. H atoms attached to C atoms were included in geometrically calculated positions for all structures using a riding model and were refined isotropically. The absolute structure of **4** has been determined by refinement of the Flack parameter 0.00(2).[39] Figures were created with DIAMOND.[40] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC Nos. 631196−631200 (**1**−**5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk, or WWW, http://www.ccdc.cam.ac.uk).

Computational Methodology. Ab initio molecular orbital calculations were carried out using the Gaussian 03W suite of programs.[41] To incorporate the effects of electron correlation, a hybrid DFT/HF method, namely, Becke's three-parameter exchange functional[42] with the Lee−Yang−Parr nonlocal correlation functional[43] (B3LYP), was used. The LANL2DZdp basis set (Wadt and Hay's LANL2DZ basis set augmented with polarization and diffuse functions)[44] was used for the full geometry optimizations. Vibrational frequency calculations were carried out to confirm that the stationary points are minima on the potential energy surface. The zero-point corrected energies of *trans*-$PhTe(OH)Cl_2$ and *cis*-$PhTe(OH)Cl_2$ are −345.415213 and −345.403290 hartrees, respectively.

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Supporting Information Available: Five CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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