# **ORGANOMETALLICS**

Note

# Synthesis and Properties of Tellurinic Anhydride–Tellurone Adducts

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**Supporting Information** 

**ABSTRACT:** The synthesis and characterization of stable tellurinic anhydride-tellurone adducts are reported. Treatment of aryltellurinic anhydride with diaryl tellurone gave pentacyclotelluroxane consisting of two molecules each of the starting tellurium oxides. The bulky aromatic substituents attached to the tellurium atoms efficiently prevent further aggregation and enable full characterization using multinuclear (<sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te) NMR and IR



spectroscopy as well as elemental analysis. For  $(TipTe)_4(Tip_2Te)_2O_{10}$  (**3TT**, Tip = 2,4,6-triisopropylphenyl), the molecular structure was unambiguously determined by an X-ray crystallographic analysis. To estimate the dissociation energies of the tellurinic anhydride–tellurone adducts, density functional theory calculations were performed, and it was found that the adducts are highly stabilized by forming a four di- $\mu$ -oxo bridge structure.

The first syntheses of aryltellurinic acids and their anhydrides were reported by Lederer<sup>1</sup> and Petragnani,<sup>2</sup> respectively. Since then, the tellurinic anhydrides have often been used in organic synthesis as mild oxidizing agents.<sup>3</sup> However, little is known about their structure because of their tendency to form random oligomeric mixtures. Recently, we succeeded in the first full characterization of diorgano tellurone, which had also been known to exist as an ill-defined oligomer, with the help of a bulky 2,4,6-triisopropylphenyl (Tip) substituent.<sup>4</sup> More recently, the second example of a welldefined tellurone, bis(8-dimethylaminonaphthyl) tellurone, was reported.<sup>5</sup> The result prompted us to prepare some bulky aryltellurinic anhydrides (vide infra); however, their <sup>1</sup>H NMR spectra still exhibited the characteristics of oligomeric compounds.

It is well-known that the Te-O double bond within an organotellurium oxide is prone to dimerize to form a stable 1,3,2,4-dioxaditelluretane ring.<sup>6</sup> For example, the X-ray crystal structures of diaryl telluroxides, such as Ph<sub>2</sub>TeO,<sup>6a</sup>  $(C_6F_5)_2$ TeO,<sup>6b</sup> Tip<sub>2</sub>TeO,<sup>6c</sup> and Mes<sub>2</sub>TeO (Mes = 2,4,6trimethylphenyl),<sup>6c<sup>1</sup></sup> show dimeric structures with a dioxaditelluretane ring. The only exception is An<sub>2</sub>TeO, which forms a linear polymeric telluroxane.<sup>7</sup> For tellurium oxoacid derivatives, Beckmann and co-workers reported the crystal structures of tellurinic and telluronic acids carrying a bulky 2,6-dimesitylphenyl substituent, which also exist as a dimer.<sup>8</sup> X-ray crystallographic studies on the polymeric tellurinic anhydrides  $[(8-Me_2NC_{10}H_6TeO)_2O]_n$  and  $[(4-MeOC_6H_4TeO)_2O]_n$  (1A), including a dioxaditelluretane link in the main chain, were also reported by the same group.9 Related examples of well-defined Te-O macrocycles involve the ionic telluroxane  $[Li(THF)_4]$ -[(i-PrTe)<sub>12</sub>O<sub>16</sub>Br<sub>4</sub>{Li(THF)Br}<sub>4</sub>Br]·2THF<sup>10</sup> and the discrete cluster  $(2-PhN=NC_6H_4Te)_6TeO_{11}^{11}$  which can be regarded as the condensation product of tellurinic acids in a broad sense.

From the above background, treatment of the tellurinic anhydride with an appropriate tellurium oxide, both of which have bulky aromatic substituents, is expected to form a spectroscopically characterizable adduct. In this study, we investigated the synthesis and characterization of tellurinic anhydride—tellurone adducts.

## RESULTS AND DISCUSSION

In accord with the reported procedure for the synthesis of 4methoxyphenyltellurinic anhydride,  $[(4-MeOC_6H_4TeO)_2O]_n$ (1A),<sup>3a,b,9b</sup> bulky aryltellurinic anhydrides 1T, 1D, and 1M, which are all new compounds, were prepared (Scheme 1). Because their <sup>1</sup>H NMR spectra are too complex to be used for their structural identification, the structures were confirmed by combustion analyses.

ArTeTeAr	ArTeCl <sub>3</sub> 10% aq NaOH, THF	· [(ArTeO) <sub>2</sub> O] <sub>n</sub>
rt, 1h	rt, overnight	<b>1</b>
	A [Ar = 4-methoxyphe T [Ar = 2,4,6-triisoprop D [Ar = 2,6-diethylphe M [Ar = 2,4,6-trimethyl	nyl (An)]: 80% sylphenyl (Tip)]: 98% nyl (Dep)]: 97% lphenyl (Mes)]: 93%

Our initial attempt to obtain the adduct of  $[(TipTeO)_2O]_n$ (1T) with Tip<sub>2</sub>TeO resulted in no reaction; however, treatment of 1T with Tip<sub>2</sub>TeO<sub>2</sub> (2T) gave the expected adduct.

When a solution of tellurone 2T in  $CDCl_3$  was treated with tellurinic anhydride 1T at room temperature, immediate and

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complete consumption of the starting materials and quantitative formation of pentacyclotelluroxane **3TT**, a 2:2 adduct of **1T** and **2T**, were observed by <sup>1</sup>H NMR spectroscopic analysis. During the process, oxidation of **1T** by strongly oxidizing **2T**<sup>4</sup> was not observed, although the related partial anhydride can be easily oxidized using  $H_2O_2$ .<sup>12</sup> The obtained adduct was chromatographically unstable, undergoing complete dissociation to **1T** and **2T**, which was ascertained by thin-layer chromatography analysis. Dissociation was also observed in a CDCl<sub>3</sub> solution of **3TT** upon addition of CD<sub>3</sub>OD. Therefore, the adduct was isolated by triturating the concentrated reaction mixture with hexane, yielding 62% **3TT** (Table 1, entry 1). The reaction could be conveniently performed in refluxing hexane, from which the adduct **3TT** was precipitated in a pure form in 68% yield (entry 2).

Table 1. Synthesis of Tellurinic Anhydride–Tellurone Adduct 3



<sup>*a*</sup>All reactions were performed for a few minutes until the starting materials were dissolved completely. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>No reaction. <sup>*d*</sup>Probably due to low solubility of the starting materials. <sup>*e*</sup>Complex mixture even after overnight reaction.

Similar treatment of 1T with bis(2,6-diethylphenyl)tellurone (Dep<sub>2</sub>TeO<sub>2</sub>, 2D) gave the corresponding adduct 3TD in 63% yield (entry 3); however, no such reaction was observed between 1T and oligomeric  $An_2TeO_2$  (2A) (entry 4).

For the reaction of  $[(DepTeO)_2O]_n$  (1D) with 2T and 2D, the corresponding adducts 3DT and 3DD were obtained in 50% and 66% yields, respectively. On the other hand, the reaction of the sterically less hindered tellurinic anhydrides 1M and 1A, having a Mes and an An group, respectively, with 2T gave a complex mixture, and the expected adduct could not be detected.

The structures of tellurinic anhydride–tellurone adducts 3 were confirmed by <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR, IR, and elemental analysis. For **3TT**, we obtained a single crystal suitable for X-ray analysis. Figure 1 shows the crystal structure of **3TT**, <sup>13</sup> which consists of two molecules each of tellurinic anhydride **1T** and tellurone **2T**. Each Te–O double bond of one tellurone is associated with one Te–O double bond of a different tellurinic anhydride to form a spiro[3.3]heptane ring, and another Te–O double bond of each tellurinic anhydride is associated with another tellurone in a similar way to furnish a pentacyclo-[9.1.1.1.<sup>1,3</sup>1.<sup>5,7</sup>1<sup>7,9</sup>]hexadecane structure. The eight Tip sub-



**Figure 1.** ORTEP plot of **3TT** with 50% probability ellipsoids for the non-hydrogen atoms. Only one orientation of the disordered *p*-isopropyl in the Tip group attached to Te3 is shown.

stituents are radially arranged around the core ring and effectively prevent further aggregation. All of the Tip groups are oriented perpendicular to the plane of the core ring system in an alternating up-and-down arrangement. Consequently, one ortho isopropyl group of each Tip substituent is located in the shielding region of the adjacent Tip moieties. In fact, the <sup>1</sup>H NMR signals of relevant methyl groups resonate at high field from -0.12 to 0.20 ppm. This characteristic <sup>1</sup>H NMR spectrum of **3TT** did not change in the temperature range 23–100 °C in toluene-*d*<sub>8</sub>, indicating that the solution structure of **3TT** is essentially similar to that in the solid state and is thermally stable.

The geometries around the Te(VI) atoms (Te1 and Te4) are octahedral and are defined by four O atoms and two C atoms. Considering the lone pair of electrons at the Te(IV) atom, the geometries around Te2, Te3, Te5, and Te6 are trigonal bipyramidal with the O<sub>3</sub>C donor set. The bond angles of anhydride linkages (Te2-O9-Te6 =  $120.9(2)^{\circ}$  and Te3-O10-Te5 =  $120.8(2)^{\circ}$ ) are slightly smaller than those reported for **1A** ( $125.6(3)^{\circ}$ )<sup>9b</sup> and the related (An<sub>2</sub>TeO)<sub>n</sub> ( $126.0(3)^{\circ}$ ),<sup>7</sup> probably due to the ring structure.

The <sup>125</sup>Te NMR spectra of adducts 3 show two resonances around 800 and 1390 ppm, as shown in Table 2; they are assigned to Te(VI) and Te(IV), respectively, in accord with an approximate integral ratio of 1:2. The chemical shift values of

Table 2. <sup>125</sup>Te NMR Chemical Shifts of 3 in CDCl<sub>3</sub>

3	$\delta_{ ext{Te(VI)}}  ext{ (ppm)}^a$	$\delta_{ m Te(IV)}~( m ppm)^a$
3TT	800	1392
3TD	797	1394
3DT	797	1388
3DD	779	1396

<sup>*a*</sup>Tip<sub>2</sub>TeO ( $\delta_{Te}$  1319 ppm) was used as an external standard.

Te(IV) are comparable with those of the structurally related tellurinic acid dimer  $[2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{Te}(\text{O})\text{OH}]_2$  ( $\delta_{\text{Te}}$  1403 ppm).<sup>8a</sup>

Figure 2 shows a schematic illustration of the inorganic telluroxane core with the bond lengths. Each dioxaditelluretane



Figure 2. Core structure of 3TT. All bond lengths are in Å.

ring consists of longer coordinative Te–O bonds (2.072–2.136 Å) and shorter Te–O bonds (1.914–1.938 Å), which are intermediate between the Te–O double bond found in 2T (1.80 Å)<sup>4</sup> and typical single bonds (Te2–O9, Te3–O10, Te5–O10, and Te6–O9) in 3TT (1.982–1.992 Å). The difference between the longer and shorter Te–O bond lengths (average 0.18 Å) is smaller than those found in the crystal structures of Ph<sub>2</sub>TeO (average 0.66 Å),<sup>6a</sup> (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TeO (0.34 Å),<sup>6b</sup> Mes<sub>2</sub>TeO (average 0.78 Å),<sup>6c</sup> Tip<sub>2</sub>TeO (average 0.67 Å),<sup>6c</sup> and 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Te(O)OH (0.25 Å),<sup>8a</sup> suggesting a relatively strong di- $\mu$ -oxo linkage.

To estimate the dissociation energies of the tellurinic anhydride–tellurone adducts, density functional theory (DFT) calculations were performed on **3TT** and **3DD** at the B3LYP/LANL2DZdp/6-31Gd level.<sup>14</sup> For **3TT**, the calculations successfully reproduced the X-ray crystal structure. The calculated vibrational frequencies of **3TT** and **3DD** assigned to the Te–O bond stretching in 400–700 cm<sup>-1</sup> are in good agreement with the experimental frequencies (see the Supporting Information), also ensuring the reliability of the calculations. We compared the molecular energies of the adducts with those of the corresponding tellurinic anhydrides and tellurones; the dissociation energies of **3TT** and **3DD** were calculated to be 319.9 and 399.0 kJ/mol, respectively. These adducts are considered to be highly stabilized by the construction of a four di- $\mu$ -oxo bridge structure.

Finally, we examined the reaction of the tellurinic anhydride–tellurone adducts with a phosphine for further structural proof. When a **3DD** solution in CDCl<sub>3</sub> was treated with an excess amount of Ph<sub>3</sub>P at room temperature for 6 days, a complete conversion to Dep<sub>2</sub>Te and DepTeTeDep, along with the formation of Ph<sub>3</sub>PO, was observed by <sup>1</sup>H NMR spectroscopy (Scheme 2). The obtained telluride and ditelluride can be regarded as reduction products of tellurone and tellurinic anhydride, respectively, although the reaction was

Scheme 2. Reaction of 3DD with Ph<sub>3</sub>P

**3DD**  $\xrightarrow{\text{Ph}_3\text{P}(\text{excess})}$  Dep<sub>2</sub>Te + DepTeTeDep + Ph<sub>3</sub>PO CDCl<sub>3</sub>, rt, 6 days rather retarded owing to the bulkiness and high stability of the adduct.

In summary, we successfully prepared stable adducts of tellurinic anhydrides with tellurones with the help of bulky aromatic substituents, which could be fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR and IR spectroscopy as well as elemental analysis. For **3TT**, the molecular structure was unambiguously confirmed by X-ray crystallography. The dissociation energies of **3TT** and **3DD** were estimated by theoretical calculations, and the adducts were found to be highly stabilized by constructing a pentacyclic telluroxane structure containing four dioxaditelluretane rings.

#### EXPERIMENTAL SECTION

The melting points were determined using a Yamato MP-21 melting point apparatus in open capillaries and are uncorrected. <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR spectra were measured on a Varian Mercury plus 400 spectrometer at 400, 100, and 126 MHz, respectively. All of the chemical shifts are reported as  $\delta$  values (ppm) relative to residual chloroform ( $\delta_{\rm H}$  7.26), the central peak of deuteriochloroform ( $\delta_{\rm C}$  77.00), and Mes<sub>2</sub>Te ( $\delta_{\rm Te}$  275) unless otherwise noted; *J* values are expressed in hertz. For <sup>125</sup>Te NMR, Tip<sub>2</sub>TeO ( $\delta_{\rm Te}$  1319) was used as a secondary external standard. Infrared spectra were measured using a JASCO FT/IR-4200 spectrometer. Elemental analyses were performed using a PerkinElmer 2400 Series II Analyzer.

All reagents and solvents were of commercial grade and were used according to supplier instructions unless otherwise mentioned. Diaryl tellurones **2T**, **2D**, and **2M** were prepared following the procedure described previously.<sup>6c</sup>

Preparation of Tellurinic Anhydride-Tellurone Adducts 3. For example, a suspension of 1T (353 mg, 0.497 mmol) and 2T (283 mg, 0.500 mmol) in hexane (10 mL) was heated for a few minutes until the starting materials dissolved completely. White solids precipitated immediately. The reaction mixture was cooled, and the solids were collected and dried under vacuum to afford the adduct 3TT (431 mg, 0.169 mmol, 68%). Recrystallization of 3TT from AcOEt gave colorless prisms suitable for X-ray crystallography. Mp: 223-225 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  -0.12 (d, J = 7 Hz, 12H), -0.06 (d, J = 7 Hz, 12H), 0.19 (d, J = 7 Hz, 12H), 0.20 (d, J = 7 Hz, 12H), 1.04 (d, J = 7 Hz, 12H), 1.05 (d, J = 7 Hz, 12H), 1.06 (d, J = 7 Hz, 12H), 1.07 (d, J = 7 Hz, 12H), 1.20 (d, J = 7 Hz, 12H), 1.31 (d, J = 7 Hz, 12H), 1.35 (d, J = 7 Hz, 12H), 1.47 (d, J = 7 Hz, 12H), 2.63 (sep, *J* = 7 Hz, 4H), 2.67 (sep, *J* = 7 Hz, 4H), 3.45 (sep, *J* = 7 Hz, 4H), 3.61 (sep, J = 7 Hz, 4H), 3.78 (sep, J = 7 Hz, 4H), 5.45 (sep, J = 7 Hz, 4H), 6.56 (d, J = 2 Hz, 4H), 6.64 (d, J = 2 Hz, 4H), 6.81 (d, J = 2 Hz, 4H), 7.05 (d, J = 2 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.0, 22.9, 23.3, 23.5, 23.6, 23.8, 23.95, 23.97, 24.7, 25.3, 25.9, 27.6, 29.6, 30.1, 30.3, 32.3, 34.1, 34.2, 119.6, 123.6, 124.1, 124.6, 145.1, 149.0, 149.4, 149.9, 150.2, 150.6, 151.1, 153.3. <sup>125</sup>Te NMR (CDCl<sub>3</sub>, Tip<sub>2</sub>TeO δ 1319): δ 800, 1392. IR (KBr, cm<sup>-1</sup>): 2959, 2927, 2866, 1462, 681, 645, 619, 448. Anal. Calcd for C120H184O10Te6: C, 56.47; H, 7.27. Found: C, 56.42; H, 7.29.

**3TD** was obtained as a white powder in 63% yield. Mp: 197–198 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  –0.01 (d, J = 7 Hz, 12H), 0.08 (t, J = 7 Hz, 12H), 0.28 (d, J = 7 Hz, 12H), 1.04 (d, J = 7 Hz, 12H), 1.05 (d, J = 7 Hz, 12H), 1.32 (dt, J = 7 and 7 Hz, 4H), 1.35 (d, J = 7 Hz, 12H), 1.32 (dt, J = 7 and 7 Hz, 4H), 1.35 (d, J = 7 Hz, 12H), 1.37 (t, J = 7 Hz, 12H), 1.45 (d, J = 7 Hz, 12H), 2.55 (dt, J = 7 and 7 Hz, 4H), 2.65 (sept, J = 7 Hz, 4H), 3.01 (dt, J = 7 and 7 Hz, 4H), 3.65 (sept, J = 7 Hz, 4H), 3.91 (sept, J = 7 Hz, 4H), 4.47 (dt, J = 7 and 7 Hz, 4H), 6.56 (dd, J = 7 and 2 Hz, 4H), 6.63 (d, J = 2 Hz, 4H), 6.82 (d, J = 2 Hz, 4H), 7.01 (dd, J = 7 and 7 Hz, 4H), 7.06 (dd, J = 7 and 2 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  15.9, 16.2, 22.9, 23.5, 23.8, 24.1, 26.0, 26.7, 27.5, 29.7, 32.8, 34.2, 120.1, 123.9, 128.4, 129.0, 129.2, 144.2, 146.7, 147.6, 149.3, 150.2, 152.5, 153.4. <sup>125</sup>Te NMR (CDCl<sub>3</sub>, Tip<sub>2</sub>TeO  $\delta$  1319):  $\delta$  797, 1394. IR (KBr, cm<sup>-1</sup>): 3049, 2957, 2931, 2868, 1456, 687, 653, 622, 440. Anal. Calcd for C<sub>100</sub>H<sub>144</sub>O<sub>10</sub>Te<sub>6</sub>: C, 52.87; H, 6.39. Found: C, 52.81; H, 6.50.

3DT was obtained as a white powder in 50% yield by recrystallization of the reaction mixture from CH<sub>2</sub>Cl<sub>2</sub>. Mp: 210-211 °C, isolated as a 2:1 complex of 3DT and 2T including four molecules of CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  –0.08 (d, I = 7 Hz, 12H), –0.01 (d, J = 7 Hz, 12H), 0.41 (t, J = 7 Hz, 12H), 1.10 (d, J = 7 Hz, 24H), 1.13  $(d, J = 7 Hz, 12H, Tip_2TeO_2), 1.16 (d, J = 7 Hz, 12H), 1.21 (d, J = 7$ Hz, 6H,  $Tip_2TeO_2$ ), 1.41 (d, J = 7 Hz, 12H), 1.44 (t, J = 7 Hz, 12H), 1.59 (dt, J = 7 and 7 Hz, 4H), 2.69 (sept, J = 7 Hz, 4H), 2.88 (dt, J = 7 and 7 Hz, 4H), 2.88 (sept, J = 7 Hz, 1H, Tip<sub>2</sub>TeO<sub>2</sub>), 3.12 (dt, J = 7 and 7 Hz, 4H), 3.30 (sept, J = 7 Hz, 4H), 3.51 (dt, J = 7 and 7 Hz, 4H), 4.09 (sept, J = 7 Hz, 2H, Tip<sub>2</sub>TeO<sub>2</sub>), 5.41 (sept, J = 7 Hz, 4H), 6.54 (d, J = 2 Hz, 4H), 6.63 (dd, J = 8 and 1 Hz, 4H), 6.84 (dd, J = 8 and 1 Hz, 4 H), 6.97 (dd, J = 8 and 8 Hz, 4H), 7.05 (d, J = 2 Hz, 4H), 7.14 (s, 2H, Tip<sub>2</sub>TeO<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.9, 17.4, 21.6, 23.6 (Tip<sub>2</sub>TeO<sub>2</sub>), 23.8, 23.8 (Tip<sub>2</sub>TeO<sub>2</sub>), 23.9, 24.3, 24.6, 25.5, 25.8, 28.6, 29.5, 29.9, 32.8 (Tip<sub>2</sub>TeO<sub>2</sub>), 34.0, 34.3 (Tip<sub>2</sub>TeO<sub>2</sub>), 123.3, 124.0, 124.8 (Tip<sub>2</sub>TeO<sub>2</sub>), 125.6, 127.9, 129.2, 138.0 (Tip<sub>2</sub>TeO<sub>2</sub>), 144.9, 147.4, 149.0, 149.5, 150.3, 150.5, 151.2, 152.3 (Tip<sub>2</sub>TeO<sub>2</sub>), 154.8  $(Tip_{1}TeO_{2})$ . <sup>125</sup>Te NMR (CDCl<sub>3</sub>, Tip\_TeO  $\delta$  1319):  $\delta$  797, 1388. IR (KBr, cm<sup>-1</sup>): 3040, 2958, 2928, 2867, 1459, 679, 645, 606, 442. Anal. Calcd for C234H342O22Cl8Te13: C, 51.57; H, 6.33. Found: C, 51.53; H, 6.58

**3DD** was obtained as a white powder in 66% yield. Mp: 195–197 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.75 (t, J = 7 Hz, 12H), 0.57 (t, J = 7 Hz, 12H), 1.35 (t, J = 7 Hz, 12H), 1.38 (t, J = 7 Hz, 12H), 1.78 (dq, J = 7 and 7 Hz, 4H), 1.95 (dq, J = 7 and 7 Hz, 4H), 2.26 (dq, J = 7 and 7 Hz, 4H), 2.85 (dq, J = 7 and 7 Hz, 4H), 2.96 (dq, J = 7 and 7 Hz, 4H), 3.18 (dq, J = 7 and 7 Hz, 4H), 3.65 (dq, J = 7 and 7 Hz, 4H), 4.60 (dq, J = 7 and 7 Hz, 4H), 6.47 (dd, J = 7 and 2 Hz, 4H), 6.49 (dd, J = 7 and 7 Hz, 4H), 7.01 (dd, J = 7 and 7 Hz, 4H), 7.06 (dd, J = 7 and 2 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.1, 16.4, 16.6, 17.2, 25.2, 25.7, 28.2, 28.9, 125.5, 127.4, 128.5, 128.9, 129.3 (overlapped), 145.6, 145.7, 145.9, 147.0, 149.6, 153.0. <sup>125</sup>Te NMR (CDCl<sub>3</sub>, Tip<sub>2</sub>TeO  $\delta$  1319):  $\delta$  779, 1396. IR (KBr, cm<sup>-1</sup>): 3049, 2957, 2930, 2870, 1455, 795, 683, 655, 607, 432. Anal. Calcd for C<sub>80</sub>H<sub>104</sub>O<sub>10</sub>Te<sub>6</sub>: C, 48.25; H, 5.26. Found: C, 48.24; H, 5.29.

**Reaction of 3DD with Ph<sub>3</sub>P.** A solution of 3DD (19.9 mg, 10.0  $\mu$ mol) and Ph<sub>3</sub>P (46.4 mg, 177  $\mu$ mol) in CDCl<sub>3</sub> (1 mL) was maintained at room temperature, and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 6 days, the broad <sup>1</sup>H NMR signals assigned to unidentified intermediates disappeared completely, and quantitative formation of Dep<sub>2</sub>Te, DepTeTeDep, and Ph<sub>3</sub>PO was observed.

**Theoretical Calculations.** All of the calculations were performed using the Gaussian 09 program package.<sup>14</sup> The starting geometries were taken from the X-ray structure of **3TT** and optimized with the DFT at the B3PW91 level. The LANL2DZdp basis set was used for Te, whereas the 6-31G(d,p) basis set was used for C, H, and O. Stationary points were confirmed to be minima by vibrational frequency calculations that gave no imaginary frequencies.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Text giving experimental details for the preparation of aryltellurinic anhydrides 1, figures giving <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR and IR spectra for tellurinic anhydride—tellurone adducts 3, and a CIF file giving X-ray crystallographic data for **3TT**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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(13) Crystal data of **3TT**:  $C_{120}H_{184}O_{10}Te_6$ ,  $M_r = 2552.37$ , crystal dimensions  $0.18 \times 0.16 \times 0.09 \text{ cm}^3$ , triclinic, a = 14.8010(10) Å, b = 18.3641(13) Å, c = 25.2862(17) Å,  $\alpha = 94.6230(10)^\circ$ ,  $\beta = 93.0820(10)^\circ$ ,  $\gamma = 109.7500(10)^\circ$ , V = 6423.5(8) Å<sup>3</sup>, T = 153(2) K, space group PI (No. 2), Z = 2,  $\rho_{calcd} = 1.32 \text{ gcm}^{-3}$ ,  $\mu$ (Mo K $\alpha$ ) = 1.394 mm<sup>-1</sup>, 38309 reflections measured, 27340 independent reflections ( $R_{int} = 0.0239$ ). The final R1 value was 0.0446 ( $I > 2\sigma(I)$ ). The final wR2( $F^2$ ) value was 0.1024 (all data). The goodness of fit on  $F^2$  was 1.011. CCDC-951783 contains supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data request/cif.

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