Inorg. Chem. **1999,** *38,* 5431−5436 **5431**

Synthesis and Reactions of *tert*-Butylimidotellurium Dihalides: X-ray Structures of $[Cl_2Te(\mu\text{-}N^tBu)_2TeCl_2]_3$ and $(^tBuO)_2Te(\mu\text{-}N^tBu)_2Te(O^tBu)_2$

Tristram Chivers,*,[†] Gary D. Enright,[‡] Nicole Sandblom,[†] Gabriele Schatte,[†] and Masood Parvez[†]

Department of Chemistry, University of Calgary, 2500 University Drive NW,
Calgary, Alberta, Canada T2N 1N4, and Steacie Institute for Molecular Sciences,
National Research Council of Canada, 110 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

Received July 16, 1999

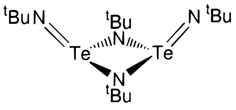
An improved synthesis of the tellurium diimide dimer $^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$ (**1**) using THF as solvent is reported. The reactions of **1** with tellurium tetrahalides (1:2 molar ratio) in THF give high yields of *tert*-butylimidotellurium dihalides $(^tBuNTeX_2)_n$ (**2a**, X = Cl, $n = 6$; **2b**, X = Br). The intermediate $^tBuNTe(\mu\text{-}N^tBu)_2TeCl_2$ (**3**) is obtained when a 3:2 molar ratio is used. The dibromide **2b** may also be prepared by halide exchange between **2a** and 2 equiv of Me_3SiBr. The crystal structure of **2a**·2THF reveals a hexamer formed by linking three $(^tBuNTeCl_2)_2$ dimers via chloride bridges. The Cl ligands in the central dimer occupy the axial positions of a distorted trigonal bipyramid on both Te atoms. In the two terminal dimers one of the Te atoms has both Cl ligands in axial positions, whereas the other Te is attached to one axial Cl substituent and one equatorial Cl substituent. There are weak Te···Cl interactions between hexamer units in the range 3.107(1)−3.704(1) Å. Crystals of **2a**·2THF are monoclinic, space group $C2/c$, $a = 35.2264(9)$ Å, $b = 11.4548(3)$ Å, $c = 14.3656(4)$ Å, $\beta = 101.645(1)°$, $V = 5677.4(3)$ Å^3, and $Z = 8$. The reaction of **2a** with 2 equiv of KO^tBu in THF produces $(^tBuO)_2Te(\mu\text{-}N^tBu)Te(O^tBu)_2$ (**4**). The crystal structure of **4** comprises a centrosymmetric dimer with a planar Te_2N_2 ring and significantly different Te−N bond lengths [1.943(4) and 2.217(4) Å]. Crystals of **4** are triclinic, space group $P\bar{1}$, $a = 9.646(5)$ Å, $b = 10.899(5)$ Å, $c = 9.439(4)$ Å, $\alpha = 94.12(4)°$, $\beta = 118.89(3)°$, $\gamma = 65.26(4)°$, $V = 778.5(7)$ Å^3, and $Z = 2$.

Introduction

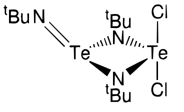
The development of tellurium−nitrogen (Te−N) chemistry has been hampered by the lack of suitable reagents that are readily prepared.[1] Recently, however, this deficiency has been ameliorated by the discovery of thermally stable tellurium(II) amides $Te[N(SiMe_3)_2]_2$[2] and $[Te(NMe_2)_2]_\infty$,[3] and the dimeric tellurium(IV) diimide $^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$ (**1**).[4] Tellurium diimide dimers may exist as *cis*[4] or *trans*[5] isomers, a feature which leads to versatile ligand behavior in complexes of **1** with coinage metals.[6] The dimerization process has been investigated through DFT calculations.[7]

The dimer **1** is also a fruitful source of novel Te−N anions, e.g., $[Te(N^tBu)_3]^{2-}$ and $[Te(N^tBu)_2(O^tBu)]^-$.[8,9] Homoleptic complexes of heavy group 15 elements, $Li\{M[Te(N^tBu)_3]_2\}$ (M = Bi, Sb), have been prepared from the former anion.[10] In this paper we describe an improved synthesis of the important reagent **1** and its redistribution reactions with tellurium tetrahalides to give the imidotellurium dihalides $(^tBuNTeX_2)_n$ (**2a**, X = Cl; **2b**, X = Br) via the intermediate **3**.

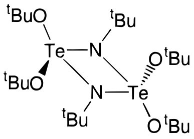
The new Te(IV)−N reagent **2a** is useful for the further development of Te−N chemistry via reactions with nucleophilic reagents. As an example, the synthesis and X-ray structure of the dimeric dialkoxytellurium imide **4** are reported.



1



3



4

Experimental Section

Reagents and General Procedures. $TeCl_4$ (AESAR), $TeBr_4$, and Me_3SiBr (all from Aldrich) were used without further purification. KO^tBu (Aldrich) was sublimed prior to use. $LiNH^tBu$ was prepared by the addition of Li^nBu to $^tBuNH_2$ in n-hexane at −10 °C. Solvents were dried with the appropriate drying agents and distilled onto fresh molecular sieves. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of argon using standard Schlenk techniques or a drybox (Innovative Technology Inc.).

---

* To whom correspondence should be addressed. Fax: (403) 289-9488. E-mail: chivers@ucalgary.ca.

[†] University of Calgary.

[‡] National Research Council of Canada.

(1) (a) Chivers, T. *J. Chem. Soc., Dalton Trans.* **1996**, 1185. (b) Chivers, T.; Gao, X.; Sandblom, N.; Schatte, G. *Phosphorus, Sulfur, Silicon* **1998**, *136−138*, 11.

(2) Björgvinsson, M.; Roesky, H. W.; Paver, F.; Stalke, D.; Sheldrick, G. M. *Inorg. Chem.* **1990**, *29*, 5140.

(3) Allan, R. E.; Gornitzka, H.; Kärcher, J.; Paver, M. A.; Rennie, M.-A.; Russell, C. A.; Raithby, P. R.; Stalke, D.; Steiner A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1996**, 1727.

(4) Chivers, T.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **1995**, *117*, 2359.

(5) (a) Chivers, T.; Gao, X.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2149. (b) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 9.

(6) Chivers, T.; Parvez, M.; Schatte, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2217.

(7) Sandblom, N.; Chivers, T.; Ziegler, T. *Inorg. Chem.* **1998**, *37*, 354.

(8) Chivers, T.; Gao, X.; Parvez, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2549.

(9) Chivers, T., Parvez, M.; Schatte, G. *Inorg. Chem.* **1996**, *35*, 4094.

(10) Chivers, T., Parvez, M.; Schatte, G. *Inorg. Chem.* **1999**, *38*, 1380.

10.1021/ic990849k CCC: $18.00

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker ACT200 spectrometer. ^{125}Te NMR and ^{13}C NMR spectra were measured on a Bruker AM400 spectrometer. ^{1}H VT-NMR spectra were obtained on a Varian XL200 spectrometer. IR spectra were measured as Nujol mulls between CsI or KBr plates on a Mattson 4020 FT-IR (4000−200 cm^{-1}) or a Mattson Genesis Series FT-IR (4000−300 cm^{-1}) spectrometer. Elemental analyses were performed by Analytical Services, Chemistry Department, University of Calgary. Electron impact mass spectra (EI-MS) were recorded on a VG 7070F instrument operating at 70 eV.

Preparation of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (1). A suspension of LiNH^{t}Bu (11.90 g, 148.6 mmol) in THF (150 mL) was added to a solution of TeCl$_4$ (10.00 g, 37.1 mmol) in THF (100 mL) cooled to −78 °C. The ^{t}BuNHLi vessel was rinsed with THF (50 mL) and the washing added to the reaction mixture, which was stirred for 3 h at −78 °C and then for 48 h at 23 °C. During this period the color of the reaction mixture changed from yellow to dark brown and finally to dark red. The solvent was removed under vacuum to give a red-orange solid. The residue was extracted with diethyl ether (300 mL), and the dark red solution was filtered. The solvent was removed under vacuum to give **1** as an orange solid (8.105 g, 15.01 mmol, 81%). Final purification of **1** (to remove LiCl) was achieved by sublimation at 85−90 °C, 5 × 10^{-3} Torr. The ^{1}H NMR spectrum was identical to that reported in the literature.[4,5b]

Preparation of [Cl$_2$Te(μ-N^{t}Bu)$_2$TeCl$_2$]$_3$ (2a). An orange solution of sublimed **1** (2.672 g, 4.95 mmol) in THF (125 mL) was slowly added to a yellow slurry of TeCl$_4$ (2.670 g, 9.91 mmol) in THF (100 mL) cooled to −60 °C. The reaction mixture was dark green, and after 16 h at 23 °C, the color changed to yellow with a small amount of black precipitate. The reaction mixture was filtered, and the solvent was removed under vacuum. The yellow-gold solid was washed with *n*-hexane (20 mL) and then diethyl ether (20 mL), yielding **2a** as a yellow-gold powder (5.131 g, 19.02 mmol, 96%), which was recrystallized from a minimum volume of THF at 23 °C to give (^{t}BuNTeCl$_2$)$_6$·2THF. Anal. Calcd for $C_{16}H_{35}Cl_6N_3OTe_3$: C, 21.81; H, 4.00; N, 4.77. Found: C, 20.83; H, 3.80; N, 4.82. ^{1}H NMR (d_8-THF): δ 1.62 (s, C(C*H*$_3$)$_3$), δ 1.77 and 3.61 (coordinated THF). ^{13}C NMR (d_8-THF): δ 33.1 (s, C(*C*H$_3$)$_3$), δ 63.9 (s, *C*(CH$_3$)$_3$). ^{125}Te NMR (d_8-THF): δ 1312 (s). FT-IR (4000−200 cm^{-1}, Nujol mull, CsI plates): 1209 w, 1174 s, 897 s, 723 s, 654 s (br), 400 w (sh), 283 s, 224 w (sh). X-ray-quality crystals of **2a** were obtained by vapor diffusion. An open vial containing a solution of **2a** (10 mg) in THF (2 mL) was placed into another vial containing *n*-hexane (5 mL). The larger vial was sealed and stored in the drybox. Yellow-orange platelike crystals were formed after 2 days.

Preparation of (^{t}BuNTeBr$_2$)$_n$ (2b). (a) Reaction of 1 and TeBr$_4$. An orange solution of sublimed **1** (0.166 g, 0.308 mmol) in THF (20 mL) was slowly added to an orange slurry of TeBr$_4$ (0.273 g, 0.610 mmol) in THF (20 mL) cooled to −60 °C. The first addition turned the mixture deep green. After the reaction was allowed to reach 23 °C, the mixture was red-orange. The solvent was removed under vacuum to give a red-orange powder (0.297 g). ^{1}H NMR (d_8-THF): δ 1.46 (s) and 1.64 (s). This mixture was recrystallized from a minimum volume of THF to give yellow-orange crystals of **2b**. ^{1}H NMR (d_8-THF): δ 1.46 (s). EI-MS (*m/z*): 639 (M$_2$ − Br)$^+$.

(b) Reaction of 2a and Me$_3$SiBr. A colorless solution of Me$_3$SiBr (0.30 mL, 0.348 g, 2.27 mmol) in THF (20 mL) was slowly added to a yellow solution of **2a** (0.290 g, 1.08 mmol) in THF (25 mL) cooled to −60 °C. The solution instantly turned orange. The reaction mixture was allowed to warm to 23 °C, and the solvent was removed under vacuum to give a red-orange powder (0.292 g). ^{1}H NMR (d_8-THF): δ 1.64 (s). Recrystallization from a minimum of THF gave yellow-orange microcrystals of **2b**. ^{1}H NMR (d_8-THF): δ 1.46 (s, ^{t}Bu), δ 1.77 and 3.61 (coordinated THF). Anal. Calcd for $C_{16}H_{35}Br_6N_3OTe_3$: C, 16.74; H, 3.07; N, 3.66. Found: C, 16.86; H, 3.21; N, 4.28. IR (4000−300 cm^{-1}, Nujol mull, CsI plates): 1289 w (sh), 1260 w (sh), 1203 w (br), 1075 s (br), 1041 s (br), 881 s, 796 s (br), 721 s (br), 658 s (br), 435 w (br), 340 w (sh).

Preparation of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeCl$_2$ (3). (a) From 1 and TeCl$_4$. An orange solution of sublimed ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (0.202 g, 0.374 mmol) in THF (25 mL) was slowly added to a yellow slurry of TeCl$_4$ (0.067 g, 0.256 mmol) in THF (10 mL) cooled to −60 °C. The reaction mixture was dark green, and after 16 h at 23 °C, the color changed to yellow-orange with a small amount of black precipitate. The reaction mixture was filtered, and the solvent was removed under vacuum to give **3** as an orange-yellow powder (0.165 g, 0.306 mmol, 61%). Anal. Calcd for $C_{12}H_{27}Cl_2N_3Te_2$: C, 26.72; H, 5.04; N, 7.79. Found: C, 26.75; H, 5.11; N, 7.48. ^{1}H NMR (d_8-THF): δ 1.53 (s, 9H, N$_t$−C(C*H*$_3$)$_3$), δ 1.58 (s, 18H, N$_b$−C(C*H*$_3$)$_3$). ^{13}C NMR (d_8-THF): δ 34.9 (s, N$_t$−C(*C*H$_3$)$_3$), δ 35.8 (s, N$_b$−C(*C*H$_3$)$_3$), δ 60.6 (s, N$_t$−*C*(CH$_3$)$_3$), δ 61.3 (s, N$_b$−*C*(CH$_3$)$_3$). ^{125}Te NMR (d_8-THF): δ 1573 (s, *Te*Cl$_2$), δ 1693 (s, *Te*═N$_t$). EI-MS (*m/z*): 526 (M − Me)$^+$. IR (4000−300 cm^{-1}, Nujol mull, CsI plates): 1220 w, 1172 s(br), 932 s(br), 917 s(br), 728 s, 696 s, 629 s, 465 w, 299 w, 224 w, 216 w, 208 s.

Table 1. Crystallographic Data for [Cl$_2$Te(μ-N^{t}Bu)$_2$TeCl$_2$]$_3$ (**2a**) and (^{t}BuO)$_2$Te(μ-N^{t}Bu)$_2$Te(O^{t}Bu)$_2$ (**4**)

	2a·THF	**4**
empirical formula	$C_{16}H_{35}Cl_6N_3OTe_3$	$C_{12}H_{27}NO_2Te$
fw	880.97	344.95
cryst syst	monoclinic	triclinic
T, °C	−100	−103
space group	*C*2/*c* (no. 15)	*P*$\bar{1}$ (no. 2)
a, Å	35.2264(9)	9.646(6)
b, Å	11.4548(3)	10.899(5)
c, Å	14.3656(4)	9.439(4)
α, deg	90	94.12(4)
β, deg	101.645(1)	118.89(3)
γ, deg	90	65.26(4)
V, Å^3	5677.4(3)	778.5(7)
Z	8	2
ρ_{calcd}, g cm^{-3}	2.061	1.472
μ(Mo Kα), cm^{-1}	36.42	19.04
λ, Å	0.71073	0.71069
R,^{a} R_w^{b}	0.025, 0.057	0.035, 0.094

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

In a separate experiment it was shown by ^{1}H NMR that **3** is the only product when ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (0.020 g, 0.074 mmol) and **2a** (0.020 g, 0.037 mmol) are allowed to react in d$_8$-THF (0.7 mL) for 1 h.

Preparation of (^{t}BuO)$_2$Te(μ-N^{t}Bu)$_2$Te(O^{t}Bu)$_2$ (4). A slurry of KO^{t}Bu (0.456 g, 4.06 mmol) in THF (20 mL) was slowly added to a yellow solution of **2a** (0.551 g, 2.04 mmol) in THF (25 mL) cooled to −60 °C. The reaction mixture was allowed to warm to 23 °C, the solvent was removed under vacuum, and the residue was extracted with diethyl ether (20 mL). The yellow solution was filtered to give a white powder, presumably KCl, which was washed with diethyl ether (3 × 5 mL). The washings were combined with the filtrate, and the solvent was removed under vacuum to give **4** as a yellow-orange powder (0.494 g, 0.716 mmol, 70%). Anal. Calcd for $C_{24}H_{54}N_2O_4Te_2$: C, 41.78; H, 7.89; N, 4.06. Found: C, 41.08; H, 7.52; N, 4.30. ^{1}H NMR (C$_6$D$_6$): δ 1.44 (s, 18H, OC(C*H*$_3$)$_3$), δ 1.74 (s, 9H, NC(C*H*$_3$)$_3$). ^{125}Te NMR (C$_7$D$_8$): δ 1620 (s, br). ^{13}C NMR (C$_7$D$_8$): δ 33.6 (s, OC(*C*H$_3$)$_3$), δ 35.3 (s, NC(*C*H$_3$)$_3$), δ 60.8 (s, N*C*(CH$_3$)$_3$), δ 76.9 (s, O*C*(CH$_3$)$_3$). IR (4000−300 cm^{-1}, Nujol mull, CsI plates): 1359 s (sh), 1232 s, 1180 s (br), 919 s (br), 897 s (br), 777 w, 757 w, 708 w, 668 w, 550 w (br), 452 w (br), 373 w (br). EI-MS (*m/z*): 349 (M + 2)$^+$.

X-ray Analysis. All measurements for **2a** were made on a Siemens SMART CCD diffractometer, and those for **4** were obtained on a Rigaku AFC6S diffractometer. Crystallographic data for **2a** and **4** are summarized in Table 1.

2a. A yellow triangular-shaped plate (0.20 × 0.20 × 0.04 mm) was coated with oil (Paratone 8277, Exxon) and mounted with a thin layer of epoxy onto a glass fiber. Cell parameters were obtained from 6755 reflections with a 2θ angle in the range 3.00−55.00°. A total of 32 698 reflections were collected. These data were merged to R_{int} (0.028) to provide 7364 unique and 5776 observed ($I > 2.00\sigma(I)$) reflections.[11] The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods and initially refined with the NRCVAX suite of

---

(11) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *32*, 384.

programs.[11] The refinement was completed using the full-matrix least-squares method on F^2 with SHELXL97-2.[12] The atoms of the heavily disordered THF molecule were allowed to reside over two sites with partial occupancy factors. The non-hydrogen atoms were refined anisotropically. The C and O atoms of the disordered THF molecule were allowed an overall isotropic displacement parameter of 0.15 Å^2, and the O−C and C−C bond distances were constrained (C−C = 1.52 Å and C−O = 1.47 Å). Hydrogen atoms for the ^{t}Bu groups were included at geometrically idealized positions and were not refined. The hydrogen atoms of the disordered THF were ignored.

4. A colorless block crystal (0.70 × 0.60 × 0.58 mm), obtained by recrystallization from *n*-hexane at 23 °C, was mounted onto a glass fiber. The cell constants and an orientation matrix for data collection were determined from the setting angles of 23 carefully centered reflections in the range $17.95° < 2\theta < 21.39°$. Scans of $1.68° + 0.34 \tan \theta$) were made at a scan speed of 16.0 deg min^{-1} to a maximum 2θ value of 50.1°. The intensities of 2752 reflections were measured, 2515 of which had $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods[13] and expanded by using Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Each of the three carbon atoms attached to C(9) was disordered over two sites with an occupancy of 0.5 at each site, and the thermal parameters for the disordered atoms were constrained.[12] Conventional atomic scattering factors, corrected for anomalous dispersion, were used,[15] and allowance was made for anomalous dispersion. All calculations for data reduction were performed using teXsan,[16] and refinement was completed by full-matrix least-squares calculations with the aid of SHELXL97-2.[12]

Results and Discussion

Synthesis of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (1). The tellurium(IV) diimide dimer **1** was first prepared by the reaction of LiNH^{t}Bu with TeCl$_4$ in an 4:1 molar ratio in *toluene*.[4,17] Under these conditions the formation of **1** is accompanied by significant amounts of the cyclic tellurium(II) imide trimer [Te(N^{t}Bu)]$_3$. The yield of **1** can reach 67% if LiNH^{t}Bu is added as a *solid* to a slurry of TeCl$_4$ in toluene at −78 °C.[18] Although this method minimizes the amount of [Te(N^{t}Bu)]$_3$ that is formed, the workup procedure is lengthy and tedious owing to the coproduction of a lithium chloride complex, {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$.[17] We have now found that the use of *THF* for the LiNH^{t}Bu−TeCl$_4$ reaction results in a significant improvement in the yield of **1** to ca. 81%. None of the reduction product [Te(N^{t}Bu)]$_3$ is formed in this solvent, and the purification process is simpler. The ^{1}H NMR spectrum of the crude product shows it to be pure **1**. However, sublimation of this product is necessary to free it from traces of LiCl which may affect the reactions of **1** with certain reagents, e.g., Ag$^+$.[18]

Preparation and Characterization of (^{t}BuNTeX$_2$)$_n$ (2a, X = Cl; 2b, X = Br). The redistribution reaction of the dimer **1** with tellurium tetrachloride or tetrabromide occurs smoothly in THF at 23 °C to give the corresponding *tert*-butylimidotellurium dihalides (eq 1). The halide exchange reaction between **2a** and trimethylsilyl bromide (eq 2) provides an alternative route to **2b**, which gives a cleaner product.

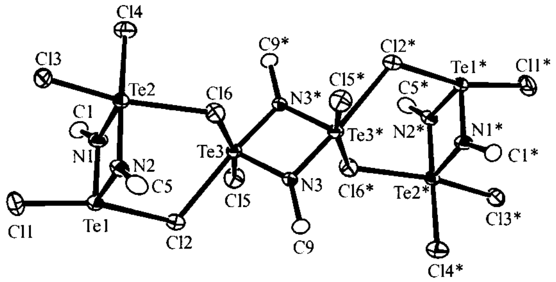


Figure 1. ORTEP drawing and atomic numbering scheme for [Cl$_2$Te(μ-N^{t}Bu)$_2$TeCl$_2$]$_3$ (**2a**). For clarity, only the α-carbon atoms of ^{t}Bu groups are shown. *Symmetry transformation: $-x + {}^3/_2, -y + {}^3/_2, -z$.

$$^t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu} + 2\text{TeX}_4 \rightarrow (4/n)[^t\text{BuNTeX}_2]_n \quad \begin{matrix}(\mathbf{2a})\ \text{X} = \text{Cl}\\ (\mathbf{2b})\ \text{X} = \text{Br}\end{matrix} \tag{1}$$

$$(1/6)[^t\text{BuNTeCl}_2]_6 \xrightarrow[-2\text{Me}_3\text{SiCl}]{+2\text{Me}_3\text{SiBr}} (1/n)[^t\text{BuNTeBr}_2]_n \tag{2}$$

The dichloride **2a** is a yellow-gold powder, which can be recrystallized from THF at 23 °C to give moisture-sensitive yellow crystals. It is sparingly soluble in acetonitrile, THF, and dichloromethane, but insoluble in diethyl ether, toluene, and *n*-hexane. The ^{1}H NMR spectrum of **2a** in d_8-THF exhibits a singlet at δ 1.62, indicating a single N^{t}Bu environment, together with resonances for THF. The ^{13}C NMR spectrum is also consistent with one type of N^{t}Bu group in solution, and the ^{125}Te NMR spectrum exhibits a singlet at δ 1312. The solid-state structure **2a** has been shown to consist of a weakly associated polymeric arrangement of hexameric units (vide infra).

The initial product in the preparation of **2b** by either route (eq 1 or 2) is a red solid. In the redistribution reaction (eq 1) this product is a mixture that exhibits singlets for N^{t}Bu groups at δ 1.46 and 1.64, whereas only the latter resonance is observed for the product of the halogen exchange reaction (eq 2). In both cases, however, recrystallization of the product from THF yields **2b** as moderately-moisture-sensitive yellow-orange crystals which, in d_8-THF, show a singlet at δ 1.46 and resonances for THF in the ^{1}H NMR spectrum. The CHN analyses for the recrystallized product are consistent with the formulation (^{t}BuNTeBr$_2$)$_6$·2THF. The EI mass spectrum of **2b** shows a group of peaks centered a $m/z = 639$ with relative intensities in good agreement with the calculated isotopic pattern for (C$_4$H$_9$NTe)$_2$Br$_3$$^+$, i.e., the loss of Br from the dimer of **2b**. We tentatively suggest that the initial product (δ 1.64) is a smaller oligomer (or, possibly, an isomer) of **2b**. The dibromide **2b** is insoluble in most organic solvents, but sparingly soluble in THF. Numerous attempts to grow crystals suitable for X-ray crystallography have produced only very thin needles.

X-ray Structure of [Cl$_2$Te(μ-N^{t}Bu)$_2$TeCl$_2$]$_3$. Recrystallization of **2a** from THF produces fragile, lamellar crystals that are very difficult to separate. An X-ray-quality crystal was eventually obtained by vapor diffusion (THF/*n*-hexane). An ORTEP drawing of **2a** is shown in Figure 1. Selected bond lengths and bond angles are summarized in Table 2.

The related compound (CF$_3$SNTeCl$_2$·THF)$_2$ has a dimeric structure based on a Te$_2$N$_2$ ring.[19] The tellurium atoms are each coordinated to one THF ligand, resulting in *pseudo*octahedral

---

(12) Sheldrick, G. M. *SHELXL97-2, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(13) SAPI91: Fan, H.-F. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, Japan, 1991.

(14) DIRDIF94: Beuskens, P. T.; Admiraal, G.; Beuskens, G.; Bosman, W. P.; Garcia-Granda, R. S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(15) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71−98.

(16) *teXsan, Single-Crystal Structure Analysis Software*, Version 1.2; Molecular Structure Corp.: The Woodlands, TX, 1992.

(17) Chivers, T.; Gao, X.; Parvez, M. *Inorg. Chem.* **1996**, *35*, 4336.

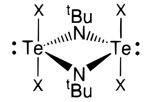
(18) Chivers, T., Parvez, M.; Schatte, G. *Inorg. Chem.* **1999**, *38*, 5171.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **2a**

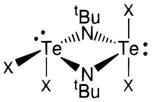
Te(1)−N(1)	1.997(3)	Te(1)−Cl(1)	2.388(1)
Te(1)−N(2)	1.943(3)	Te(1)−Cl(2)	2.892(1)
Te(2)−N(1)	2.016(3)	Te(2)−Cl(3)	2.416(1)
Te(2)−N(2)	2.076(3)	Te(2)−Cl(4)	2.662(1)
Te(3)−N(3)	1.980(2)	Te(2)−Cl(6)	2.798(1)
Te(3)−N(3)[b]	2.025(2)	Te(3)−Cl(2)	2.854(1)
		Te(3)−Cl(5)	2.437(1)
		Te(3)−Cl(6)	2.729(1)
Te(1)···Cl(3)[a]	3.704(1)		
Te(1)···Cl(4)[a]	3.107(1)		
Te(2)[a]···Cl(2)	3.463(1)		
N(2)−Te(1)−N(1)	78.70(11)	N(3)[b]−Te(3)−Cl(5)	95.24(7)
N(2)−Te(1)−Cl(1)	96.34(8)	N(3)−Te(3)−Cl(6)	93.52(7)
N(1)−Te(1)−Cl(1)	98.80(8)	N(3)[b]−Te(3)−Cl(6)	89.92(7)
Cl(2)−Te(1)−Cl(1)	161.65(3)	Cl(5)−Te(3)−Cl(6)	167.63(3)
Cl(2)−Te(1)−N(2)	101.69(8)	N(3)−Te(3)−Cl(2)	97.02(7)
Cl(2)−Te(1)−N(1)	88.11(8)	N(3)[b]−Te(3)−Cl(2)	172.97(7)
N(1)−Te(2)−N(2)	75.24(10)	Cl(5)−Te(3)−Cl(2)	89.24(3)
N(1)−Te(2)−Cl(3)	94.55(8)	Cl(6)−Te(3)−Cl(2)	86.76(3)
N(2)−Te(2)−Cl(3)	96.43(8)	Te(3)−Cl(6)−Te(2)	117.21(3)
N(1)−Te(2)−Cl(4)	91.74(8)	C(1)−N(1)−Te(1)	121.8(2)
N(2)−Te(2)−Cl(4)	165.54(8)	C(1)−N(1)−Te(2)	134.0(2)
Cl(3)−Te(2)−Cl(4)	90.77(3)	Te(1)−N(1)−Te(2)	103.14(12)
N(1)−Te(2)−Cl(6)	97.58(8)	C(5)−N(2)−Te(1)	130.9(2)
N(2)−Te(2)−Cl(6)	87.71(7)	C(5)−N(2)−Te(2)	126.2(2)
Cl(3)−Te(2)−Cl(6)	167.82(3)	Te(1)−N(2)−Te(2)	102.87(12)
Cl(4)−Te(2)−Cl(6)	87.82(3)	C(9)−N(3)−Te(3)	132.34(19)
N(3)−Te(3)−N(3)[b]	76.99(10)	C(9)−N(3)−Te(3)[b]	124.46(18)
N(3)−Te(3)−Cl(5)	98.58(8)	Te(3)−N(3)−Te(3)[b]	103.01(10)

[a] Symmetry operation: $+x$, $-y + 1$, $+z + 1/2$. [b] Symmetry operation: $-x + {}^{3}/_{2}$, $-y + {}^{3}/_{2}$, $-z$.

geometry. By contrast, the core structure of **2a** is a centrosymmetric hexamer composed of two terminal Te_2N_2 rings ($\overline{\text{Te1}-\text{N1}-\text{Te2}-\text{N2}}$) (and its symmetry equivalent) flanking a central Te_2N_2 ($\overline{\text{Te3}-\text{N3}-\text{Te3}^*-\text{N3}^*}$) ring. The three Te_2N_2 rings are bridged by chlorine atoms Cl2 and Cl6 (and their symmetry equivalents). There are two *noncoordinated* THF molecules for each hexameric unit in the lattice. The Cl ligands of the central dimer occupy axial positions in the distorted trigonal bipyramid around the Te atoms (**A**). In the terminal dimers the two Cl substituents inhabit one axial position and one equatorial position at one of the Te atoms and both axial positions at the other Te atom (**B**).



A



B

In contrast to the folded conformation of the Te_2N_2 ring in **1**,[4] the central Te_2N_2 ring in **2a** is perfectly planar, while the terminal Te_2N_2 rings deviate only slightly from planarity. The NTeNTe torsional angles are 0.0° and 1.7(1)°, respectively. The geometry at the bridging nitrogens is essentially planar: $\sum\angle(N(1)) = 359.0°$, $\sum\angle(N(2)) = 359.9°$, $\sum\angle(N(3)) = 359.8°$; cf. 340.3° and 343.6° in **1**.[4] The Te−N distances are in the range 1.943(2)−2.076(3) Å with a mean value of 2.006 Å; cf. 2.081 Å for the endocyclic Te−N bonds in **1**.[4] Short Te−N bond lengths are also a characteristic feature of bisamidotellurium dichlorides, e.g., $[(Me_3Si)_2N]_2TeCl_2$.[20] All of the $\angle$(TeNTe) bond angles in the ring are ca. 103°, while the values of $\angle$(NTeN) range from 75.3(1)° to 78.7(1)°.

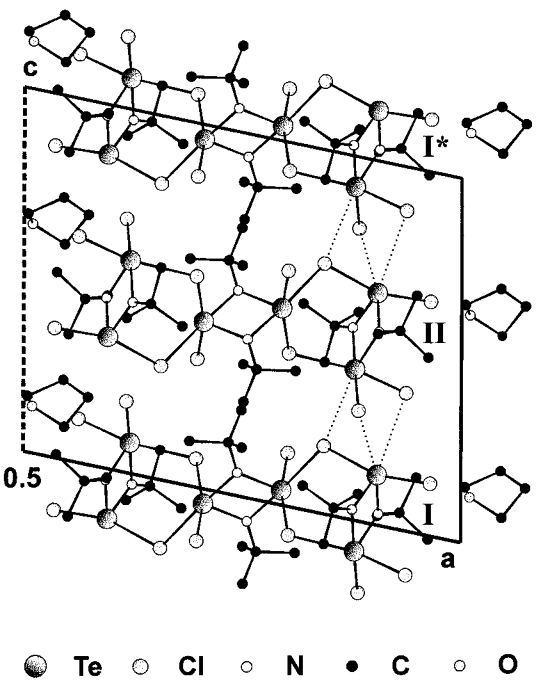


Figure 2. Half of the unit cell of $[Cl_2Te(\mu\text{-}N^tBu)_2TeCl_2]_3$ (**2a**) viewed down the *b* axis showing Te···Cl contacts between hexameric units.

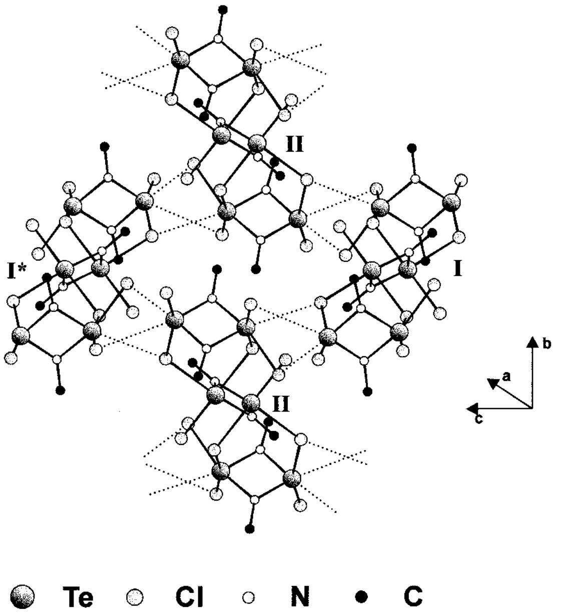


Figure 3. Extended structure of $[Cl_2Te(\mu\text{-}N^tBu)_2TeCl_2]_3$ (**2a**) showing the spiral arrangement of hexameric units. For clarity, only the α-carbon atoms of ^{t}Bu groups are shown and THF molecules have been omitted.

Before the coordination geometry of the Te atoms is discussed, it should be noted that there are weak Te···Cl interactions between hexameric units in **2a** involving two of the tellurium atoms, Te(1) and Te(2). Two views of the unit cell are necessary to appreciate all the features of the extended three-dimensional structure of **2a**. A view down the *b* axis (Figure 2) shows parallel chains of terminal $Cl_2Te(\mu\text{-}N^tBu)_2TeCl_2$ units bridged by central $Cl_2Te(\mu\text{-}N^tBu)_2TeCl_2$ dimers to give the hexameric units I, II, and I*. An alternative view along the *a* axis (Figure 3) reveals a zigzag-shaped polymeric chain, which is the result of an overlap of hexameric units belonging to the outer parallel chains (in the *ac* plane), while the position of the central hexameric unit (in the *ac* plane) is unchanged. The

---

(19) Boese, R.; Dworak, J.; Haas, A.; Pryka, M. *Chem. Ber.* **1995**, *128*, 477.

central hexameric unit (II) is related to the two outer units (I and I*) by a *c*-glide, which gives rise to a spiral arrangement.

Neglecting the weak Te···Cl interactions, Te(1) is four-coordinate whereas Te(2) and Te(3) are both five-coordinate. The terminal Te−Cl bonds are relatively short: Te(1)−Cl(1) = 2.388(1) Å, Te(2)−Cl(3) = 2.416(1) Å, Te(2)−Cl(4) = 2.662(1) Å, and Te(3)−Cl(5) = 2.437(1) Å. These values can be compared with Te−Cl bond lengths of 2.519 Å in $[(Me_3Si)_2N]_2TeCl_2$[20] and 2.672 and 2.585 Å and 2.614 and 2.592 Å in $(R_3PN)_2TeCl_2$ (R = Me[21a] and Ph,[21b] respectively). The dichlorides $(Ph_3PN)_2TeCl_2$[21b] and $(Ph_2CN)_2TeCl_2$[22] are monomers, whereas $(Me_3PN)_2TeCl_2$ is a dimer with very weak Te···Cl interactions (3.669 Å).[21a] The bisamido derivative $[(Me_3Si)_2N]_2TeCl_2$ has an extended network,[20] as do $MeN[PhBN(Me)]_2TeCl_2$[23] and $(Ph_2SN)_2TeCl_2$,[22] but the Te···Cl distances of 3.824 and 3.869 Å are close to the sum of the van der Waals radii for Te and Cl (3.81 Å[24a] or 4.0 Å[24b]). In **2a** the weak contacts between hexamer units are Te(1)···Cl(4)* = 3.107, Te(1)···Cl(3)* = 3.704, and Te(2)*···Cl(2) = 3.463 Å. The Cl atoms Cl(2) and Cl(6) each bridge two Te atoms in the hexameric units almost symmetrically (2.892(1) and 2.854(1) Å and 2.728(1) and 2.798(1) Å, respectively). Consideration of the trends in Te−Cl bond lengths in **2a** (see Table 2) suggests that each tellurium has one covalently bonded, axial chlorine (Cl(1), Cl(3), and Cl(5) for Te(1), Te(2), and Te(3), respectively); the remaining chlorine ligands have substantial ionic character. They serve to link the dimeric units (Cl(2) and Cl(6)) and to provide bridges in the extended structure (Cl(2) and Cl(4)).

The properties and structure of the imidotellurium dichloride **2a** are in sharp contrast with those of their S or Se analogues. The compound $^tBuNSCl_2$ is a yellow oil.[25] In the case of selenium, derivatives of the type $RNSeCl_2$ are known only for R = CF_3, C_2F_5.[26] They are pale yellow liquids which decompose at room temperature to give, inter alia, RN=NR and $SeCl_4$.[26] The observation of a singlet in the ^1H NMR spectrum of **2a** in d_8-THF suggests that the hexameric arrangement observed in the solid state dissociates, presumably to form dimers; cf. $(CF_3SNTeCl_2\cdot THF)_2$.[19]

Preparation of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeCl$_2$ (3). In an attempt to isolate an intermediate in the formation of **2a**, the reaction between **1** and $TeCl_4$ was carried out in a 3:2 molar ratio (eq 3). The product **3** was isolated as an orange-yellow powder,

$$3\,{}^{t}BuNTe(\mu\text{-}N^{t}Bu)_2TeN^{t}Bu + 2TeCl_4 \rightarrow 4\,{}^{t}BuNTe(\mu\text{-}N^{t}Bu)_2TeCl_2 \quad (3)$$

3

which is soluble in *n*-hexane, benzene, diethyl ether, and THF. The identity of **3** was established on the basis of CHN analyses, the observation of $M - Me^+$ as the strongest ion in the mass spectrum, IR spectroscopy, and multinuclear NMR spectroscopy. The ^1H NMR spectrum in d_8-THF shows two resonances at δ 1.58 and 1.53 in the integrated ratio 2:1 corresponding to bridging and terminal $N^tC_4H_9$ groups, respectively. Consistently, the ^{13}C NMR spectrum also shows two different types of N^tBu groups. The ^{125}Te NMR spectrum of **3** exhibits two singlets at δ 1575 and 1693. The former is tentatively assigned to the $TeCl_2$ group by comparison with the chemical shifts for $[(Me_3Si)_2N]_2TeCl_2$[20] and $(Ph_3PN)_2TeCl_2$,[21b] δ 1510 and 1604, respectively. However, these NMR spectra were recorded in different solvents. The spectroscopic data for **3** are consistent with the formulation $^tBuNTe(\mu\text{-}N^tBu)_2TeCl_2$, and the high solubility of **3** in organic solvents suggests that chloride bridges, if they exist, are very weak. Thus, it can be viewed as the cycloaddition product of the putative monomers $^tBuN{=}Te{=}N^tBu$ and $^tBuN{=}TeCl_2$.

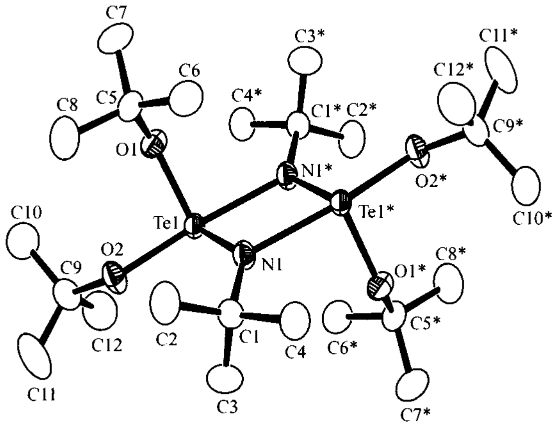


Figure 4. ORTEP drawing (50% probability ellipsoids) and atomic numbering scheme for $(^tBuO)_2Te(\mu\text{-}N^tBu)_2Te(O^tBu)_2$ (**4**). *Symmetry transformation: $-x, -y, -z + 1$.

Finally we note that the reaction of equimolar amounts of the tellurium diimide dimer **1** and **2a** in THF produces **3** quantitatively, as demonstrated by the ^1H NMR spectrum of the reaction mixture. The disadvantage of this synthesis of **3** compared to the method shown in eq 3 is that it requires the prior preparation of **2a**.

Preparation and X-ray Structure of (^{t}BuO)$_2$Te(μ-N^{t}Bu)$_2$Te(O^{t}Bu)$_2$ (4). The imidotellurium dichloride **2a** is a potentially useful reagent for the development of Te−N chemistry. As an example, the metathetical reaction of **2a** with 2 equiv of potassium *tert*-butoxide proceeds smoothly in THF at room temperature to give **4** in 71% yield (eq 4). The product **4** is

$$(^2/_6)(^tBuNTeCl_2)_6 + 4KO^tBu \rightarrow (^tBuO)_2Te(\mu\text{-}N^tBu)_2Te(O^tBu)_2 + 4KCl \quad (4)$$

4

obtained as a yellow powder, which is soluble in *n*-pentane, hexane, diethyl ether, and THF. Exposure of solutions of **4** to air produces a fine black precipitate, presumably elemental tellurium. The ^1H NMR spectrum of **4** shows two singlets at δ 1.44 and 1.74 in the integrated ratio 2:1, which are readily assigned to the *tert*-C_4H_9 groups bound to O and N, respectively. The ^{13}C NMR spectrum also exhibits two types of $-C(CH_3)_3$ groups with δ 33.6 and 76.9 $[OC(CH_3)_3]$ and δ 35.3 and 60.8 $[NC(CH_3)_3]$. The ^{125}Te NMR spectrum of **4** in C_7H_8 shows a broad resonance at δ 1620.

An X-ray structural determination of **4** revealed a centrosymmetric dimeric structure (Figure 4). Selected bond distances and bond angles are given in Table 3. The Te_2N_2 ring is a perfectly

---

(20) Pietikäinen, J.; Laitinen, R. S.; Valkonen, J. *Acta Chem. Scand.*, in press.

(21) (a) Folkerts, H.; Dehnicke, K.; Magull, J. *Z. Naturforsch., Sect. B* **1995**, *50b*, 573. (b) Roesky, H. W.; Münzenberg, J.; Bohra, R.; Noltemeyer, M. *J. Organomet. Chem.* **1991**, *418*, 339.

(22) Münzenberg, J.; Roesky, H. W.; Noltemeyer, M.; Besser, S.; Herbst-Irmer, R. *Z. Naturforsch., Sect. B* **1993**, *B48*, 199.

(23) Koch, H.-J.; Roesky, H. W.; Besser, S.; Herbst-Irmer, R. *Chem. Ber.* **1993**, *126*, 571.

(24) (a) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1. (b) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Itaka, NY, 1960; Chapter 7, p 260.

(25) Scherer, O. J.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **1977**, *432*, 173.

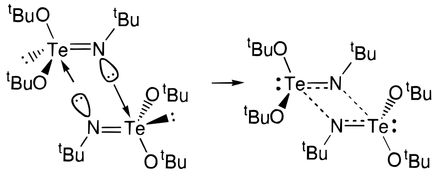
(26) Thrasher, J. S.; Bauknight, C. W., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1985**, *24*, 1598.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

Te(1)−O(1)	1.929(3)	O(1)−C(5)	1.450(6)
Te(1)−O(2)	2.024(3)	O(2)−C(9)	1.455(5)
Te(1)−N(1)	1.943(4)	N(1)−C(1)	1.496(6)
Te(1)−N(1)[a]	2.217(4)		
O(1)−Te(1)−N(1)	108.86(16)	C(5)−O(1)−Te(1)	135.4(3)
O(1)−Te(1)−O(2)	92.54(15)	C(9)−O(2)−Te(1)	121.8(3)
N(1)−Te(1)−O(2)	91.33(15)	C(1)−N(1)−Te(1)	129.7(3)
O(1)−Te(1)−N(1)[a]	89.23(15)	C(1)−N(1)−Te(1)[a]	124.9(3)
N(1)−Te(1)−N(1)[a]	75.90(16)	Te(1)−N(1)−Te(1)[a]	104.1(2)
O(2)−Te(1)−N(1)[a]	166.97(13)		

[a] See footnote *b* in Table 2.

Scheme 1



planar parallelogram (torsion angle N(1)*−Te(1)−N(1)−Te(1)* = 0.0°, ∠(NTeN) = 75.9(2)°, ∠(TeNTe) = 104.1(2)°). There is a substantial (14%) difference in the Te−N bond lengths, which are 1.943(4) and 2.217(4) Å (cf. |*d*(Te−N)| = 2.081(8) Å in **1**).[4] The predicted tellurium(IV)−nitrogen single and double bond values are 2.05 and 1.83 Å, respectively.[27] Thus, the structure of **4** can be viewed as two ^{t}BuN═Te(O^{t}Bu)$_2$ monomers associated through a weaker interaction than that observed in tellurium diimide dimers.[4,5] Although the axial Te−N bonds are expected to be longer than their equatorial counterparts, the substantial inequality in the Te−N bond distances suggests that the monomer units retain substantial double bond character. This idea is reinforced by the fact that the bridging nitrogen atoms in **4** are almost planar (∑∠(N(1)) = 358.7°; cf. |∑∠(N$_{\text{bridging}}$)| = 341.9° in **1**[4]). A schematic depiction of the dimerization of two (^{t}BuO)$_2$Te═N^{t}Bu monomers is shown in Scheme 1. It is conceivable that sufficiently bulky alkoxy or aryloxy groups attached to tellurium could stabilize a monomeric tellurium imide.

The tellurium atoms in **4** adopt a seesaw (pseudo-trigonal-bipyramidal) geometry in which the axial sites are occupied by one O^{t}Bu group and one N^{t}Bu group. The equatorial positions are occupied by one O^{t}Bu group, one N^{t}Bu group, and a lone pair whose influence is evident from the values of ∠O(2)−Te(1)-N(1)*) and ∠O(1)−Te(1)−N(1)), which are 167.0(1)° and 108.9(2)°, respectively. The axial and equatorial Te−O bond lengths, 2.024(3) vs 1.929(3) Å differ by 5%, a difference substantially smaller than that observed for the Te−N distances. The apparent equivalence of the axial and equatorial O^{t}Bu groups in the ^{1}H NMR spectrum of **4** at room temperature might indicate a facile exchange process similar to that established for tetraalkoxytelluranes.[28,29] Although the O^{t}Bu resonance is broadened at 195 K, it does not resolve into two separate peaks. Thus, the activation energy for the exchange process must be very low. The alternative explanation that the two resonances are isochronous seems less likely.

Conclusions

The facile preparation of the imidotellurium dichloride [Cl$_2$Te(μ-N^{t}Bu)$_2$TeCl$_2$]$_3$ provides a useful new reagent for the development of Te−N chemistry as exemplified by the preparation of (^{t}BuO)$_2$Te(μ-N^{t}Bu)$_2$Te(O^{t}Bu)$_2$. The structure of this dimeric bisalkoxytellurium imide suggests the possibility of generating a monomeric tellurium imide by the attachment of sufficiently bulky OR or OAr groups to tellurium.

Acknowledgment. We thank NSERC (Canada) for financial support and Professor R. S. Laitinen for a preprint of ref 20 prior to publication.

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

IC990849K

---

(27) Björgvinsson, M.; Roesky, H. W. *Polyhedron* **1991**, *10*, 2353.

(28) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Hsu, Y. F. *J. Am. Chem. Soc.* **1981**, *103*, 2340.

(29) Gottlieb, H. E.; Hoz, S.; Elyashiv, I.; Albeck, M. *Inorg. Chem.* **1994**, *33*, 808.