Investigations of the $TeCl_4$−^tBuNHLi Reaction: Synthesis, X-ray Structures, and Fluxional Behavior of the Tellurium−Nitrogen Compounds $[Li_2Te(N^tBu)_3]_2$, $\{[LiTe(N^tBu)_2(NH^tBu)]_2LiCl\}_2$, and $\{Te_2(N^tBu)_4[LiTe(N^tBu)_2(NH^tBu)]LiCl\}_2$

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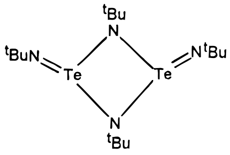
The reaction of ^tBuNHLi with $TeCl_4$ in toluene at −78 °C produces $^tBuNTe(\mu\text{-}N^tBu)_2TeN^tBu$ (**1**) (55%) or $[(^tBuNH)Te(\mu\text{-}N^tBu)_2TeN^tBu]Cl$ (**2**) (65%) for 4:1 or 7:2 molar ratios, respectively. The complex $\{Te_2(N^tBu)_4[LiTe(N^tBu)_2(NH^tBu)]LiCl\}_2$ (**5**) is obtained as a minor product (23%) from the 4:1 reaction. It is a centrosymmetric dimer in which each half consists of the tellurium diimide dimer **1** bonded through an exocyclic nitrogen atom to a molecule of $LiTe(N^tBu)_2(NH^tBu)$ which, in turn, is linked to a LiCl molecule. Crystals of **5** are monoclinic, of space group $C2/c$, with $a = 27.680(6)$ Å, $b = 23.662(3)$ Å, $c = 12.989(2)$ Å, $\beta = 96.32(2)°$, $V = 8455(2)$ Å^3, and $Z = 4$. The final R and R_w values were 0.046 and 0.047. At 65 °C in toluene solution, **5** dissociates into **1**, LiCl, and $\{[LiTe(N^tBu)_2(NH^tBu)]_2LiCl\}_2$ (**4**), which may also be prepared by treatment of $[Li_2Te(N^tBu)_3]_2$ (**6**) with 2 equiv of HCl gas. The centrosymmetric structure of **6** consists of a distorted hexagonal prism involving two pyramidal $Te(N^tBu)_3^{2-}$ anions linked by four Li atoms to give a $Te_2N_6Li_4$ cluster. Crystals of **6** are monoclinic, of space group $P2_1/c$, with $a = 10.194(2)$ Å, $b = 17.135(3)$ Å, $c = 10.482(2)$ Å, $\beta = 109.21(1)°$, $V = 1729.0(5)$ Å^3, and $Z = 2$. The final R and R_w values were 0.026 and 0.023. VT ^1H and ^7Li NMR studies reveal that, unlike **1**, compounds **2**, **4**, and **6** are fluxional molecules. Possible mechanisms for these fluxional processes are discussed.

Introduction

The history of tellurium−nitrogen (Te−N) chemistry dates back more than 70 years to the report of the synthesis of an explosive binary tellurium nitride (probably Te_3N_4) from $TeBr_4$ and liquid ammonia.[1] Although the structure of Te_3N_4 is still unknown,[2] several novel Te(IV)−N compounds were recently prepared from the reactions of $TeCl_4$ with Si−N reagents and structurally characterized. In 1990, Roesky et al. described the reaction of $TeCl_4$ with $Me_3SiNSNSiMe_3$ to give $N[Te(NSN)Cl]_3{\cdot}3DMF$, which contains the μ_3-nitrido Te_3N_4 structural motif.[3] In related work, Haas et al. have shown that $TeCl_4$ reacts with Me_3SiNSO to give $Cl_{4-x}Te(NSN)_xTeCl_{4-x}$ ($x = 1, 2$).[4] Lithiated or silylated amine derivatives may also be used to incorporate carbon[5a] or phosphorus[5b] into Te(IV)−N rings. The reaction of $N(SiMe_3)_3$ with 2 equiv of $TeCl_4$, followed by treatment with AsF_5, yields the dimeric Te(IV) cation $[Cl_3TeN[\mu\text{-}Te(Cl)]_2NTeCl_3]^{2+}$, the first N−Te−Cl cation, presumably via "$TeNCl_5$".[6] By contrast, the reaction of $TeCl_4$ with 4 equiv of $LiN(SiMe_3)_2$ results in reduction to the tellurium(II) compound $Te[N(SiMe_3)_2]_2$,[7a] which may be oxidized with AsF_5 to the corresponding cation radical.[7b]

The reactions of $^tBuNH_2$ with sulfur(IV) or selenium(IV) halides provide a facile route to the corresponding chalcogen diimides $^tBuN{=}E{=}N^tBu$ (E = S,[8] Se[9]). In a preliminary communication,[10] we reported that the treatment of $TeCl_4$ with ^tBuNHLi generates the three products **1**−**3** in amounts that depend on the molar ratio of the reactants.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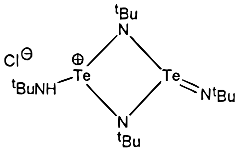
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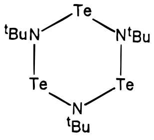
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Further investigations of this reaction have now revealed the formation of two other Te−N compounds **4** and **5**. The complex **5** has previously been obtained by the treatment of $[Li_2Te(N^tBu)_3]_2$, **6**, with anhydrous HCl gas.[11] In this article we report the full details of our studies of the products of the $TeCl_4$−^tBuNHLi system including (a) new synthetic procedures for **1** and **2**, (b) the isolation and characterization of **4** and **5**, (c) the X-ray structure of **5**, (d) an improved structure of **6** (the structure described in the preliminary report[12] was disordered), and (e) variable-temperature ^1H and ^7Li NMR studies of the fluxional molecules **2**, **4**, and **6**.

Experimental Section

$TeCl_4$ (Aldrich) was used as received. ^tBuNHLi was prepared from anhydrous $^tBuNH_2$ (commercial sample dried over molecular sieves) and ^nBuLi in hexane (Aldrich). $[Li_2Te(N^tBu)_3]_2$ was prepared from $Te_2(N^tBu)_4$[10] and ^tBuNHLi by the literature procedure.[12] Solvents were

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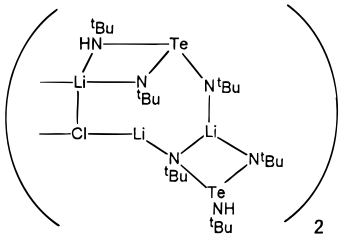

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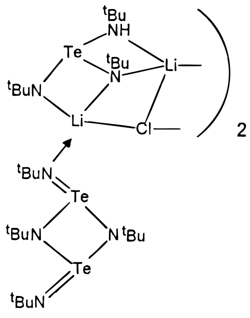

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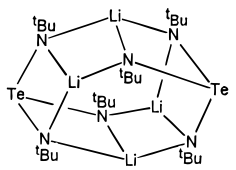

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dried with the appropriate drying agents and distilled immediately before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of argon.

^{1}H NMR spectra were recorded on Bruker ACE 200 and AMX 400 spectrometers, and chemical shifts are reported relative to Me$_4$Si in C$_6$D$_6$ or C$_6$D$_5$CD$_3$. ^{7}Li NMR spectra were obtained on a Bruker AMX 400 spectrometer at 155.508 MHz, and chemical shifts are given relative to 1.0 M LiClO$_4$ in D$_2$O. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, The University of Calgary.

Preparation of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (1). Solid ^{t}BuNHLi (11.90 g, 148.6 mmol) was added to a solution of TeCl$_4$ (10.0 g, 37.1 mmol) in toluene (170 mL) at −78 °C. The mixture was stirred at −78 °C for 12 h and then allowed to reach room temperature. The orange slurry was centrifuged, and the supernatant was decanted into a flask in an N$_2$-filled glovebox. The remaining orange solid was treated with toluene (100 mL), and the resultant slurry was centrifuged. The ^{1}H NMR spectrum of a small aliquot of the combined toluene solutions show it to contain mainly Te$_2$(N^{t}Bu)$_4$ (**1**), a small amount of {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]$_2$}, and a trace of (TeN^{t}Bu)$_3$ (**3**). The solution was heated at 60 °C for 24 h, and the solvent was removed under vacuum. The solid residue was extracted with hexanes (300 mL). The solution was filtered, and the filtrate volume was reduced to *ca.* 10 mL, whereupon orange crystals formed. These crystals were redissolved by warming the concentrated hexane solution slightly. After 24 h at 23 °C, the hexane solution produced orange crystals of pure **1**, which were separated from the mixture by decantation, washed quickly with cold pentane (10 mL), and dried under vacuum. A second crop of **1** was obtained by removing hexane from the mother liquor under vacuum, dissolving the residue in toluene (20 mL), heating the toluene solution to 60 °C for 24 h, removing toluene under vacuum, and extracting the residue with hexanes, followed by crystallization at 23 °C. The combined yield of **1** was 5.5 g, 55%. Anal. Calcd for C$_{16}$H$_{36}$N$_4$Te$_2$: C, 35.61; H, 6.72; N, 10.38. Found: C, 35.74; H, 6.74; N, 10.37. The ^{1}H NMR data were identical to those previously reported for **1**.[10]

Preparation of [(^{t}BuNH)Te(μ-N^{t}Bu)$_2$TeN^{t}Bu]Cl (2). Solid ^{t}BuNHLi (3.12 g, 39.0 mmol) was added to a solution of TeCl$_4$ (3.00 g, 11.1 mmol) at −78 °C. The mixture was stirred for 12 h at −78 °C. Solvent was removed from the orange slurry under vacuum, and the residue was extracted with CH$_2$Cl$_2$ (150 mL). The CH$_2$Cl$_2$ solution was filtered through a fine frit to remove LiCl, and the filtrate was pumped to dryness. The residue was dissolved in THF (60 mL), and the resultant solution was pumped slowly to dryness while the product crystallized. The solid was treated with hexanes (50 mL), and the slurry was filtered to give **2** as a yellow solid, which was washed with hexanes (3 × 15 mL) and dried under vacuum. The yield of pure **2** was 2.0 g, 65%. Anal. Calcd for C$_{16}$ H$_{37}$ClN$_4$Te$_2$: C, 33.35; H, 6.47; N, 9.72. Found: C, 32.74; H, 5.87; N, 9.48. The ^{1}H NMR data were in good agreement with those reported for **2** in ref 10.

Table 1. Crystallographic Data for **5** and **6**

	5	**6**
formula	(C$_{28}$H$_{64}$Li$_2$N$_7$ClTe$_3$)$_2$	(C$_{12}$H$_{27}$N$_3$TeLi$_2$)$_2$
fw	1862.00	709.70
space group	*C*2/*c* (No. 15)	*P*2$_1$/*c* (No. 14)
a, Å	27.680(6)	10.194(2)
b, Å	23.662(3)	17.135(3)
c, Å	12.989(2)	10.482(2)
β, deg	96.32(2)	109.21(1)
V, Å^3	8455(2)	1729.0(5)
Z	4	2
T, °C	−73	−73
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.463	1.363
μ, cm^{-1}	21.44	17.07
R[a]	0.046	0.026
R$_w$[b]	0.047	0.023

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$.

Preparation of {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$ (5). A toluene/hexane solution of LiNH^{t}Bu [prepared from ^{t}BuNH$_2$ (15.80 mL, 150.3 mmol) and ^{n}BuLi (2.5 M in hexanes, 60.1 mL)] was added to a solution of TeCl$_4$ (10.0 g, 37.1 mmol) in toluene (250 mL) at −78 °C. The mixture was stirred and allowed to reach 23 °C slowly (1.5 h) and then stirred for a further 3 h. The orange slurry was centrifuged to separate the supernatant and the solid residue, which was then treated with toluene (200 mL), and the resultant slurry was centrifuged again. The combined toluene extracts were pumped to dryness. The residue was washed with hexanes (2 × 150 mL) to give an orange solid (1.0 g). The hexane washings were concentrated to 30 mL and then cooled to 5 °C to give orange crystals, which were washed with cold hexanes (−10 °C, 3 × 20 mL) and dried under vacuum. The combined yield of {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$ (**5**) was 2.7 g (23% based on TeCl$_4$). Anal. Calcd for C$_{28}$H$_{64}$ClLi$_2$N$_7$Te$_3$: C, 36.12; H, 6.93; N, 10.53. Found: C, 34.27; H, 6.77; N, 10.23. ^{1}H NMR (in C$_6$D$_6$, 296 K): δ 2.18 (s, br, 1H), 1.68 (s, 9H), 1.58 (s, br, 27H), 1.36 (s, 9H), 1.28 (s, 18H). ^{7}Li NMR (in C$_6$D$_6$, 296 K): δ 2.23 (s). X-ray-quality crystals of **5** were obtained from a saturated hexane solution at 23 °C after 1 month.

Preparation of {[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]$_2$LiCl}$_2$ (4). (a) Decomposition of {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$ (5). A solution of **5** (1.00 g, 0.537 mmol) in toluene was heated at 65 °C for 2 h. The solution was cooled to 23 °C and filtered. Solvent was removed from the filtrate under vacuum, and the residue was dissolved in hexanes (80 mL). The resulting solution was allowed to evaporate slowly under an atmosphere of N$_2$ to give large yellow crystals of **4** (0.378 g, 0.255 mmol, 95%), which were washed with hexanes (3 × 15 mL) and dried under vacuum. ^{1}H NMR (in C$_7$D$_8$, 300−340 K): δ 2.09 (s, br, 1H), 1.54 (s, br, 18H), 1.34 (s, 9H). ^{7}Li NMR (in C$_7$D$_8$, 296 K): δ 2.17 (s). Anal. Calcd for C$_{24}$H$_{56}$ClLi$_3$N$_6$Te$_2$: C, 38.94; H, 7.63; N, 11.35. Found: C, 38.67; H, 7.55; N, 11.44.

(b) Reaction of [Li$_2$Te(N^{t}Bu)$_3$]$_2$ with HCl Gas. Dry HCl gas (10.70 mL at 296K and 1 atm, 0.440 mmol) was added slowly to a stirred solution of [Li$_2$Te(N^{t}Bu)$_3$]$_2$ (0.156 g, 0.220 mmol) in toluene (30 mL) at −78 °C. The pale yellow reaction mixture was allowed to reach 23 °C and filtered, and the filtrate was pumped to dryness. The yield of **4** was 0.148 g, 91%. The ^{1}H and ^{7}Li NMR spectra were in good agreement with the spectra of **4** prepared by method a.

X-ray Analyses. (a) 5. A dark red prism (0.60 × 0.60 × 0.50 mm) of **5** was obtained from hexane solution at 23 °C and was mounted in a capillary tube. All measurements were made on a Rigaku AFC6S diffractometer. Cell constants and an orientation matrix obtained from a least-squares refinement using the setting angles of 25 reflections with 2θ in the range 30−40° corresponded to a *C*-centered monoclinic cell. Crystal data are given in Table 1. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 8.0°/min, scan width (1.63 + 0.34 tan θ)°, and monochromatic Mo Kα radiation in the range 4.0 < 2θ < 50.0°. The intensities of 7721 reflections were measured, of which 5212 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects. The positional parameters are given in Table 2. The structure was solved by direct methods[13] and expanded using Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In

Table 2. Positional Parameters and B(eq) Values for **5**

atom	x	y	z	B_{eq}, Å^2
Te(1)	0.12323(2)	0.14025(3)	0.70927(5)	2.32(1)
Te(2)	0.19815(3)	0.04575(3)	0.80611(5)	2.84(2)
Te(3)	0.00670(2)	0.30680(3)	0.42348(5)	2.40(2)
Cl(1)	0.06647(9)	0.2716(1)	0.7389(2)	2.90(6)
N(1)	0.1349(3)	0.0554(3)	0.7085(6)	2.4(2)
N(2)	0.1939(3)	0.1315(3)	0.7806(6)	3.2(2)
N(3)	0.1248(3)	0.1696(3)	0.5742(5)	2.4(2)
N(4)	0.2406(3)	0.0257(4)	0.7093(7)	4.6(3)
N(5)	0.0000(3)	0.2393(3)	0.5059(5)	2.3(2)
N(6)	−0.0129(3)	0.3558(3)	0.5252(6)	2.6(2)
N(7)	0.0758(3)	0.3087(3)	0.4628(6)	2.4(2)
C(1)	0.0978(4)	0.0115(4)	0.6961(8)	3.3(3)
C(2)	0.1213(5)	−0.0436(5)	0.6666(13)	7.6(4)
C(3)	0.0731(5)	0.0015(6)	0.7946(10)	6.8(4)
C(4)	0.0594(5)	0.0284(5)	0.6088(9)	5.1(4)
C(5)	0.2155(5)	0.1729(5)	0.8578(9)	4.5(3)
C(6)	0.2085(5)	0.2314(5)	0.8129(11)	7.1(4)
C(7)	0.2700(5)	0.1605(5)	0.8763(11)	6.6(4)
C(8)	0.1947(5)	0.1710(6)	0.9608(11)	7.9(5)
C(9)	0.1593(4)	0.1558(4)	0.4984(8)	3.1(3)
C(10)	0.1712(5)	0.0944(5)	0.4900(9)	5.0(3)
C(11)	0.2075(5)	0.1883(6)	0.5278(10)	7.1(5)
C(12)	0.1382(4)	0.1769(5)	0.3946(8)	4.7(3)
C(13)	0.2786(4)	−0.0178(5)	0.7290(9)	4.0(3)
C(14)	0.2944(7)	−0.0300(8)	0.6234(13)	11.7(7)
C(15)	0.3230(6)	0.0057(7)	0.7902(14)	10.2(6)
C(16)	0.2621(6)	−0.0707(6)	0.7734(19)	14.9(8)
C(17)	−0.0275(4)	0.1905(4)	0.4624(7)	2.8(2)
C(18)	0.0045(4)	0.1527(5)	0.3997(9)	5.0(4)
C(19)	−0.0391(5)	0.1554(5)	0.5539(9)	5.1(4)
C(20)	−0.0743(5)	0.2059(5)	0.3957(10)	5.7(4)
C(21)	−0.0558(4)	0.3944(4)	0.5320(8)	3.2(3)
C(22)	−0.0579(4)	0.4255(5)	0.6350(9)	4.5(3)
C(23)	−0.0524(4)	0.4390(4)	0.4472(9)	4.1(3)
C(24)	−0.1023(4)	0.3598(5)	0.5059(9)	4.2(3)
C(25)	0.1048(4)	0.3535(4)	0.4270(9)	3.3(3)
C(26)	0.0887(7)	0.4111(6)	0.4388(23)	19(1)
C(27)	0.1140(9)	0.3481(10)	0.3176(13)	17.0(9)
C(28)	0.1537(6)	0.3508(8)	0.4771(18)	14.5(8)
Li(1)	−0.0112(6)	0.2802(7)	0.6389(12)	2.8(4)
Li(2)	0.0772(6)	0.2404(7)	0.5561(12)	2.8(4)

the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Waber,[15] and allowance was made for anomalous dispersion.[16] All calculations were performed using teXsan.[17]

(b) 6. A colorless plate (0.66 × 0.40 × 0.17 mm) of **6** was obtained by recrystallization from toluene at −20 °C.[18] Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares fit of the setting angles of 25 reflections with 2θ in the range 19.7−40°. Crystal data are given in Table 1. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 8.0°/min, scan width $(1.63 + 0.34 \tan \theta)°$, Mo Kα radiation in the range $4.0 < 2\theta < 50.0°$. The intensities of 3186 reflections were measured, of which 1899 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects. The positional parameters are given in Table 3. The structure was solved and expanded by using Fourier techniques.[14] Refinement was carried out in a manner similar to that described for **5**.

Table 3. Positional Parameters and B(eq) Values for **6**

atom	x	y	z	B_{eq}, Å^2
Te(1)	0.23567(3)	0.00399(2)	0.45298(3)	2.460(6)
N(1)	0.3666(4)	−0.0395(2)	0.6218(3)	2.70(9)
N(2)	0.3464(4)	0.0937(2)	0.4284(4)	3.04(10)
N(3)	0.6911(4)	0.0656(2)	0.6581(4)	2.65(9)
C(1)	0.3186(5)	−0.0449(3)	0.7410(5)	2.8(1)
C(2)	0.2813(7)	0.0351(4)	0.7843(6)	5.9(2)
C(3)	0.1930(6)	−0.0981(4)	0.7150(6)	5.7(2)
C(4)	0.4401(6)	−0.0788(4)	0.8548(5)	4.9(2)
C(5)	0.2712(5)	0.1681(3)	0.3835(5)	3.1(1)
C(6)	0.3833(6)	0.2278(3)	0.3858(6)	5.1(2)
C(7)	0.1684(6)	0.1625(3)	0.2402(6)	4.4(2)
C(8)	0.1950(6)	0.1960(3)	0.4775(6)	5.1(2)
C(9)	0.7885(5)	0.1175(3)	0.7571(5)	3.3(1)
C(10)	0.8621(7)	0.1736(4)	0.6915(7)	6.2(2)
C(11)	0.8970(7)	0.0721(4)	0.8669(6)	7.4(2)
C(12)	0.6994(7)	0.1635(3)	0.8224(6)	5.2(2)
Li(1)	0.5668(9)	−0.0174(7)	0.6854(9)	4.8(3)
Li(2)	0.5508(9)	0.1097(5)	0.4939(9)	4.0(2)

Results and Discussion

Syntheses of ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN^{t}Bu (1) and [(^{t}BuNH)Te((μ-N^{t}Bu)$_2$TeN^{t}Bu]Cl (2). The reaction of ^{t}BuNHLi with TeCl$_4$ provides a rich source of Te−N compounds, none of which have S or Se analogues. The products obtained depend markedly upon reaction conditions, especially the molar ratio of reagents. In a preliminary communication,[10] we reported that the tellurium diimide dimer **1** is the major product (41%) when this reaction is carried out in a 4:1 molar ratio, while the HCl adduct **2** is obtained in 63% yield for a 7:2 molar ratio. In both reactions the cyclic tellurium(II) imide [Te(N^{t}Bu)]$_3$ (**3**) was obtained as a minor product. In view of the importance of **1** for the development of Te−N chemistry, we have varied the reaction conditions in order to optimize the yields of this reagent. We find that the yield of **1** can be increased to 55% if ^{t}BuNHLi is added as a *solid* to a slurry of TeCl$_4$ in toluene at −78 °C and the reaction is allowed to proceed slowly at this temperature. This procedure minimizes the amount of the tellurium (II) heterocycle (**3**) that is formed, but another product {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$ (**5**) can be detected in the reaction mixture by ^{1}H NMR. The isolation and X-ray structure of this new complex are described below. The improved synthetic protocol gives **2** in 65% yield when a 7:2 molar ratio (^{t}BuNHLi:TeCl$_4$) is used.

Synthesis and X-ray Structure of {Te$_2$(N^{t}Bu)$_4$[LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]LiCl}$_2$ (5). Complex **5** was isolated in 23% yield when the reaction of a toluene solution of ^{t}BuNHLi with TeCl$_4$ was carried out in a 4:1 molar ratio in toluene at −78 °C followed by warming to 23 °C. The procedure for the separation of **5** from **1**, the major product, and **3** depends on the very limited solubility of **5** in cold hexanes (see Experimental Section). Both **1** and **3** are very soluble in cold hexanes.

The ^{1}H NMR spectra of **5** in the temperature range 190−300 K revealed a very complex fluxional behavior. However, at 300 K the ^{1}H NMR spectrum showed singlets at δ 1.68, 1.58, 1.36, and 1.28 with relative intensities 1:3:1:2, indicating the presence of *seven* ^{t}Bu groups, and a broad singlet at δ 2.18 attributable, on the basis of its relative intensity, to an NH proton.

The structure of **5** was determined by X-ray diffraction, and an ORTEP diagram is depicted in Figure 1. Selected bond lengths and bond angles are given in Table 4. Complex **5** is a centrosymmetric dimer. Each half of the dimer consists of one molecule each of Te$_2$(N^{t}Bu)$_4$, LiTe(N^{t}Bu)$_2$(NH^{t}Bu), and LiCl. The tellurium diimide dimer Te$_2$(N^{t}Bu)$_4$ is linked through one of its exocyclic N atoms to the Li atom of LiTe(N^{t}Bu)$_2$(NH^{t}Bu) which, in turn, is chelated to the Li atom of a LiCl molecule. The halves of the dimer are connected through a

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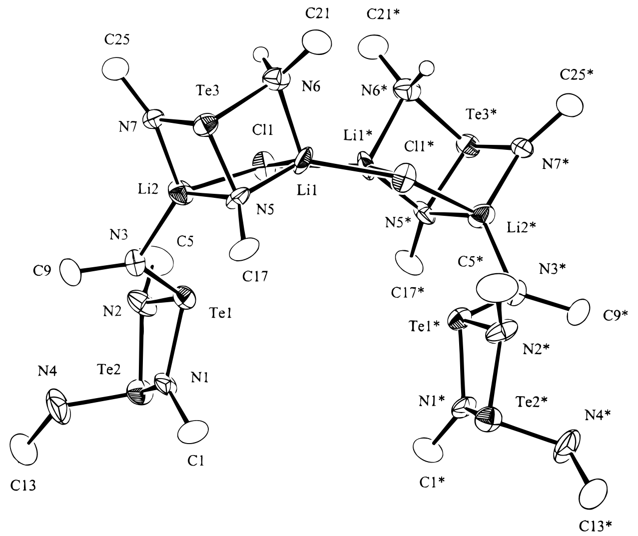

Figure 1. ORTEP diagram and atomic numbering scheme for $\{Te_2(N^tBu)_4[LiTe(N^tBu)_2(NH^tBu)]LiCl\}_2$ (**5**). For clarity only the α-carbon atoms of ^tBu groups are shown.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) in **5**[a]

	Bond Lengths		
Te(1)−N(1)	2.035(7)	Te(1)−N(2)	2.079(8)
Te(1)−N(3)	1.892(7)	Te(2)−N(1)	2.057(7)
Te(2)−N(2)	2.058(8)	Te(2)−N(4)	1.874(8)
Te(3)−N(5)	1.944(7)	Te(3)−N(6)	2.081(7)
Te(3)−N(7)	1.926(7)	Cl(1)−Li(1)	2.39(2)
Cl(1)−Li(1*)	2.33(1)	Cl(1)−Li(2)	2.53(2)
N(1)−C(1)	1.46(1)	N(2)−C(5)	1.48(1)
N(3)−C(9)	1.48(1)	N(3)−Li(2)	2.13(2)
N(4)−C(13)	1.47(1)	N(5)−C(17)	1.46(1)
N(5)−Li(1)	2.03(2)	N(5)−Li(2)	2.16(2)
N(6)−C(21)	1.49(1)	N(6)−Li(1)	2.16(2)
N(7)−C(25)	1.44(1)	N(7)−Li(2)	2.02(2)
	Bond Angles		
M(1)−Te(1)−N(2)	76.2(3)	N(1)−Te(1)−N(3)	109.8(3)
N(2)−Te(1)−N(3)	109.4(3)	N(1)−Te(2)−N(2)	76.2(3)
N(1)−Te(2)−N(4)	99.7(3)	N(2)−Te(2)−N(4)	99.8(4)
N(5)−Te(3)−N(6)	89.5(3)	N(5)−Te(3)−N(7)	91.5(3)
N(6)−Te(3)−N(7)	96.9(3)	Li(1)−Cl(1)−Li(1*)	75.2(6)
Li(1)−Cl(1)−Li(2)	73.0(5)	Li(1)−Cl(1)−Li(2)	144.7(6)
Te(1)−N(1)−Te(2)	103.4(3)	Te(1)−N(1)−C(1)	126.4(6)
Te(2)−N(1)−C(1)	122.1(6)	Te(1)−N(2)−Te(2)	101.8(4)
Te(1)−N(2)−C(5)	121.8(7)	Te(2)−N(2)−C(5)	122.0(7)
Te(1)−N(3)−C(9)	128.1(6)	Te(1)−N(3)−Li(2)	108.3(5)
C(9)−N(3)−Li(2)	122.5.(7)	Te(2)−N(4)−C(13)	123.3(7)
Te(3)−N(5)−C(17)	120.9(6)	Te(3)−N(5)−Li(1)	96.3(5)
Te(3)−N(5)−Li(2)	90.3(5)	C(17)−N(5)−Li(1)	125.7(7)
C(17)−N(5)−Li(2)	125.5(7)	Li(1)−N(5)−Li(2)	88.6(7)
Te(3)−N(6)−C(21)	121.6(6)	Te(3)−N(6)−Li(1)	88.5(5)
C(21)−N(6)−Li(1)	122.6(7)	Te(3)−N(7)−C(25)	120.4(6)
Te(3)−N(7)−Li(2)	95.3(6)	C(25)−N(7)−Li(2)	144.2(8)
Cl(1)−Li(1)−Cl(1*)	103.9(6)	Cl(1)−Li(1)−N(5)	102.0(7)
Cl(1)−Li(1)−N(6)	109.8(7)	Cl(1)−Li(1)−N(5)	102.0(7)
Cl(1)−Li(1)−N(6)	109.8(7)	Cl(1)−Li(1)−N(5)	135.2(8)
Cl(1)−Li(1)−N(6)	118.7(8)	Cl(1)−Li(1)−N(5)	135.2(8)
Cl(1)−Li(1)−N(6)	118.7(8)	N(5)−Li(1)−N(6)	85.0(6)
Cl(1)−Li(1)−N(6)	105.1(6)	Cl(1)−Li(2)−N(5)	94.2(6)
Cl(1)−Li(2)−N(7)	109.5(7)	N(3)−Li(2)−N(5)	127.0(9)
N(3)−Li(2)−N(7)	131.8(8)	N(5)−Li(2)−N(7)	82.9(6)

[a] Starred atoms are related to the unstarred atoms by −*x*, *y*, $^3/_2 - z$.

four-membered Li_2Cl_2 ring. The trapping of a LiCl molecule was reported recently for $(^iPr_2NLi)_2LiCl(TMEDA)_2$,[19] but in that case a single LiCl unit bridged the two (dialkylamido)lithium molecules. The structural parameters of the $Te_2(N^tBu)_4$ unit in **5** are not significantly different from those found for the uncoordinated dimer **1**.[10] The endocyclic Te−N bond lengths are in the range 2.035(7)−2.079(8) Å with a mean value of 2.057 Å (*cf.* estimated values of 2.05 and 1.83 Å for single and double tellurium−nitrogen bonds, respectively).[20] The coordination of one of the terminal N^tBu groups has little effect on the exocyclic Te−N bond lengths, which are slightly longer than the estimated double-bond value [Te(1)−N(3) = 1.892(7) and Te(2)−N(4) = 1.874(8) Å]. The pyramidal $Te(N^tBu)_2(NH^tBu)^-$ anion has one long Te−N bond [Te(3)−N(6) = 2.081(7) Å], which involves the ^tBuNH group, and two short Te−N bonds (mean value 1.935(7) Å). Similar trends in Te−N bond lengths were observed for the two different $Te(N^tBu)_2(NH^tBu)^-$ anions in **4**.[11] The pyramidal $Te(N^tBu)_2(NH^tBu)^-$ anion [$\angle N\hat{T}eN$ = 89.5(3)−96.9(3)°] in **5** is chelated unsymmetrically to both lithium atoms Li(1) and Li(2) [*d*(Li−N) = 2.03(2) and 2.16(2) for Li(1), 2.02(2) and 2.16(2) Å for Li(2)]. The Li(2)−Cl(1) distance of 2.53(2) Å is substantially longer than the mean value of 2.36(2) Å in the Li_2Cl_2 ring [*cf.* mean values of 2.38(1) for **4**[11] and 2.408(3) Å for $(^iPr_2NLi)_2LiCl(TMEDA)_2$].[19]

Synthesis of $\{[LiTe(N^tBu)_2(NH^tBu)]_2LiCl\}_2$ (4). Variable-temperature NMR studies of **5** in C_7D_8 revealed that the dimer $Te_2(N^tBu)_4$ is formed by dissociation when the solution is warmed gently. Consequently, we attempted to generate $LiTe(N^tBu)_2(NH^tBu)$ by heating toluene solutions of **5** at 65 °C. This procedure generated **4** in essentially quantitative yield according to eq 1. Complex **4** may also be obtained in >90% yield by

$$2\{Te_2(N^tBu)_4[LiTe(N^tBu)_2(NH^tBu)]\cdot LiCl\}_2 \rightarrow \{[LiTe(N^tBu)_2(NH^tBu)]_2\cdot LiCl\}_2 + 4Te_2(N^tBu)_4 + 2LiCl \quad (1)$$

the treatment of **6** with 2 equiv of dry HCl gas in toluene at −78 °C, and the X-ray structure has been reported.[11]

It is reasonable to envisage that $LiTe(N^tBu)_2(NH^tBu)$ is an intermediate (prior to deprotonation) in the formation of **6** from the reaction of dimer **1** with 4 equiv of ^tBuNHLi.[12] Consequently, we have carried out the reaction of $Te_2(N^tBu)_4$ with 2 equiv of ^tBuNHLi in toluene at −78 °C in an attempt to generate and isolate the $Te(N^tBu)_2(NH^tBu)^-$ anion as its lithium derivative. The ^1H NMR spectrum of the reaction mixture in C_6D_6 revealed the presence of $[Li_2Te(N^tBu)_3]_2$ and unreacted $Te_2(N^tBu)_4$ in addition to resonances at δ 1.35 and 1.50, with relative intensities 1:2, which we tentatively attribute to $LiTe(N^tBu)_2(NH^tBu)$. Unfortunately, this product could not be separated from $[Li_2Te(N^tBu)_3]_2$ because of their similar solubilities.

X-ray Structure and Fluxional Behavior of $[Li_2Te(N^tBu)_3]_2$ (6). We have previously established the hexagonal prismatic structure of the $Te_2N_6Li_4$ cluster in **6**, but the structure was disordered with respect to the positions of two of the lithium atoms.[12] We have now carried out a second structural determination of **6** on a single crystal obtained by recrystallization from toluene of a sample recovered from an unsuccessful reaction of **6**.[18] Although toluene was also used as the recrystallization solvent in the previous structural determination,[11] the new X-ray analysis provides a different space group ($P2_1/c$ vs *Pnma*) with four rather than eight molecules in the unit cell, which is smaller by a factor of *ca.* $^1/_2$ along the *a* axis. The new structure refined to $R = 0.026$ and $R_w = 0.023$. An ORTEP drawing of **6** is shown in Figure 2, and pertinent geometrical data are summarized in Table 5. Although the

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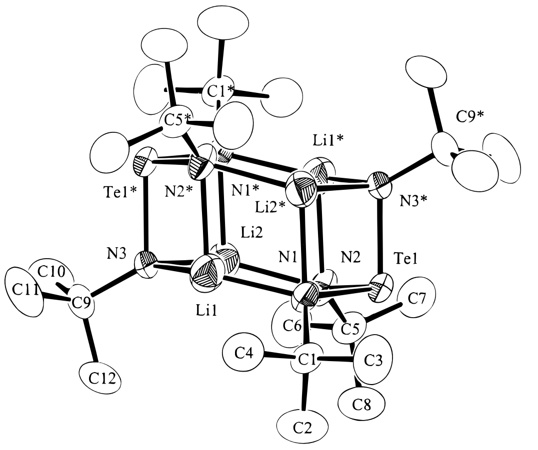

Figure 2. ORTEP diagram and atomic numbering scheme for [Li$_2$Te(N^{t}Bu)$_3$]$_2$ (**6**).

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) in **6**^{a}

Bond Lengths			
Te(1)−N(1)	1.978(4)	Te(1)−N(2)	1.973(4)
Te(1)−N(3*)	1.977(4)	N(1)−C(1)	1.487(5)
N(1)−Li(1)	1.964(9)	N(1)−Li(2*)	2.073(9)
N(2)−C(5)	1.483(6)	N(2)−Li(2)	1.987(10)
N(3)−C(9)	1.474(6)	N(3)−Li(1)	1.99(1)
N(3)−Li(2)	1.990(9)	N(2)−Li(1*)	2.147(10)
Bond Angles			
N(1)−Te(1)−N(2)	99.4(2)	N(1)−Te(1)−N(3*)	91.4(2)
N(2)−Te(1)−N(3*)	92.8(2)	Te(1)−N(1)−C(1)	117.6(3)
Te(1)−N(1)−Li(1)	123.4(3)	Te(1)−N(1)−Li(2*)	88.8(3)
C(1)−N(1)−Li(1)	108.6(4)	C(1)−N(1)−Li(2*)	139.9(4)
Li(1)−N(1)−Li(2*)	74.6(4)	Te(1)−N(2)−C(5)	116.9(3)
Te(1)−N(2)−Li(2)	130.0(3)	C(5)−N(2)−Li(2)	111.4(4)
Te(1)−N(3*)−C(9*)	118.7(3)	Te(1)−N(3*)−Li(1*)	92.0(3)
Te(1)−N(3)−Li(2*)	91.3(3)	C(9)−N(3)−Li(1)	130.1(4)
C(9)−N(3)−Li(2)	120.4(4)	Li(1)−N(3)−Li(2)	94.9(4)
N(1)−Li(1)−N(3)	136.8(6)	N(1)−Li(2*)−N(2*)	107.4(4)
N(1)−Li(2*)−N(3*)	88.4(4)	N(2)−Li(2)−N(3)	128.3(5)
Te(1)−N(2)−Li(1*)	87.5(3)	C(5)−N(2)−Li(1*)	127.7(4)
Li(2)−N(2)−Li(1*)	72.5(4)	N(1)−Li(1)−N(2*)	105.4(5)
N(3)−Li(1)−N(2*)	87.5(3)		

^{a} Starred atoms are related to the unstarred atoms by 1 − *x*, −*y*, 1 − *z*.

structural parameters involving Te atoms [|*d*(Te−N)| = 1.976(4) Å and |∠N−Te−N| = 94.5(2)°] are similar to those previously reported for the disordered structure,[11] the accuracy of the Li−N distances is significantly improved, as might be expected since the disorder involved the Li atoms. Both Li atoms, Li(1) and Li(2), are three-coordinate and form two short Li−N linkages (mean values 1.977(10) and 1.988(10) Å, respectively) and one relatively long Li−N distance (2.147(10) and 2.073(9) Å) in the Te$_2$N$_6$Li$_4$ cluster. The long Li−N bonds connect the two TeNLiNLiN hexagons of the distorted hexagonal prism. Hexagonal prismatic structures based on an A$_6$X$_6$ cluster (A = main group metal, X = non-metal) are known for [(THF)MgNPh]$_6$,[21] (RAlNR′)$_6$,[22] [^{t}BuC(=CH$_2$)OLi]$_6$,[23,24][PhSn(O)(μ-O$_2$CC$_6$H$_{11}$)]$_6$,[25] and (NaO^{t}Bu)$_6$.[26]

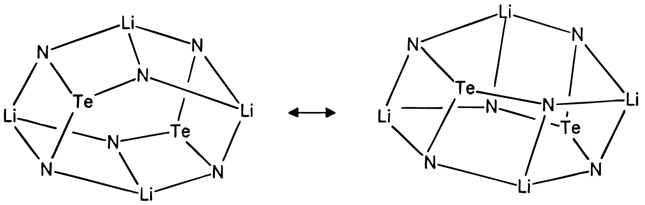

Figure 3. Proposed fluxional process for **6**. ^{t}Bu groups on nitrogen atoms are omitted for clarity.

To our knowledge, **6** represents the first hexagonal prismatic cluster with an A$_4$B$_2$X$_6$ core.[27] It has C_{2h} symmetry with the crystallographically inequivalent lithium atoms, Li(1) and Li(2), related by a C_2 axis which passes through the center of the four-membered Li$_2$N$_2$ rings. Consequently, the ^{7}Li NMR spectrum of **6** in C$_7$D$_8$ solution consists of a singlet at δ 5.7 throughout the temperature range 185−298 K. However, the ^{1}H NMR spectrum (a singlet at δ 1.34) in C$_7$D$_8$ is also invariant within this temperature. On the basis of symmetry considerations, two resonances in the ratio 2:1 are expected for the inequivalent ^{t}Bu groups. Since the dissociation of **6** into monomers in the noncoordinating solvent C$_7$D$_8$ is highly unlikely, we propose the concerted stretching and contraction of the two Li(1)−N(2) interactions between the two six-membered rings of the hexagonal prism, as illustrated in Figure 3, to explain this observation. The Li(1)−N(2) distances of 2.147(10) Å represent the longest and, presumably, weakest lithium−nitrogen bonds. However, a similar process involving the Li(2)−(N(1) bonds would also result in equivalence of all N^{t}Bu Groups. Consistent with the apparently low activation energy for this process, these deformations require a relatively minor perturbation of the Te$_2$N$_6$Li$_4$ cluster.

Fluxional Behavior of 2 and 4. The tellurium diimide dimer **1** exhibits no exchange between bridging and terminal ^{t}BuN groups up to 370 K.[10] By contrast, the protonation of one of the terminal ^{t}BuN groups results in a highly fluxional structure. As indicated in Figure 4, the ^{1}H NMR spectrum of **1** in C$_7$D$_8$ at 298 K exhibits a singlet for all four ^{t}Bu groups at δ 1.63, in addition to the broad resonance for the NH group at δ 4.09. Upon cooling of the solution, the resonance at δ 1.63 broadens and collapses. At 200 K, the expected three resonances for the inequivalent ^{t}Bu groups of the static structure of **2** in the integrated ratio 2:1:1 are observed at δ 1.84, 1.69, and 1.67. On the basis of relative intensities, the former resonance can readily be assigned to the bridging N^{t}Bu groups. Upon warming of the solution back to 298 K, the reverse of these spectral changes is observed. In order to account for the equivalence of all four N^{t}Bu groups, two fluxional processes must be involved. As indicated in Figure 5, we propose a rapid 1,3-proton shift between terminal and bridging nitrogen atoms,[28] followed by exchange between the resultant bridging ^{t}BuNH and a terminal ^{t}BuN group. The protonation of nitrogen atoms in inorganic heterocycles is known to result in a substantial lengthening (and, hence, weakening) of the bonds involving the protonated N atoms.[29,30] In the case of **2**, a 1,3-proton shift would result in a further weakening of the already relatively weak bridging Te−N bonds.

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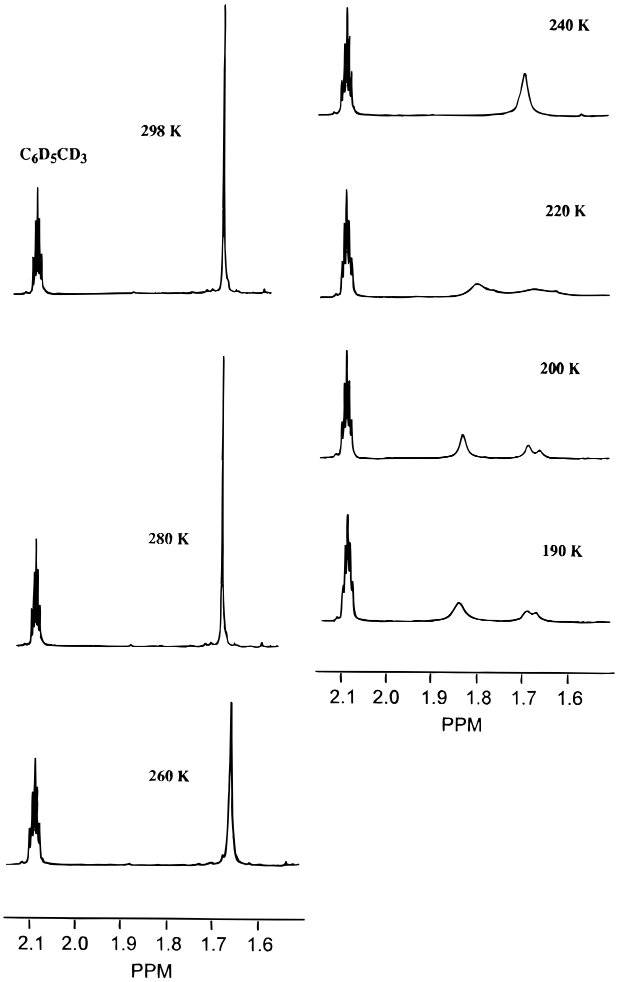

Figure 4. VT ^{1}H NMR spectra for a C$_7$D$_8$ solution of [(^{t}BuNH)Te(μ-N^{t}Bu)$_2$TeN^{t}Bu]Cl (**2**).

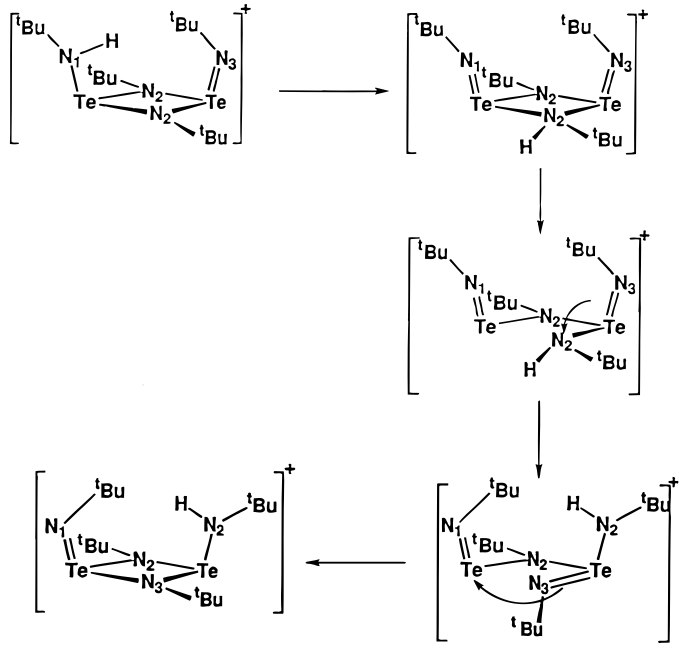

Figure 5. Proposed fluxional processes for **2**.

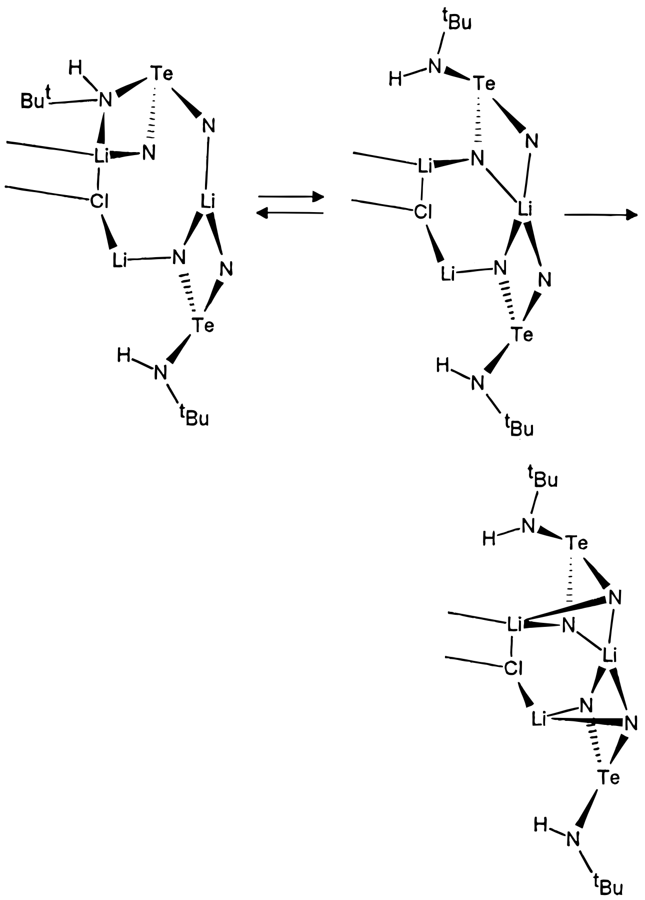

Figure 6. Formation of monomeric [LiTe(N^{t}Bu)$_2$(NH^{t}Bu)]$_2$LiCl.

The VT ^{1}H and ^{7}Li NMR data for **4** in C$_7$D$_8$ (see preliminary communication for details)[11] also indicate a fluxional structure. The changes that are observed are complex but the main features are as follows: (a) the two types of Te(N^{t}Bu)$_2$(NH^{t}Bu)$^-$ anions are not distinguished even at 200 K; (b) three equally intense ^{t}Bu resonances are observed at 200 K, and these collapse to give two resonances (with an integrated ratio of 2:1) upon warming; (c) at 185 K two ^{7}Li resonances are observed with relative intensities 1:2, which collapse to a single resonance at 300 K. The fluxional behavior of **4** may involve a combination of the following processes: (a) Li–N bond breaking and bond formation, (b) rapid proton shifts, and (c) dissociation into monomer units. The precise sequence of events will be difficult to elucidate, but dissociation to a monomeric structure that would account for the low-temperature observation of three equally intense ^{1}H NMR resonances and two ^{7}Li resonances (2:1) is depicted in Figure 6.

Conclusion. The reaction of ^{t}BuNHLi with TeCl$_4$ in a 4:1 molar ratio in toluene provides a rich source of thermally stable Te–N compounds, the most important of which is the tellurium diimide dimer Te$_2$(N^{t}Bu)$_4$, **1**. The HCl adduct **2** and the closely related pair of complexes **4** and **5** can be viewed respectively as the result of a deficiency and an excess of ^{t}BuNHLi in this reaction. Complexes **1**, **2**, **4**, **5**, and **6** are without precedent in chalcogen imide chemistry; they demonstrate the propensity for multiply bonded Te–N compounds to dimerize. The facile fluxional behavior observed for **2**, **4**, and **6** reflects the weakness of certain Te–N bonds combined, in the case of **2**, with rapid proton shifts.

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Supporting Information Available: Tables giving X-ray experimental details, atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances, bond angles, and torsion angles (21 pages). Ordering information is given on any current masthead page.

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