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3-(Phenyltellanyl)propylammonium chloride and its reactions

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ABSTRACT

$PhTe(CH_2)_3NH_3Cl$ (**1**) is readily converted to $[PhTeX_2(CH_2)_3NH_3]X$ (X = Cl: **2**, X = Br: **3**) either by reactions with X_2 (X = Cl, Br) or by air oxidation after treatment with concentrated HX (X = Cl, Br). Similar reactions with HI or I_2 resulted in the formation of unattractive viscous oils only.

Solutions of compound **1** are stable on air under slightly acidic conditions, but undergo a reaction with CO_2 from the air under formation of the corresponding carbamate, when aqueous ammonia or NEt_3 are added. The reaction is more efficient when CO_2 is bubbled through the solution. The ion pair $[PhTe(CH_2)_3NH_3]^+[PhTe(CH_2)_3NHCO_2]^-$ is formed from such solutions in high yields. The products have been studied spectroscopically and by X-ray diffraction.

1. Introduction

The coordination chemistry of tellurium-containing ligands has been stimulated by the use of so-called hybrid ligands, which contain in addition of the tellurium donor site other coordinating units. They frequently contain 'hard' donor atoms such as nitrogen or oxygen, which extends the coordination ability of such ligand systems and allows the formation of stable complexes with a large number of metal ions [1–5]. Tellurated alkylamines are important building blocks for the synthesis of such ligands, since they allow access e.g. to *Te*,*N*,*O*- or *Te*,*N*,*N*-containing chelators. Some of them are shown in Chart 1.

The synthesis of 3-(aryltellanyl)propylamines from appropriate diarylditellurides, $NaBH_4$ and 3-chloropropylamine hydrochloride is well-described [6], but relatively less is known about their stability under certain conditions, which are relevant for their use as building blocks for the synthesis of hybrid ligand systems. Air-oxidation of the tellurium atoms of $3\text{-}\{(4\text{-}MeOC_6H_4)Te\}(CH_2)_3NH_2$ and $2\text{-}\{(4\text{-}MeOC_6H_4)Te\}(CH_2)_2NH_2$ was observed, when the compounds were poured into HCl for the formation of the corresponding hydrochlorides. While the reaction occurred rapidly in a MeOH/5 M HCl mixture for the ethylene derivative, the conversion of the propyleneamine required 11 M HCl and a reaction time of 3–4 h [7]. These findings lead us to further experiments about the stability of $[PhTe(CH_2)_3NH_3]Cl$ (**1**) and its conversion into the corresponding tellurium(IV) dihalides.

2. Results and discussion

2.1. Reactions of 1 with HX and X_2 (X = Cl, Br, I) and molecular structures of the products

The treatment of solutions of $PhTe(CH_2)_3NH_2$ in methanol with 6 M solutions of HCl or HBr on air results in the oxidation of the tellurium(II) compound and the precipitation of the tellurium(IV) propylammonium salts $[PhTeCl_2(CH_2)_3NH_3]^+Cl^-$ (**2**) and $[PhTeBr_2(CH_2)_3NH_3]^+Br^-$ (**3**) (Scheme 1). The colorless (chloride) or pale yellow (bromide) products are obtained by this simple procedure in reasonable yields as has been reported previously for the chlorides $[3\text{-}\{(4\text{-}MeOC_6H_4)TeCl_2\}(CH_2)_3NH_3]^+Cl^-$ and $[2\text{-}\{(4\text{-}MeOC_6H_4)TeCl_2\}(CH_2)_2NH_3]^+Cl^-$ [7]. The reactions are completed within a few minutes with the unsubstituted phenyltellurides. With respect to the relatively long reaction time reported in [8], this fact suggests an influence not only of the lengths of the alkyl chain, but also of the nature of the substitution of the aryl ring on the reactivity of the tellurium atom. It is also remarkable that the reaction with HBr ensures a complete halide exchange and forms pure **3** within a short time. Alternatively, the oxidation products **2** and **3** can be obtained by the 'classical' reactions using Cl_2 or Br_2 as oxidants. The yields of the later routes are somewhat better for both halides.

The progress of the oxidation can readily be checked by NMR spectroscopy. The ^{125}Te NMR signal shifts upon oxidation from 472 ppm in the starting material **1** to 968 ppm for the dichloride **2** and 939 ppm for the dibromide **3**, respectively. Similar downfield shifts can be observed for the ^{13}C NMR signals of the $TeCH_2$ groups and the *ipso* carbon atoms of the phenyl rings. The corresponding

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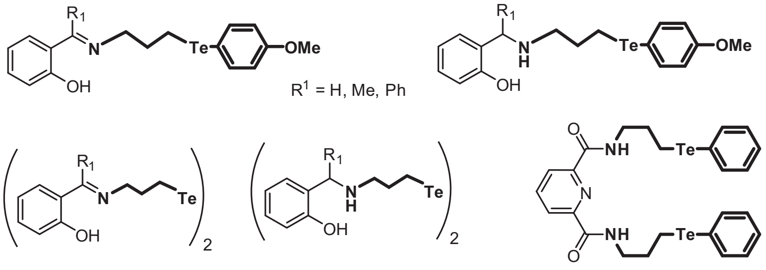
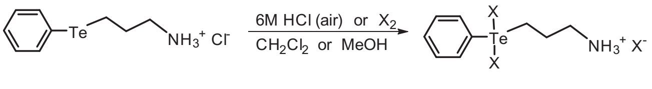


Chart 1. Representative ligands with 3-(phenyltellanyl)propylamine derivatives.



1 **2** (X = Cl) **3** (X = Br)

Scheme 1. Syntheses of compounds **2** and **3**.

signals, which appear in the spectrum of the tellurium(II) compound at 5.0 and 111.6 ppm [6], are shifted to 24.4 and 129.8 ppm in **2** or 25.2 and 127.8 ppm in **3**.

Positive mode electron spray mass spectra show intense peaks for fragments, which are formed by the abstraction of one or two HX molecules, while the molecular ions cannot be detected (compound **2**) or only with a very low intensity (compound **3**).

The molecular structures of the two ammonium salts are virtually identical. For this reason, only that of compound **3** is shown in Fig. 1. Selected bond lengths and angles of both compounds are summarized in Table 1. The molecular labeling scheme of **3** has also been adopted for the chloride. The first coordination spheres of the tellurium atoms show the typical V-shaped arrangement of the substituents. The Te–C bond lengths are consistent with values reported before for Te–C(aryl) and Te–C(alkyl) bonds [7–9]. Also the Te–Cl and Te–Br bonds are unexceptional. The hydrogen atoms of the ammonium group establish weak hydrogen bonds between 2.502 Å and 2.611 Å to the surrounding Br^- counter ions. A similar situation is also found in the structure of **2**, where H···Cl bonds between 2.313 Å and 2.805 Å are found. Further intermolecular contacts, which complete the coordination sphere of the tellurium atoms of both compounds to a pseudo octahedron will be discussed later.

While reactions of **1** with HCl, HBr, Cl_2 and Br_2 gave the tellurium(IV) dihalides in satisfactory yields, we were not able to isolate the corresponding oxidation products during reactions of **1** with HI or I_2. All our attempts ended in the formation of unattractive brown–black (HI) or yellow–orange (I_2) oily products. This finding is somewhat surprising, since a large number of arylalkyl tellurides have been oxidized by iodine before in excellent yields [10,11].

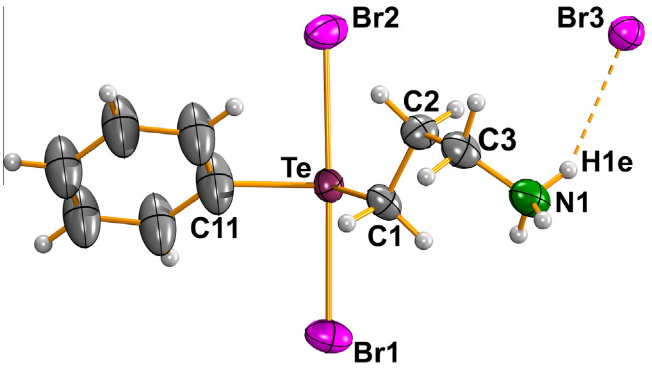


Fig. 1. Ellipsoid representation of the molecular structure of **3** [19]. Thermal ellipsoids represent 50% probability.

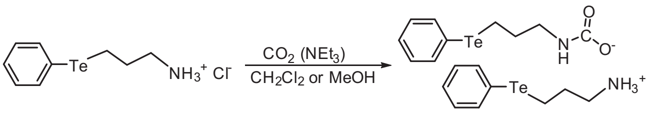
Table 1
Selected bond lengths (Å) and angles (°) in **2** (X = Cl) and **3** (X = Br).

	2	**3**		**2**	**3**
Te–C11	2.117(1)	2.108(6)	Te–X1	2.490(2)	2.653(1)
Te–C1	2.145(7)	2.158(5)	Te–X2	2.513(2)	2.686(1)
C1–C2	1.52(1)	1.516(8)	C3–N1	1.48(1)	1.486(9)
C2–C3	1.52(1)	1.514(8)			
C11–Te–C1	93.4(5)	98.0(3)	C1–Te–X1	86.0(2)	87.1(2)
C11–Te–X1	85.0(6)	92.7(3)	C1–Te–X2	93.8(2)	94.7(2)
C11–Te–X2	93.8(2)	86.7(3)	X1–Te–X2	177.9(1)	178.17(3)

2.2. Reactions of **1** with CO_2

Exposure of solutions of **1** to air results in the formation of reasonable amounts of the ion pair $[PhTe(CH_2)_3NH_3]^+[PhTe(CH_2)_3NHCOO]^-$ (**4**). A similar reaction was observed when solid samples of **1** were stored on air for several months: The colorless solid slowly converted into a viscous oil, from which finally colorless single crystals of **4** could be isolated. The straightforwardness of the observed reactions motivated us to study them more in detail.

A more rational and rapid synthesis of **4** was found with the treatment of solutions of **1** in methanol or CH_2Cl_2, which contain NEt_3 as supporting base, with CO_2 gas (Scheme 2). After bubbling CO_2 through such solutions, the conversion of 50% of $[PhTe(CH_2)_3NH_3]^+$ into $[PhTe(CH_2)_3NHCOO]^-$ is completed after a few minutes. Prolonged reaction times or reactions with powdered dry ice do not result in higher conversion rates. The progress of such reactions can readily be observed by ^1H NMR spectroscopy, where the $-NH_3^+$ signal of **1** in $CDCl_3$ is detected at 1.06 ppm [6] and two additional signals appear during the reaction, which can be assigned to the NH protons in $[PhTe(CH_2)_3NH_3]^+$ (3.85 ppm) and $[PhTe(CH_2)_3NHCOO]^-$ (4.48 ppm). While the signal of the carbamate NH proton appears in the expected range for alkylammonium carbamates [12], the downfield shift of the $-NH_3^+$ signal in the cation is remarkable and can be regarded as a hint for the formation of cation/anion interactions even in solution. This interpretation is supported by the fact that the formation of the carbamate stops at a conversion rate of 50%. All our attempts to produce higher yields of the carbamate with Na^+ or NBu_4^+ as counter ions failed.



1 **4**

Scheme 2. Synthesis of compound **4**.