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Journal of Organometallic Chemistry 642 (2002) 186–190

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and molecular structures of dimeric assemblies of telluronium salts derived from o-$C_6H_4(CH_2TeMe)_2$ and PhMeTe

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Received 6 July 2001; accepted 3 September 2001

Abstract

The ditelluroether, o-$C_6H_4(CH_2TeMe)_2$ reacts with excess MeI in acetone to afford the bis(triorganotelluronium iodide), o-$C_6H_4(CH_2TeMe_2I)_2$, in high yield which has been characterised by ^1H-, $^{13}C\{^1H\}$- and $^{125}Te\{^1H\}$-NMR spectroscopy, microanalysis and X-ray crystallography. The crystal structure of this species reveals a weakly associated dimer, assembled through a series of secondary Te···I interactions to give a pseudo-cubane Te_4I_4 core, involving three-coordinate (pyramidal) iodine and six-coordinate (distorted octahedral) tellurium. The o-xylyl backbone units are oriented across the diagonal of two opposite faces of the cubane. This is the first crystallographic study of a triorganotelluronium halide salt derived from a ditelluroether. The crystal structure of $PhTeMe_2I$ shows a weakly associated μ^2-diiodo bridged dimer, in this case with two-coordinate iodine and five-coordinate, distorted square pyramidal tellurium. The stereochemical activity of the Te-based lone pair is discussed for each system and the structures are compared with other related species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tellurium; Telluronium; X-ray structures; Secondary interactions

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1. Introduction

We have been interested for some time in the synthesis and coordination chemistry of polydentate and macrocyclic telluroether ligands [1–6]. This interest stems mainly from the quite different ligating behaviour of these compounds compared to their sulfur and selenium analogues. Thus, for example, it is clear that telluroethers are significantly better ligands (improved σ-donor capacity) than thio- or seleno-ethers to low valent transition metal centres [7,8]. The syntheses of multidentate telluroethers are generally non-trivial, owing to the high reactivity or instability of the required Te-containing precursors and intermediates. Also, the products themselves tend to be air-sensitive and extremely malodorous oils. It is often more convenient therefore, to characterise new telluroethers as their telluronium derivatives (formed through treatment with dihalogens or with alkyl halides) due to their air-stability. Various classes of organotelluronium halides are known, from species of general formula $RTeX_3$, through R_2TeX_2 (often formed from telluroether R_2Te by the former route) to R_3TeX (from R_2Te and RX). These compounds are often structurally very interesting owing to the frequent occurrence of secondary Te···X interactions which result in dimeric or higher oligomeric assemblies [9]. Recently, in the course of our studies on the synthesis and properties of new telluroethers, we synthesised o-$C_6H_4(CH_2TeMe)_2$ [2]. As part of its characterisation we prepared the MeI derivative, o-$C_6H_4(CH_2TeMe_2I)_2$. In this paper we report the preparation and structural characterisation of this compound, together with the mono-tellurium species $PhTeMe_2I$. While a number of R_3TeX species have been structurally characterised, no crystallographic data have been reported for examples derived from di- or polytelluroethers.

2. Results and discussion

The ditelluroether o-$C_6H_4(CH_2TeMe)_2$ reacts readily with excess MeI in acetone solution to afford the telluronium salt o-$C_6H_4(CH_2TeMe_2I)_2$ in high yield as a

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PII: S0022-328X(01)01229-3

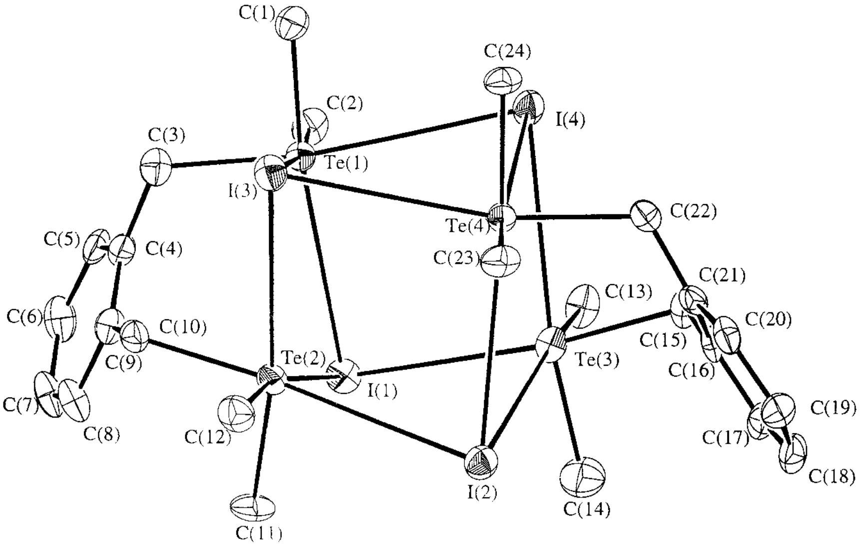

Fig. 1. View of the structure of o-$C_6H_4(CH_2TeMe_2I)_2$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity.

white powder. As for other telluronium salts and unlike the parent telluroether, this compound is air stable both in solution and in the solid state. Microanalytical data, together with ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy, confirms the identity of the product. The ^{125}Te{^{1}H}-NMR spectrum reveals a single resonance at 526 ppm for o-$C_6H_4(CH_2TeMe_2I)_2$, indicative of a single product. This shift is significantly to high frequency of the parent ditelluroether compound (264 ppm), consistent with conversion from formally Te(II) to Te(IV).

In order to establish the structure of this species, a single crystal X-ray analysis was undertaken. The structure shows (Fig. 1, Table 1) that o-$C_6H_4(CH_2TeMe_2I_2)_2$ exists as a weakly associated dimer. This is assembled through an array of intramolecular and intermolecular secondary Te···I interactions (ranging between 3.531(2) and 3.828(2) Å) to give a distorted pseudo-cubane Te_4I_4 core, in which each R_3Te^+ centre interacts with three formally I^- centres in a severely distorted octahedral environment, while each iodo centre is associated with three Te atoms in a distorted pyramidal geometry (there are no Te–I–Te angles greater than 83.3°). The Te···I distances in this compound are similar to the corresponding distances attributed to secondary interactions in other telluronium iodides [10–12]. The distortion of the Te_4I_4 cubane core is reflected in the Te–I–Te and I–Te–I bond angles presented in Table 1. The I–Te–I angles are more obtuse than the C–Te–C angles, possibly indicating the direction of the Te-based lone pair, out of the open triangular face formed by the three iodines. The o-xylyl backbone units lie across two opposite diagonal faces of the cubane core. The Te···Te distances within the o-xylyl bridged units are 3.943 and 3.995 Å, these are similar to the corresponding distances in [MnCl(CO)$_3${o-$C_6H_4(CH_2TeMe)_2$}] and [W(CO)$_4${o-$C_6H_4(CH_2TeMe)_2$}], suggesting that the o-xylyl unit provides a fairly rigid inter-tellurium linkage [2]. Interestingly, the species Et_3TeX (X = Cl or Br) also adopt distorted pseudo-cubane arrangements, although in these species the cubane core is derived from weakly associated tetramers (Te···Cl = 3.448(4) Å; Te···Br = 3.564 Å) [10,11]. In contrast, Me_3TeI is an ion-paired

Table 1
Selected bond lengths (Å) and angles (°) for [o-$C_6H_4(CH_2TeMe_2I)_2$]·1/2CHCl$_3$

Bond lengths			
I(1)–Te(1)	3.828(2)	Te(1)–C(1)	2.12(1)
I(1)–Te(2)	3.780(1)	Te(1)–C(2)	2.12(1)
I(1)–Te(3)	3.548(2)	Te(1)–C(3)	2.18(1)
I(2)–Te(2)	3.572(3)	Te(2)–C(10)	2.20(1)
I(2)–Te(3)	3.768(1)	Te(2)–C(11)	2.14(1)
I(2)–Te(4)	3.787(1)	Te(2)–C(12)	2.13(1)
I(3)–Te(1)	3.779(1)	Te(3)–C(13)	2.13(1)
I(3)–Te(2)	3.652(1)	Te(3)–C(14)	2.12(1)
I(3)–Te(4)	3.595(3)	Te(3)–C(15)	2.19(1)
I(4)–Te(1)	3.531(2)	Te(4)–C(22)	2.18(1)
I(4)–Te(3)	3.647(2)	Te(4)–C(23)	2.10(1)
I(4)–Te(4)	3.686(1)	Te(4)–C(24)	2.14(1)
Bond angles			
Te(1)–I(1)–Te(2)	62.43(2)	Te(1)–I(1)–Te(3)	80.48(5)
Te(2)–I(1)–Te(3)	80.43(3)	Te(2)–I(2)–Te(3)	80.29(2)
Te(2)–I(2)–Te(4)	75.04(4)	Te(3)–I(2)–Te(4)	63.85(2)
Te(1)–I(3)–Te(2)	64.07(2)	Te(1)–I(3)–Te(4)	76.16(2)
Te(2)–I(3)–Te(4)	76.47(4)	Te(1)–I(4)–Te(3)	83.28(5)
Te(1)–I(4)–Te(4)	78.13(3)	Te(3)–I(4)–Te(4)	66.02(2)
I(1)–Te(1)–I(3)	113.70(2)	I(1)–Te(1)–I(4)	91.07(5)
I(3)–Te(1)–I(4)	97.74(2)	I(1)–Te(2)–I(2)	92.27(3)
I(1)–Te(2)–I(3)	117.95(2)	I(2)–Te(2)–I(3)	99.33(4)
I(1)–Te(3)–I(2)	92.86(2)	I(1)–Te(3)–I(4)	93.86(5)
I(2)–Te(3)–I(4)	114.73(3)	I(2)–Te(4)–I(3)	96.48(4)
I(3)–Te(4)–I(4)	98.31(3)		

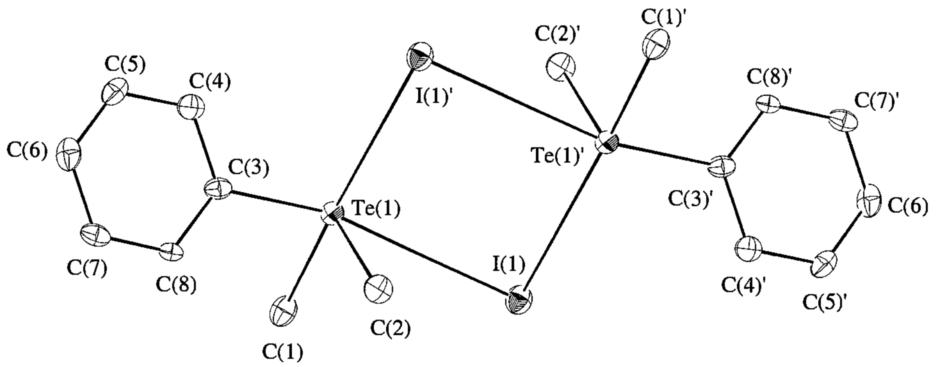

Fig. 2. View of the structure of [$PhTeMe_2I$] with numbering scheme adopted. Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity.

monomer (Te···I = 3.702 Å), [12] while Et_3TeI is a weakly associated dimer with two μ^2-bridging iodo ligands (Te···I = 3.813(5), 3.861(5) Å) [10].

In light of the unusual pseudo-cubane structure observed for the iodo-compound in our work, which also constitutes the first structural characterisation of a bis(triorganotelluronium) salt derived from a ditelluroether, we were interested to investigate whether other related species would exhibit similar structural features and the role of the linking unit between the Te centres. We therefore, attempted to crystallise the MeI derivatives of *o*-$C_6H_4(TeMe)_2$, $MeTe(CH_2)_3TeMe$ and $MeC(CH_2TeMe)_3$, all of which have been spectroscopically characterised previously. However, owing to the very poor solubilities of these telluronium salts in common solvents, we were unable to obtain suitable crystals of any of these, even from carefully layered acetone solutions of MeI and the telluroether, which deposited only fine microcrystalline powders. However, we did obtain crystals of $PhTeMe_2I$, prepared by layering neat MeI onto PhTeMe. This compound was characterised by ^1H-, $^{13}C\{^1H\}$- and $^{125}Te\{^1H)$-NMR (565 ppm) spectroscopy and microanalytical data. The crystal structure of $PhTeMe_2I$ confirms (Fig. 2Table 2) the presence of the tellurium(IV) centre, giving a $PhTeMe_2^+$ unit. This is then associated with a similar telluronium cation unit through weak, secondary interactions with two formally I^- centres, giving a centrosymmetric μ^2-diiodo bridged dimer with Te···I distances of 3.6591(7) and 3.7584(8) Å. Each Te atom is in a distorted square pyramidal environment derived from three R groups and two iodine atoms, with the Te-based lone pair stereochemically active and occupying the void. The iodine atoms are two-coordinated, unlike those in *o*-$C_6H_4(CH_2TeMe_2I)_2$ above, and the dimeric structure resembles that of Et_3TeI discussed above [12].

These results show that the structure of *o*-$C_6H_4(CH_2TeMe_2I)_2$ is quite different from those seen for the simple R_3TeI (R = Me or Et). This may be derived from the presence of the *o*-xylyl inter-tellurium linkage. As synthetic routes to a wider range of polydentate and macrocyclic telluroethers develop, we can anticipate that the telluronium halide derivatives of these will exhibit a range of unusual structural motifs.

3. Experimental

Infrared spectra were recorded as CsI discs using a Perkin–Elmer 1710 spectrometer over the range 4000–200 cm^{-1}. Mass spectra were run by positive ion electrospray (MeCN solution) using a VG Biotech platform. ^1H-NMR spectra were recorded in $CDCl_3$ using a Bruker AM300 spectrometer. $^{13}C\{^1H\}$- and $^{125}Te\{^1H\}$-NMR spectra were recorded in CH_2Cl_2 or Me_2SO containing ca. 10–15% $CDCl_3$ using a Bruker DPX400 spectrometer operating at 100.6 or 126.3 MHz, respectively and are referenced to tetramethylsilane and external neat Me_2Te, respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service.

Table 2
Selected bond lengths (Å) and angles (°) for [$PhTeMe_2I$]

Bond lengths	
I(1)′–Te(1)	3.7584(8)
I(1)–Te(1)	3.6591(7)
Te(1)–C(1)	2.128(8)
Te(1)–C(2)	2.132(9)
Te(1)–C(3)	2.132(7)
Bond angles	
Te(1)–I(1)–Te(1)′	78.68(2)
I(1)–Te(1)–I(1)′	101.32(2)
I(1)–Te(1)–C(1)	78.7(3)
I(1)–Te(1)–C(2)	173.9(2)
I(1)–Te(1)–C(3)	85.2(2)
I(1)–Te(1)–C(1)	77.3(2)
I(1)–Te(1)–C(2)	78.8(2)
I(1)–Te(1)–C(3)	168.3(2)
C(1)–Te(1)–C(2)	95.4(3)
C(1)–Te(1)–C(3)	94.7(3)
C(2)–Te(1)–C(3)	93.7(3)

Table 3
Crystallographic parameters

Complex	$[o\text{-}C_6H_4(CH_2TeMe_2I)_2]\cdot 1/2CHCl_3$	$[PhTeMe_2I]$
Formula	$C_{12.5}H_{15.5}Cl_{1.5}I_2Te_2$	$C_8H_{11}ITe$
Formula weight	732.99	361.68
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	18.05(2)	8.9319(3)
b (Å)	13.34(1)	9.9545(4)
c (Å)	33.907(9)	11.7192(4)
β (°)	90.17(4)	104.201(2)
U (Å^3)	8162.5(1)	1010.14(6)
Z	16	4
μ(Mo–K$_\alpha$) (cm^{-1})	60.69	59.37
Unique observed reflections	7532	2195
Observed reflections with $[I_o > 2\sigma(I_o)]$	4899	1580
Parameters	325	91
R [a]	0.037	0.040
R_w [b]	0.043	0.044

[a] $R = \Sigma (|F_{obs}|_i - |F_{calc}|_i)/\Sigma |F_{obs}|_i$.

[b] $R_w = [\Sigma w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\Sigma w_i|F_{obs}|_i^2]$.

3.1. Preparations

3.1.1. $[o\text{-}C_6H_4(CH_2TeMe_2I)_2]$

To a degassed acetone solution of $o\text{-}C_6H_4(CH_2TeMe)_2$ (0.10 g, 0.26 mmol) was added an acetone solution (10 cm^3) containing excess MeI. The mixture was stirred at room temperature for 2 h, the resultant white powder being filtered and washed with diethyl ether. Yield 0.15 g, 88%. Calc. for $C_{12}H_{20}I_2Te_2$: C, 21.4; H, 3.0%. Found: C, 20.9; H, 2.6. ^{1}H-NMR: δ 7.25 (m, 4H), 4.68 (s, 2H), 3.96 (s, 2H), 1.57 (s, 12H) ppm. ^{13}C{^{1}H}-NMR: δ 134.4, 132.2, 129.2, 30.8, 12.8 ppm. ^{125}Te{^{1}H}-NMR: δ 526 (s) ppm.

3.2. $[PhTeMe_2I]$

Procedure as above. White powder. Yield 94%. Calc. for $C_8H_{11}TeI_1$. C: 26.6; H, 3.1%. Found: C, 26.1; H, 3.2%. ^{125}Te{^{1}H}-NMR: δ 565 ppm (s) (lit. 550—Ref. [4]).

3.3. X-ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 3. Colourless crystals of $[o\text{-}C_6H_4(CH_2TeMe_2I)_2]\cdot 1/2CHCl_3$ were grown by infusion of diethyl ether into a solution of the compound in CHCl$_3$, while those of [PhTeMe$_2$I] were obtained by dropwise addition of neat MeI to PhMeTe. Data collection for the former used a Rigaku AFC7S four-circle diffractometer ($T = 150$ K), while the latter used an Enraf Nonius Kappa CCD diffractometer ($T = 120$ K) and with graphite-monochromated Mo–K$_\alpha$ X-radiation ($\lambda = 0.71073$ Å). Although the programme indicated an orthorhombic cell for $[\{o\text{-}C_6H_4(CH_2TeMe_2I)_2\}_2]\cdot 1/2CHCl_3$, the Laue check failed and a precession simulation did not show the mirror symmetry which would make the cell orthorhombic, hence the data were collected and the structure solved and refined assuming a monoclinic cell. Otherwise structure solution and refinement were routine [13–16]. Selected bond lengths and angles are given in Tables 1 and 2.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166604 and 166605 for compounds $[o\text{-}C_6H_4(CH_2TeMe_2I)_2]\cdot 1/2CHCl_3$ and [PhTeMe$_2$I] 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 www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the EPSRC for support and Professor M.B.H. for access to the Kappa CCD diffractometer.

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