

**Tellurium–Nitrogen Double Bonds and a Novel  $\text{Te}_3\text{N}_3$  Ring: Formation and Structures of  $[(^t\text{BuNH})(^t\text{BuN})_3\text{Te}_2]\text{Cl}$ ,  $(^t\text{BuN}=\text{Te}=\text{N}^t\text{Bu})_2$ , and  $(^t\text{BuNTe})_3$**

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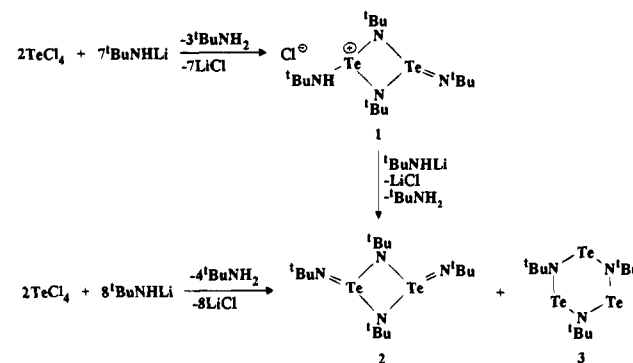
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Interest in tellurium compounds is expanding rapidly. Such compounds have applications in the semiconductor industry, and they often exhibit unique structures or reactivities that are unknown in sulfur or selenium chemistry.<sup>1–3</sup> Part of this interest has focused on tellurium involved in multiple bonds with other elements, e.g., carbon,<sup>4</sup> phosphorus,<sup>5</sup> or transition metals.<sup>6</sup> Although attention has been directed to tellurium–nitrogen derivatives recently, compounds containing  $\text{Te}=\text{N}$  double bonds, e.g.,  $^t\text{BuN}=\text{Te}=\text{N}^t\text{Bu}$ , are unknown.<sup>7,8</sup>

The reactions of primary amines with sulfur(IV) or selenium(IV) provide a facile route to the corresponding diimides  $\text{RN}=\text{E}=\text{NR}$  ( $\text{E} = \text{S}, \text{Se}$ ), which are of interest from the structural viewpoint as well as in organic synthesis and as ligands for transition metals.<sup>9</sup> The first sulfur(IV) diimide,  $^t\text{BuN}=\text{S}=\text{N}^t\text{Bu}$ , was prepared from *tert*-butylamine and  $\text{SCL}_4$ ,<sup>10</sup> and a similar approach can be used to generate thermally unstable  $^t\text{BuN}=\text{Se}=\text{N}^t\text{Bu}$ , a useful reagent for the allylic amination of olefins and acetylenes.<sup>11</sup> In this Communication, we report that the reaction of  $^t\text{BuNHLi}$  with  $\text{TeCl}_4$  leads to the formation of  $[(^t\text{BuNH})(^t\text{BuN})_3\text{Te}_2]\text{Cl}$  (**1**), which exhibits the first genuine example of a  $\text{Te}=\text{N}$  double bond,  $(^t\text{BuN}=\text{Te}=\text{N}^t\text{Bu})_2$  (**2**), the first  $\text{N},\text{N}'$ -diorganotellurium diimide, and  $(^t\text{BuNTe})_3$  (**3**), the first cyclic tellurium imide.

The reaction of  $\text{TeCl}_4$  with  $^t\text{BuNHLi}$  in toluene at  $-100\text{ }^\circ\text{C}$  (followed by slow warming to  $23\text{ }^\circ\text{C}$ ) gives rise to three products, **1**, **2**, and **3**, in amounts that depend on the molar ratio of the reactants.<sup>12</sup> When that ratio was 2:7, the major product **1** was isolated in 63% yield as very moisture-sensitive yellow crystals<sup>12a</sup> (see Scheme 1). The identity of **1** was established by X-ray crystallography,<sup>13</sup> and the molecular structure is shown in Figure 1. Compound **1** is an  $\text{HCl}$  adduct of the dimer of the hitherto unknown tellurium diimide  $^t\text{BuN}=\text{Te}=\text{N}^t\text{Bu}$ . The most

Scheme 1



significant feature of the structure of **1** is the  $\text{Te}(1)-\text{N}(3)$  distance of  $1.840(9)\text{ \AA}$ , which is close to the estimated value of  $1.83\text{ \AA}$  for a  $\text{Te}(\text{IV})=\text{N}$  double bond.<sup>14</sup> There are several examples of compounds containing short  $\text{Te}-\text{N}$  bonds,<sup>14–17</sup> but the shortest value reported is  $1.900(5)\text{ \AA}$ .<sup>15</sup> Thus **1** exhibits the first example of a genuine  $\text{Te}=\text{N}$  double bond. The other exocyclic  $\text{Te}-\text{N}$  bond length of  $1.980(9)\text{ \AA}$  and the endocyclic  $\text{Te}-\text{N}$  bond lengths, which are in the range  $2.00(1)-2.112(8)\text{ \AA}$ , are closer to the value of  $2.04\text{ \AA}$  expected for a  $\text{Te}(\text{IV})-\text{N}$  single bond.<sup>18</sup> The sums of the endocyclic bond angles at  $\text{N}(1)$  and  $\text{N}(2)$  are  $349.4$  and  $349.5^\circ$ , respectively, indicating a

(12) (a) **1**: A solution of  $^t\text{BuNHLi}$  (1.04 g, 13.0 mmol) in toluene (30 mL) at  $-30\text{ }^\circ\text{C}$  was added slowly under argon to a vigorously stirred solution of  $\text{TeCl}_4$  (1.00 g, 3.71 mmol) in toluene (30 mL) at  $-100\text{ }^\circ\text{C}$ . An orange color developed immediately. The mixture was allowed to reach  $23\text{ }^\circ\text{C}$  slowly (1 h), stirred for a further 2 h, and then filtered through a fine frit. The solid product was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20\text{ mL}$ ), and then solvent was removed under vacuum to give a yellow-orange residue which was combined with the residue obtained after removal of toluene from the filtrate and then dissolved in THF (30 mL). The volume of this solution was reduced to ca. 10 mL under vacuum. After 12 h at  $5\text{ }^\circ\text{C}$ , yellow crystals of **1** were isolated and washed with hexane. A second crop of **1** was obtained upon cooling the combined mother liquor and hexane washings. Total yield of **1** was 0.674 g, 1.17 mmol, 63%; mp  $189\text{ }^\circ\text{C}$  dec;  $^1\text{H NMR}$  ( $\text{C}_7\text{D}_8$ , 190 K)  $\delta$  4.0 (s br, 1H, NH), 1.84 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.69 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 1.67 (s, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{125}\text{Te NMR}$  (toluene,  $\text{D}_2\text{O}$  insert, 296 K  $\delta$  1744 (s) (ref  $\text{K}_2\text{TeO}_3$  in  $\text{D}_2\text{O}$ ). (b) **2** and **3**: A solution of  $^t\text{BuNHLi}$  (12.0 g, 150 mmol) in a mixture of toluene (80 mL) and hexane (60 mL) at  $-20\text{ }^\circ\text{C}$  was added by cannula under argon to a vigorously stirred solution of freshly sublimed  $\text{TeCl}_4$  (10.0 g, 37.1 mmol) in toluene (150 mL) at  $-100\text{ }^\circ\text{C}$ . The reaction mixture was allowed to warm slowly to  $23\text{ }^\circ\text{C}$ , and then the orange slurry was stirred for 24 h. The solution was filtered through a glass frit, and solvent was removed under vacuum to give a sticky dark orange residue. The solid over the frit was extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 50\text{ mL}$ ). The  $\text{CH}_2\text{Cl}_2$  solution was filtered, solvent was removed from the filtrate, and the residue was extracted with hexanes ( $4 \times 70\text{ mL}$ ). The volume of the hexane solution was reduced to 10 mL to give orange crystals of **2** (3.19 g). The orange residue obtained after the separation of **3** (*vide infra*) was sublimed at  $85\text{ }^\circ\text{C}/5 \times 10^{-3}$  Torr to give 0.91 g of **2**. The total yield of **2** was 4.10 g, 7.59 mmol, 41%; mp  $100-102\text{ }^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 296K)  $\delta$  1.68 (s, 18H), 1.25 (s, 18H). The hexane mother liquor was combined with a hexane solution (60 mL) of the sticky dark orange residue (*vide supra*). The volume of this combined solution was reduced to 10 mL, and, after 12 h at  $5\text{ }^\circ\text{C}$ , dark orange crystals of **3** (0.63 g) were obtained. A second crop of **3** (0.65 g) was obtained from pentane solutions at  $-20\text{ }^\circ\text{C}$  of the residue obtained upon removal of solvent from the mother liquor. The crystals of **3** were washed several times with cold pentane to remove traces of **2**. The total yield of **3** was 1.28 g, 2.15 mmol, 17%; mp  $132\text{ }^\circ\text{C}$  dec;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.22 (s). Satisfactory C, H, and N analyses were obtained for **1**, **2**, and **3**.

(13) Details of the crystal structure determinations of **1**, **2**, and **3** can be found in the supplementary material.

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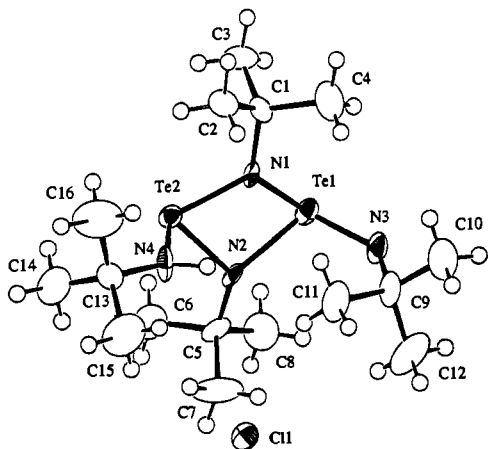
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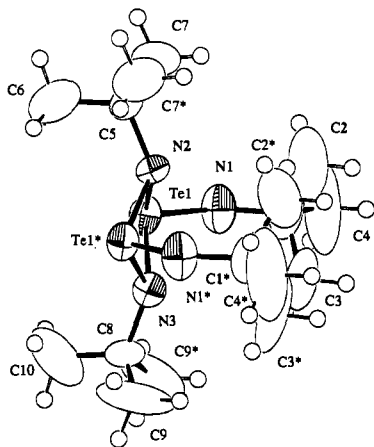
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**Figure 1.** ORTEP view of **1** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (deg): Te(1)–N(1) 2.112(8), Te(1)–N(2) 2.092(10), Te(1)–N(3) 1.840(9), Te(2)–N(1) 2.00(1), Te(2)–N(2) 2.003(8), Te(2)–N(4) 1.980(9), N(1)–Te(1)–N(2) 73.0(3), N(1)–Te(2)–N(2) 77.4, Te(1)–N(1)–Te(2) 99.5(4), Te(1)–N(2)–Te(2) 100.1(4), Te(1)–N(3)–C(9) 134.8(7), and Te(2)–N(4)–C(13) 129.9(7).



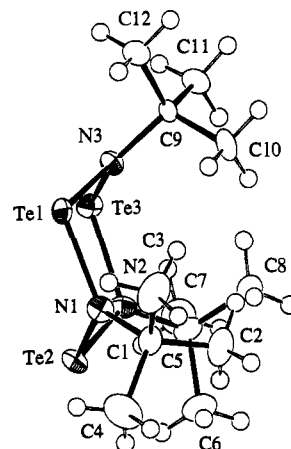
**Figure 2.** ORTEP view of **2** showing numbering scheme. Selected bond lengths (Å) and angles (deg): Te(1)–N(1) 1.876(10), Te(1)–N(2) 2.080(8), Te(1)–N(3) 2.082(8), N(1)–Te(1)–N(2) 113.7(5), N(1)–Te(1)–N(3) 113.1(5), N(2)–Te(1)–N(3) 75.6(4), Te(1)–N(2)–Te(1)\* 101.1(6), Te(1)–N(3)–Te(1)\* 101.0(6), and Te(1)–N(1)–C(1) 130.9(80). Asterisks indicate symmetry-related atoms.

tendency toward planarity. The  $^1\text{H}$  NMR spectrum of **1** in  $\text{C}_7\text{D}_8$  at 298 K exhibits a singlet for all four 'Bu groups at  $\delta$  1.63, in addition to the broad resonance for the NH group at  $\delta$  4.09. At 190 K, however, the expected three resonances in the integrated ratio 2:1:1 ( $\delta$  1.84, 1.69, and 1.67) are observed.<sup>12a</sup>

When the molar ratio of  $\text{TeCl}_4$  to 'BuNHLi was 1:4, the two products **2** and **3** were isolated in 41% and 17% yields, respectively.<sup>12b</sup> In a separate experiment, the reaction of **1** with an equimolar amount of 'BuNHLi in toluene at  $-78^\circ\text{C}$  was shown to produce **2** in 98% yield (see Scheme 1). A pure sample of **2** was obtained as orange, X-ray quality crystals by sublimation at  $75^\circ\text{C}/10^{-4}$  Torr. **2** was confirmed to be the dimer ('BuNTeN'Bu)<sub>2</sub> by an X-ray structural determination (see Figure 2).<sup>13</sup> The exocyclic imido substituents in **2** are in a *cis* orientation with respect to the folded  $\text{Te}_2\text{N}_2$  ring.

The relatively high thermal stability of the dimeric tellurium diimide **2**<sup>12b</sup> is noteworthy in comparison with the thermal lability of selenium diimides,<sup>11,19–21</sup> which are thought to exist as monomers.<sup>19</sup> The dimer **2** melts without decomposition at

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**Figure 3.** ORTEP view of **3** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (deg): mean values, Te–N 2.033(6), N–Te–N 104.6(2), and Te–N–Te 112.6(3).

$100\text{--}102^\circ\text{C}$ .<sup>12b</sup> By contrast, 'BuN=Se=N'Bu' decomposes slowly at room temperature to give the eight-membered ring ('BuN)<sub>2</sub>Se<sub>6</sub>.<sup>19</sup> The  $^1\text{H}$  NMR spectrum of **2** in  $\text{C}_7\text{D}_8$  exhibits two equally intense singlets at  $\delta$  1.68 and 1.25 throughout the temperature range 298–370 K, indicating no exchange between bridging and terminal 'BuN groups. A second pair of equally intense singlets at  $\delta$  1.59 and 1.28, which represent *ca.* 20% of the total signal, is also observed. We tentatively attribute these resonances to the *trans* isomer of **2**.<sup>22</sup>

X-ray quality dark orange crystals of **3** were obtained from a diethyl ether solution.<sup>13</sup> As indicated in Figure 3, compound **3** consists of a six-membered  $\text{Te}_3\text{N}_3$  ring in a chair conformation with Te–N distances in the narrow range 2.017(6)–2.044(6) Å, indicative of Te(II)–N single bonds (cf.  $d(\text{Te}–\text{N}) = 2.049\text{--}(2)$  Å in  $\text{Te}[\text{N}(\text{SiMe}_3)_2]_2$ ).<sup>23</sup> The endocyclic bond angles at Te and N fall within the ranges 103.1(1)–106.0(2) and 111.9(3)–113.0(3) $^\circ$ , respectively. The geometry at the three nitrogen atoms is essentially planar ( $\Sigma\angle\text{N}(1) = 359.5^\circ$ ;  $\Sigma\angle\text{N}(2) = 357.5^\circ$ ;  $\Sigma\angle\text{N}(3) = 359.1^\circ$ ). Although the cyclic selenium imides ('BuN)<sub>2</sub>Se<sub>6</sub> and ('BuN)<sub>6</sub>Se<sub>9</sub> are known,<sup>24</sup> there are no precedents in chalcogen imide chemistry for a six-membered  $\text{E}_3\text{N}_3$  ring.

The development of Te–N chemistry should be facilitated by the simple preparation of the novel reagents **1**, **2**, and **3** described herein.

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**Supplementary Material Available:** Tables of crystallographic data for [(BuNH)(BuN)<sub>3</sub>Te<sub>2</sub>]Cl, [BuNTeN'Bu]<sub>2</sub>, and [BuNTe]<sub>3</sub> (24 pages); observed and calculated structure factors (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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