Synthesis, Structure and Selective Chlorination of Bis(*N*-borane-dimethylaminopropyl)telluride¹⁾

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Abstract. The reaction of Te powder, NaBH₄ and Me₂N(CH₂)₃Cl·HCl provided the title compound [H₃BNMe₂-(CH₂)₃]₂Te (1), whose selective chlorination with SO₂Cl₂ lead to the formation of [ClH₂BNMe₂(CH₂)₃]₂TeCl₂ (2) and [Cl₃BNMe₂(CH₂)₃]₂TeCl₂ (3), respectively. Compounds 1-3 were

characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction.

Keywords: Tellurium; Boron; NMR spectroscopy; Crystal structure

Introduction

Hypercoordinate organometallic compounds comprising the potentially intramolecularly coordinating dimethylaminopropyl group are known for many of the heavier *p*-block elements including Sn, Pb and Sb [1-5]. In an effort to synthesize related hypercoordinate Te complexes we attempted the preparation of bis(dimethylaminopropyl)telluride, but only obtained a persistent *N*-borane adduct thereof, whose selective chlorination with SO₂Cl₂ has been studied in greater detail.

Results and Discussion

The one-pot reaction of Te powder, NaBH₄ and $Me_2N(CH_2)_3Cl$ ·HCl in aqueous THF solution afforded bis(*N*-borane-dimethylaminopropyl)telluride, [H₃BNMe₂-(CH₂)₃]₂Te (1), as pale yellow crystalline solid in 59 % yields (Scheme 1). The formation of 1 can be rationalized by the reduction of the Te powder by NaBH₄ to give Na₂Te, which twice underwent nucleophilic replacement of a Cl atom attached to α -C atom of a dimethylaminopropyl group, while BH₃, the by-product of the reduction, formed a coordinative bond with the N atoms. The molecular structure of 1 is shown in Figure 1. Selective bond parameters are collected in Table 1 while crystal and refinement data are listed

* Prof. Dr. Jens Beckmann Institut für Chemie und Biochemie Freie Universität Berlin Fabeckstraße 34–36 D-14195 Berlin Tel. Int. code +49 (0)30-838-54697 Fax. Int. code +49 (0)30-838-52440 Email: beckmann@chemie.fu-berlin.de in Table 2. The two *N*-borane-dimethylaminopropyl groups are crystallographically independent. The Te-C and B-N bond lengths are equal within experimental error and in average 2.160(3) and 1.623(4) Å, respectively. The smallest intermolecular Te···Te distance at 4.040(2) Å is close to the sum of the van der Waals radii (4.12 Å). Bis(*N*-borane-dimethylaminopropyl)telluride 1 is very soluble in most organic solvents. The ¹¹B and ¹²⁵Te NMR spectrum (CDCl₃) of 1 gives rise to resonances at δ –10.3 and 262.9, respectively.



Scheme 1

Attempts at removing borane from $[H_3BNMe_2-(CH_2)_3]_2$ Te (1) by oxidation with H_2O_2 or protolysis with concentrated HCl solution failed and led to complete disintegration of the material. In case of the protolysis the



¹⁾ This paper contains parts of the Bachelor thesis of Nicolai Schnurbusch.



Figure 1 Molecular structure of $[H_3BNMe_2(CH_2)_3]_2$ Te (1) showing 40 % probability displacement ellipsoids and the atom numbering.

formation of elemental Te was noticed, while all other decomposition products remained unaccounted for.

The chlorination of $[H_3BNMe_2(CH_2)_3]_2$ Te (1) with two equivalents of SO₂Cl₂ produced a complex reaction mixture, from which only one product, namely [ClH₂BNMe₂(CH₂)₃]₂TeCl₂ (2), was isolated by fractional crystallisation. When the same reaction was repeated with three equivalents of SO₂Cl₂ the yield of 2 improved from 12 % to 63 % (Scheme 1). When the chlorination of 1 was repeated with seven equivalents of SO₂Cl₂ all B-H bonds were replaced by B-Cl bonds and [Cl₃BNMe₂(CH₂)₃]₂TeCl₂ (3) was obtained in 88 % yield (Scheme 1). It worth mentioning that the halogenation of simple borane alkylamine adducts by a number of different reagents was reported pre-

Table 1Selected bond parameters [Å, °] of 1-3.

	1.0.5 toluene	2	3
Te1-C10	2.163(3)	2.142(3)	2.146(9)
Te1-C20	2.157(3)	2.134(3)	2.143(1)
Te1-Cl1		2.569(3)	2.536(3)
Te1-Cl2		2.459(3)	2.443(3)
Te1…Cl1a		3.382(2)	3.702(2)
B1-N1	1.626(4)	1.615(4)	1.64(2)
B2-N2	1.619(4)	1.611(4)	1.62(2)
B1-Cl10		1.880(4)	1.83(1)
B1-Cl11			1.84(1)
B1-C12			1.83(1)
B2-C120		1.880(4)	1.83(1)
B2-Cl21			1.81(1)
B2-Cl22			1.84(1)
C10-Te1-C20	97.2(1)	98.9(1)	90.0(4)
C10-Te1-Cl1		86.6(1)	89.5(3)
C10-Te1-Cl2		91.5(1)	89.5(3)
C20-Te1-Cl1		87.1(1)	85.1(3)
C20-Te1-Cl2		90.3(1)	89.8(3)
Cl1-Te1-Cl2		176.51(3)	174.8(2)

viously [6]. No evidence was found that an excess of SO_2Cl_2 causes cleavage of Te-C bonds, which contrasts the previous observation that the exhaustive halogenation of dialkyltellurids produces mixtures of dialkyltellurium dihalides and alkyltellurium trihalides [7]. To the best of our knowledge not a single example of a haloborane alkylamine adduct has yet been characterized by X-ray crystallography. The molecular structure of **2** and **3** are shown in Figures 2 and 3. Selective bond parameters are collected in Table 1, whe-

Table 2 Crystal data and structure refinement of 1-3.

	1.0.5 toluene	2	3	
Formula	$C_{27}H_{60}B_4N_4Te_2$	$C_{10}H_{28}B_2Cl_4N_2Te$	C ₁₀ H ₂₄ B ₂ Cl ₈ N ₂ Te	
Formula weight, g mol ^{-1}	739.25	467.36	605.13	
Crystal system	monoclinic	triclinic	triclinic	
Crystal size, mm	0.5 imes 0.1 imes 0.05	0.3 imes 0.1 imes 0.05	0.1 imes 0.05 imes 0.05	
Space group	$P2_1/c$	P-1	P-1	
a, Å	16.312(3)	6.541(5)	6.4856(10)	
b, Å	5.9780(12)	11.073(11)	12.4030(19)	
<i>c</i> , Å	20.588(4)	14.167(16)	14.228(3)	
α , °	90	81.75(8)	94.728(14)	
β , °	111.822(4)	81.81(8)	99.691(14)	
v. °	90	76.28(7)	98.937(13)	
V, Å ³	1863.7(6)	980.2(17)	1107.5(3)	
Z	2	2	2	
$\rho_{\rm calcd}$, Mg m ⁻³	1.317	1.584	1.815	
T, K	173	200	200	
μ (Mo K α), mm ⁻¹	1.585	2.052	2.305	
<i>F</i> (000)	748	464	592	
θ range, deg	1.34 to 30.50	0.90 to 29.17	3.23 to 29.19	
Index ranges	$-23 \le h \le 22$	$-8 \le h \le 8$	$-8 \le h \le 8$	
	$-8 \le k \le 8$	$-15 \le k \le 13$	$-16 \le k \le 16$	
	$-29 \le 1 \le 23$	$-16 \le l \le 19$	$-17 \le l \le 19$	
No. of reflns collected	21404	7613	8388	
Completeness to θ_{max}	99.9 %	89.7 %	89.5 %	
No. indep. reflns	5694	4743	5354	
No. obsd reflns with $(I \ge 2\sigma(I))$	4472	4159	1926	
No. refined params	205	188	208	
GooF (F^2)	1.128	1.020	0.647	
$R_1(F)(I \ge 2\sigma(I))$	0.0374	0.0272	0.0597	
wR_2 (F^2) (all data)	0.1094	0.0697	0.1047	
$(\Delta/\sigma)_{\rm max}$	0.003	0.002	< 0.001	
Largest diff peak/hole, e $Å^{-3}$	3.801 / -1.051	0.567 / -1.151	0.647 / -0.996	



Figure 2 Molecular structure and supramolecular association of $[ClH_2BNMe_2(CH_2)_3]_2TeCl_2$ (2) showing 40 % probability displacement ellipsoids and the atom numbering (Symmetry code used to generate equivalent atoms: a = 1-x, 2-y, 2-z).



Figure 3 Molecular structure and supramolecular association of $[Cl_3BNMe_2(CH_2)_3]_2TeCl_2$ (3) showing 40 % probability displacement ellipsoids and the atom numbering. (Symmetry code used to generate equivalent atoms: a = 1-x, 1-y, 1-z).

reas crystal and refinement data are listed in Table 2. The average Te-C bond length of **2** and **3** being 2.137(8) Å is somewhat shorter that in the parent compound **1**. The mean B-N bond length of **2** and **3** being 1.615(4) Å and 1.630(16) Å, respectively, are comparable with that of **1**. The two Te-Cl bond lengths of **2** (2.569(3) and 2459(3) Å) and **3** (2.536(3) and 2.443(3) Å) are somewhat different due

to the involvement of the Cl1 atom into intermolecular secondary Te···Cl interactions. In the crystal lattice the individual molecules of 2 and 3 form centrosymmetric dimers. The secondary Te…Cl bond length of 2 being 3.382(2) Å is shorter than that of **3** being 3.702(2) Å. The solubility of **2** and 3 in organic solvents differs substantially. Compound **2** is rather soluble in CH_2Cl_2 and diethyl ether, but only poorly soluble in CHCl₃. Compound 3 is only poorly soluble in the same solvents, but readily dissolves in acetone. The ¹²⁵Te NMR chemical shifts of **2** and **3** are δ 862.9 (CD₂Cl₂) and 910.3 (acetone-d₆), respectively. Compound 2 gives rise to a very broad ¹¹B NMR resonance at δ -3.5, whereas the corresponding ¹¹B NMR signal of 3 at δ 11.0 was sharp. It is worth mentioning that the ¹H resonances of the borane moieties were detected neither for 1 nor 2. However, the presence of B-H bonds was unambiguously confirmed by IR spectra (KBr), which revealed indicative signals between \tilde{v} 2266–2368 cm⁻¹ for 1 and \tilde{v} 2471-2386 cm⁻¹ for 2 that were assigned to symmetric and asymmetric B-H stretching vibrations [8].

The attempted removal of the chloroborane moieties by the base hydrolysis of 2 and 3 failed and produced only ill-defined products.

Experimental Section

General. Te powder, NaBH₄ and Me₂N(CH₂)₃Cl·HCl were commercially available and used as received. NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and are referenced against Me₄Si, Me₂Te and BF₃·Et₂O. IR spectra were recorded with a 5 SXC Nicolet DTGS FT-IR spectrometer. Microanalyses were obtained from a Vario EL elemental analyser.

Synthesis of [H₃BNMe₂(CH₂)₃]₂Te (1). To a magnetically stirred suspension of Te powder (3.23 g, 25.3 mmol) and NaOH (2.23 g, 55.8 mmol) in THF (44 mL) and water (440 µL), solid NaBH₄ (2.11 g, 55.8 mmol) was slowly added at 0 °C against a gentle flow of argon. After 2 h, the mixture was allowed to warm to room temperature and stirred for 3 h. Then, a solution of 3-dimethylaminopropylchloride hydrochloride (7.98 g, 50.6 mmol) in H₂O (50 mL) was slowly added. The reaction mixture was stirred overnight at room temperature and was then diluted with aqueous NaOH solution (0.2 M, 200 ml). The product was extracted with $CHCl_3$ (2 × 100 mL) The combined organic layers were washed with water (2 \times 50 mL), saturated NaCl solution (2 \times 50 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residual oil was diluted in CHCl₃ (20 mL). Addition of toluene (40 mL) induced crystallisation of 1.0.5 toluene as pale yellow needles. Attempts to crystallize the product from other solvents failed. The co-crystallized toluene was removed in high vacuum to give 1 as pale yellow solid (4.91 g, 59 %, mp. 83 °C). Anal. Calcd. for C₁₀H₃₀B₂N₂Te (327.62): C, 36.66; H, 9.23; N, 8.55; Found: C, 36.52; H, 9.12; N, 8.38 %.

¹**H-NMR** (CDCl₃) δ = 2.8 (4H, t; NC*H*₂), 2.6 (4H, t; TeC*H*₂), 2.6 (12H, s; N(*CH*₃)₂), 2.2 (4H, m; CH₂CH₂CH₂). ¹³**C-NMR** (CDCl₃) δ = 65.7 (N*C*H₂), 51.3 (N(*C*H₃)₂), 26.0 (CH₂CH₂CH₂), - 1.3 (¹*J*(¹³C-¹²⁵Te) 161 Hz; Te*C*H₂). ¹¹B-NMR (CDCl₃) δ = -10.3. ¹²⁵Te-NMR (CDCl₃) δ = 262.9. **IR**: \tilde{v} (B-H) = 2368 s, 2355 (shoulder), 2312 s, 2289 m, 2266 s cm⁻¹.

Synthesis of [CIH₂BNMe₂(CH₂)₃]₂TeCl₂ (2). A Schlenk flask connected with a gas outlet was charged with 1 (600 mg, 1.83 mmol),

dissolved in CHCl₃ (20 mL) and cooled to 0 °C. Under vigorous stirring, a slight excess of SO₂Cl₂ (776 mg, 5.75 mmol) was slowly added *via* a syringe. After 15 min, the mixture was allowed to warm to room temperature and stirring was continued for 60 min. The colourless precipitate was collected and dissolved in CH₂Cl₂ (20 mL). A very small amount of insoluble material was filtered off. Hexane was added (30 mL) and the solvent was slowly evaporated to yield **2** as colourless crystals (0.54 g, 63 %, mp. 119 °C). Anal. Calcd. for C₁₀H₂₈B₂N₂Cl₄Te (467.41): C, 25.70; H, 6.04; N, 5.99; Found: C, 25.65; H, 5.77; N, 5.75 %.

¹**H-NMR** (acetone-d₆) δ = 3.9 (4H, t; NC*H*₂), 3.6 (4H, t; TeC*H*₂), 3.2 (12H, s; N(*CH*₃)₂), 3.1 (4H, m; CH₂C*H*₂CH₂). ¹³**C-NMR** (CD₂Cl₂) δ = 60.0 (NC*H*₂), 48.0 (N(*CH*₃)₂), 42.5 (TeC*H*₂), 19.6 (CH₂C*H*₂C*H*₂). ¹¹**B-NMR** (CD₂Cl₂) δ = -3.5 (very broad). ¹²⁵**Te-NMR** (CD₂Cl₂) δ = 862.9. **IR**: \tilde{v} (B-H) = 2471 (shoulder), 2453 s, 2386 m cm⁻¹.

Synthesis of $[Cl_3BNMe_2(CH_2)_3]_2TeCl_2$ (3). A Schlenk flask connected with a gas outlet was charged with 1 (500 mg, 1.53 mmol), dissolved in CH₂Cl₂ (15 mL) and cooled to 0 °C. Under vigorous stirring, a slight excess of SO₂Cl₂ (1.65 g, 12.2 mmol) was slowly added *via* a syringe. After 15 min, the mixture was allowed to warm to room temperature and stirring was continued for 60 min. The colourless precipitate was collected and dissolved in acetone (20 mL). A very small amount of insoluble material was filtered off. Ethanol was added (30 mL) and the solvent was slowly evaporated to yield **3** as colourless crystals (0.82 g, 88 %, mp. 140 °C (dec.)). Anal. Calcd. for C₁₀H₂₄B₂N₂Cl₈Te (605.19): C, 19.85; H, 4.00; N, 4.63; Found: C, 19.98; H, 3.92; N, 4.58 %.

¹**H-NMR** (acetone-d₆) δ = 4.9 (4H, t; NCH₂), 4.6 (4H, t; TeCH₂), 4.2 (12H, s; N(CH₃)₂), 4.1 (4H, q; CH₂CH₂CH₂). ¹³**C-NMR** (acetone-d₆) δ = 59.5 (NCH₂), 45.6 (N(CH₃)₂), 40.6 (TeCH₂), 19.6 (CH₂CH₂CH₂). ¹¹**B-NMR** (acetone-d₆) δ = 11.0. ¹²⁵**Te-NMR** (acetone-d₆) δ = 910.3.

X-ray crystallography

Intensity data were collected on Bruker SMART 1000 CCD area detector (1) and a STOE IPDS 2T area detector (2, 3), equipped with graphite-monochromated Mo-K α (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [9]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002 [10]. Full-matrix least-squares

refinements on F^2 , using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. The co-crystallized toluene molecule of 1.0.5 toluene was disordered over two positions. H atoms attached to C atoms were included in geometrically calculated positions for all structures using a riding model and were refined isotropically. H atoms attached to B atoms were located in the last refinement cycle and refined isotropically. Figures were created with DIAMOND [11]. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 641951-641953(1-3). 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; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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