Isolation of a Catenated Organotelluride Anion in the Sodium Borohydride Reduction of Diphenylditelluride

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Summary: Far more complex than anticipated is the widely utilized reductive cleavage of diorganoditellurides with sodium borohydride. The isolation and characterization of $[Pn(C_6H_5)_4][(TeC_6H_5)_3]$ *(Pn = P, As) suggests that diphenylditelluride is reactive toward the hydride as well as to the phenyltellurolate anion.*

Introduction

Until very recently, a marked difference between the metal compounds of polytellurides and those of organic compounds of tellurium was the lack of examples with catenated tellurium in a linear arrangement in the latter. Angles about tellurium atoms of ca. 90° or 180° are a common motif in many metal compounds of polytellurides,[1,2] which has in some cases been attributed to electron-rich three-center or hypervalent bonding.[3,4] This “nonclassical”[5] behavior gives rise to an array of aesthetically exciting and theoretically demanding polytelluride ions ranging from discrete entities to infinite one-, two-, and three-dimensional networks.[1,2] In contrast, examples of organopolytellurides are still rare with most attention given to diorganoditellurides. While a variety of diorganoditellurides have been fully characterized, some prominent examples are cited here;[6−9] to our knowledge, the only examples containing a higher degree of catenation are a few diorganotritellurides: R_2Te_3, where R = tris(trimethylsilyl)methyl,[10] 2-(2-pyridyl)phenyl,[11] and [3]ferrocenophane.[12] As would be expected, the tritellurium units in these compounds are nonlinear. In addition, a strongly bent tri(*tert*-butyl)phosphoryltritellurium cation[13] and a pentakis(trimethylsilyl)methyltritellurium cation with a slightly bent Te−Te−Te chain (159.5°)[14] were reported.

Last year's discovery of [bis[hydrotris(3,5-dimethylpyrazolyl)borate]samarium(III)] tri(tellurophenolate) utilizing a reaction normally employed to prepare lanthanide chalcogenolates is the only example of an organotellurium compound with a nearly linear arrangement in the tritellurium chain.[15] We report here that the $[(TeC_6H_5)_3]^-$ anion can be isolated during the sodium borohydride reduction of diphenylditelluride and confirm the principal findings of structural details by X-ray structure studies on single crystals of the isotypous tetraphenylphosphonium and tetraphenylarsonium salts.

Experimental Section

Chemicals and Instrumentation. Sodium borohydride, tetraphenylphosphonium bromide, tetraphenylarsonium chloride, phenyllithium (1.0 M in ether), and tellurium powder were newly purchased from Aldrich and used without further purification. Diphenylditelluride was prepared by quenching and air oxidation of lithium tellurophenolate obtained from the reduction of tellurium with phenyllithium in dry ether.[16] Ethanol was procured from Fisher and distilled from sodium metal.

Single-crystal diffraction data was collected on a Siemens Smart platform diffractometer (graphite monochromated, λ(Mo Kα) = 0.710 73 Å). All experimental work was performed under an inert atmosphere using deoxygenated solvents. The concentration of filtered ethanolic solutions of sodium borohydride was obtained by titration of diphenylditelluride (0.500 g) in ethanol. Typically, the sodium borohydride solution was dropwise added via a buret to the red slurry of diphenylditelluride until the mixture remained colorless.

Synthesis of Salts of the Tri(tellurophenolate) Anion (1^-). (A) An ethanolic solution of sodium borohydride (20 mL, 0.1 M, 2.0 mmol) was added to a red suspension of diphenylditelluride (1.21 g, 3 mmol) in ethanol (20 mL). A red solution resulted after the mixture was stirred for 45 min at 21 °C. To this solution was added an ethanolic solution (40 mL) of tetraphenylphosphonium bromide (0.84 g, 2 mmol) or tetraphenylarsonium chloride (0.84 g, 2 mmol) at 21 °C. After filtration through a bed of Celite, the deep red solution was stored at −10 °C for 3−4 months, whereupon large cubic blood-red crystals precipitated. After decantation of the pale red liquid, the crystalline product was collected: $[P(C_6H_5)_4]$**1** (0.824 g, 0.86 mmol, 43%) or $[As(C_6H_5)_4]$**1** (0.910 g, 0.91 mmol, 45%).

(B) Alternately, a colorless ethanolic solution of sodium tellurophenolate (1 mmol), prepared by treating diphenylditelluride (0.205 g, 0.5 mmol) with a solution of sodium

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borohydride (10 mL, 0.1 M in ethanol, 1.0 mmol), was added to a suspension of diphenylditelluride (0.410 g, 1.0 mmol) in ethanol (20 mL). A red solution resulted after the mixture was stirred for 45 min at 21 °C. To this solution was added a solution of tetraphenylphosphonium bromide (0.42 g, 1 mmol) or tetraphenylarsonium chloride (0.42 g, 1 mmol) at 21 °C in ethanol (40 mL). After filtration through a bed of Celite, the deep red solution was stored at −10 °C for 3−4 months, whereupon large cubic blood-red crystals precipitated. After the pale red liquid was decanted off, the crystalline product was collected: $[P(C_6H_5)_4]$**1** (0.487 g, 0.51 mmol, 51%) or $[As(C_6H_5)_4]$**1** (0.522 g, 0.52 mmol, 52%).

Characterization of $[P(C_6H_5)_4][(TeC_6H_5)_3]$. Mp: 120 °C dec. Anal. Calcd for $C_{42}H_{35}PTe_3$: C, 52.9; H, 3.7. Found: C, 51.3; H, 3.6.

Characterization of $[As(C_6H_5)_4][(TeC_6H_5)_3]$. Mp: 145 °C. Anal. Calcd for $C_{42}H_{35}AsTe_3$: C, 50.6; H, 3.5. Found: C, 50.0; H, 3.6.

Crystal Structure Study. Single crystals of $[P(C_6H_5)_4]$**1** (in parentheses: $[As(C_6H_5)_4]$**1**) were obtained from their ethanol solutions. The single crystals selected for data collection were mounted with a trace of silicone oil on a 0.1 mm glass capillary. A total of 25 283 (20 541) X-ray diffraction data were collected with a Siemens Smart platform diffractometer using three different ϕ settings and 0.3° increment ω scans $2\theta < 56.59°$ (59.52°). The unit cell parameters were obtained from least-squares fit of 8192 (8192) reflections. Corrections for absorption and decay were applied using SADABS.[17] Solution by direct methods using SHELXS-86[18] and refinement by full matrix least squares on F^2 using all 9128 with $R_{int} = 0.0368$ (9771 with $R_{int} = 0.0355$) unique data using SHELXL-93.[19] The final refinements included anisotropic thermal parameters for all non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms ("riding" on idealized positions) and converged to $wR_2 = 7.58\%$ (6.04%) (F^2, all data) and $R_1 = 3.14\%$ (2.70%) (F, 7793 (8053) reflections with $I > 2\sigma(I)$). Crystallographic data for the two compounds is summarized in Table 1.

Results and Discussion

Synthesis. Anaerobic treatment of diphenylditelluride with sodium borohydride in a 3:2 stoichiometry produced deep red solutions of sodium tri(tellurophenolate), $Na[(TeC_6H_5)_3]$ (Na**1**).

$$3(TeC_6H_5)_2 + 2NaBH_4 \rightarrow 2Na[(TeC_6H_5)_3] + 2BH_3 + H_2 \quad (1)$$

Attempts to isolate the product by precipitation resulted in the formation of red powders even when the product was slowly precipitated from reaction mixture at −20 °C. The complex anion was isolated in pure crystalline form, after metathesis with tetraphenylphosphonium bromide or tetraphenylarsonium chloride and filtration of the reaction mixture, as tetraphenylphosphonium tri(tellurophenolate), $[P(C_6H_5)_4]$**1**, or tetraphenylarsonium tri(tellurophenolate), $[As(C_6H_5)_4]$**1**, respectively. Rapid precipitation of the product resulted in coprecipitation of diphenylditelluride as red-orange needles along with small blood-red cubic crystals of the product. In contrast, slow cooling of saturated reaction mixtures to −20 °C provided large blood-red cubic crystals of the salts within 4 months. Alternatively, we treated diphenylditelluride with sodium tellurophenolate in a 1:1 stoichiometry (eq 2) and after metathesis obtained the same product as in the reaction illustrated in eq 1.

Table 1. Crystallographic Data for $[(C_6H_5)_4P]$1 and $[(C_6H_5)_4As]$1

empirical form.	$C_{42}H_{35}PTe_3$	$C_{42}H_{35}AsTe_3$
formula wt (g/mol)	953.47	997.42
space grp (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)
a (Å)	9.4626(1)	9.4734(1)
b (Å)	28.8510(2)	28.8035(2)
c (Å)	13.9600(2)	14.1073(1)
β (deg)	104.177(1)	104.285(1)
V (Å^3)	3695.08(7)	3730.39(5)
Z	4	4
T (K)	180	180
λ (Å)	0.71073	0.71073
ρ(calcd) (g/cm^3)	1.714	1.776
μ (mm^{-1})	2.424	3.239
transmission coeff	0.678−0.990	0.561−0.746
R_1 (on F)[a]	0.0314	0.0270
wR_2 (on F^2)[b]	0.0758[c]	0.0604[d]

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.2508P]$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.2362P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

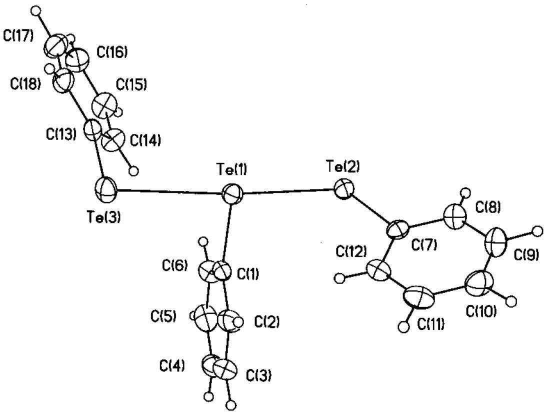

Figure 1. ORTEP plot and numbering scheme of the complex anion $[(TeC_6H_5)_3]^-$, **1**$^-$, of $[P(C_6H_5)_4][(TeC_6H_5)_3]$ with 50% probability ellipsoids.

$$(TeC_6H_5)_2 + NaTeC_6H_5 \rightarrow Na[(TeC_6H_5)_3] \quad (2)$$

Both salts of **1** dissolve readily in ethanol, toluene, and chloroform to provide air-sensitive red solutions. Rapid precipitation of the product from these solvents lead to the precipitation of small blood red cystals of **1**$^-$ and orange needles of diphenylditelluride. These observations suggest the tri(tellurophenolate) anion may partially dissociate in solution to diphenylditelluride and tellurophenolate anion. Several of the large red crystals were dissolved in toluene-d_8, which provided ^{125}Te NMR spectra containing only a broad signal at ca. 374 ppm of poor signal-to-noise ratio, which may be a further indication for a dynamic process in solution.

Crystal Structures of $[P(C_6H_5)_4]$1 and $[As(C_6H_5)_4]$1. Structural analyses of $[P(C_6H_5)_4][(TeC_6H_5)_3]$ and $[As(C_6H_5)_4][(TeC_6H_5)_3]$ by X-ray crystallography revealed discrete anions of $[(TeC_6H_5)_3]^-$ and cations. The cations are not unusual where the central atom is slightly distorted from tetrahedral geometry. Figure 1 shows the structure of the anion, $[(TeC_6H_5)_3]^-$, of $[P(C_6H_5)_4][(TeC_6H_5)_3]$ along with the numbering scheme. The numbering scheme for the anion of $[As(C_6H_5)_4]$**1** is the same. Table 2 contains selected distances and angles

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Table 2. Selected Bond Lengths (Å and Angles (deg) for [Cation][$(TeC_6H_5)_3$], Where [Sm(PZ)] Denotes [Bis[hydrotris(3,5-dimethylpyrazolyl)borate]samarium(III)][15]

	[$P(C_6H_5)_4$]	[$As(C_6H_5)_4$]		[Sm(PZ)]
Te(1)−Te(2)	2.9485(3)	2.9508(2)	Te(2)−Te(3)	2.939(1)
Te(1)−Te(3)	3.0352(3)	3.0406(2)	Te(1)−Te(2)	3.113(1)
Te(1)−C(1)	2.130(3)	2.132(2)	Te(2)−C(37)	2.14(1)
Te(2)−C(7)	2.125(3)	2.121(2)	Te(1)−C(31)	2.136(10)
Te(3)−C(13)	2.123(3)	2.128(3)	Te(3)−C(45)	2.127(11)
C(1)−Te(1)−Te(2)	90.37(7)	90.44(7)	C(37)−Te(2)−Te(3)	89.63(25)
C(1)−Te(1)−Te(3)	90.75(7)	90.86(7)	C(37)−Te(2)−Te(3)	84.96(25)
Te(2)−Te(1)−Te(3)	172.843(8)	172.917(8)	Te(1)−Te(2)−Te(3)	172.92(3)
C(7)−Te(2)−Te(1)	103.94(8)	103.57(7)	C(43)−Te(3)−Te(2)	102.73(25)
C(13)−Te(3)−Te(1)	93.12(7)	92.84(7)	C(31)−Te(1)−Te(2)	91.97(25)

along with those of [bis[hydrotris(3,5-dimethylpyrazolyl)borate]samarium(III)] tri(tellurophenolate).[15] The [$(TeC_6H_5)_3$]$^-$-anion shows a nearly linear chain of three tellurium atoms of tellurophenolate fragments: Te(2)−Te(1)−Te(3) angle is 172.843(8) in [$P(C_6H_5)_4$][$(TeC_6H_5)_3$] and 172.917(8) in [$As(C_6H_5)_4$][$(TeC_6H_5)_3$]. A slightly bent T-shaped geometry is observed for the central three coordinate tellurium atom such that C(1)−Te(1)−Te(2) is ca. 90.4° and C(1)−Te(1)−Te(3) is ca. 90.8°. Noteworthy, this is a rare example of a T-shaped organotellurium compound, where the constituent angles are greater than 90°. An asymmetry exists in the linear chain where Te(1)−Te(2) is ca. 2.95 Å and Te(1)−Te(3) is ca. 3.04 Å. These are considerably longer than in the classical di- and tritellurides. Here the Te−Te distances are ca. 2.7 Å as for example in diphenylditelluride,[20] several tritelluride anions,[21−23] diorganotritellurides[24] and cationic tritellurodiphosphanes.[25] However, comparable Te−Te interactions are observed in several compounds containing *pseudo*-T-shaped Te_3 moieties; for example [$AgTe_7$]$^{3-}$, [$HgTe_7$]$^{2-}$, [Te_6]$^{3-}$, and [([1,3,5-$(CH_3)_3C_6H_5$]$_2$Te)$_2$Te[1,3,5-$(CH_3)_3C_6H_5$]]$^+$.[26−28] For the terminal two-coordinate tellurium atoms in **1**$^-$ an angular geometry is obtained with C(7)−Te(2)-Te(1) of ca. 103.9° (103.6°) and C(13)−Te(3)-Te(1) of ca. 93.1° (92.8°). The lengths of the Te−C-bonds show very little variation and average to 2.126 (2.127) Å with the bond Te(1)−C(1) of the central unit being slightly longer. These agree well with the Te−C bond lengths of related compounds.[29−31]

Concluding Remarks. In a broader context, these observations provide new insights into the process whereby organotelluride anions are prepared by the reduction of diorganoditellurides, which is a very common entry to organotelluride chemistry. Apparently, during this process both the reducing agent and the organotelluride anion as it is prepared can interact with the diorganoditelluride. More intriguing, by analogy to the isoelectronic polyiodide system, is the possibility that [$(TeC_6H_5)_3$]$^-$ is the first member of a new class of compounds consisting of the trimerization of Te−R-units.

Structurally, the central tellurium atom of [$(TeC_6H_5)_3$]$^-$ possesses topological similarities to that in a number of dihalogeno- and dipseudohalogenotellurium(II) complexes.[29,30,32] In addition, this structural motif extents to some organoselenium and even organosulfur compounds.[33−35] A truly interesting aspect of this compound, and one best handled by theoreticians, is the interpretation of the electronic situation in the tellurium chain and must remain unanswered. While the formulation of the reaction according to eq 2 suggests a simple addition of [TeC_6H_5]$^-$ to a $(TeC_6H_5)_2$ molecule as exemplified by the triiodide ion formation from I^- and I_2, the similarity of tri(tellurophenolate) and phenyldithiocyanatotellurate(II)[32] is suggestive of an intramolecular redox reaction.[36] This remarkable feature places the [$(TeC_6H_5)_3$]$^-$-anion in line with analogous organic compounds of the heavier elements of groups 15−17 and xenon, for which hypervalency is discussed.

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Supporting Information Available: Two X-ray crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

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