Cooperative THF Ring-Opening by $B(C_6F_5)_3$ and a Tellurium Diimide Dimer

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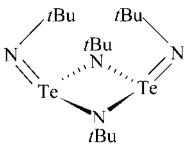
Dedicated to the memory of Professor Ron Snaith

Keywords: N ligands / Ring opening / Lewis acids / Boron / Tellurium

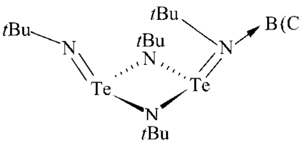
The tellurium diimide dimer [tBuNTe(μ-NtBu)$_2$TeNtBu] (**1**) and $B(C_6F_5)_3$ form a 1:1 adduct which instigates THF ring-opening to give [tBuNTe(μ-NtBu)$_2$TeN(tBu)$(CH_2)_4OB(C_6F_5)_3$] (**3**) quantitatively; complex **3** is also formed rapidly when **1** is added to a THF solution of $B(C_6F_5)_3$.

The perfluorinated borane $B(C_6F_5)_3$ was first reported in 1963.[1] During the past decade this strong Lewis acid has attracted wide attention as a co-catalyst for olefin polymerization.[2] While early work established that $B(C_6F_5)_3$ forms 1:1 adducts with NH_3 and NMe_3,[1] more recent studies with nitrogen bases have included cyano derivatives,[3] imidazole,[4] pyridines,[5] amines,[6] and the anions CN^- [7] and NH_2^-.[8] As part of our studies of the Lewis base behaviour of the tellurium diimide dimer tBuNTe(μ-NtBu)$_2$TeNtBu (**1**),[9] we have investigated the reaction of this bidentate ligand with $B(C_6F_5)_3$. We report here the formation of the 1:1 adduct **2**, which engenders rapid THF ring-opening to produce [tBuNTe(μ-NtBu)$_2$TeN(tBu)$(CH_2)_4OB(C_6F_5)_3$] (**3**). Complex **2** is also generated when **1** is added to a THF solution of $B(C_6F_5)_3$. Although various transition-metal and uranium complexes promote THF ring-opening,[10] main-group element Lewis acids are rarely involved[11,12] and, to the best of our knowledge, this is the first example involving $B(C_6F_5)_3$.

The reaction of **1** with $B(C_6F_5)_3$ in a 1:1 molar ratio in *n*-pentane at 23 °C produced the adduct **2** as a moisture-sensitive yellow-orange adduct in almost quantitative yield. The same reaction with a 1:2 molar ratio affords an equimolar mixture of **2** and $B(C_6F_5)_3$. The ^{11}B NMR chemical shift of **2** ($\delta = -6.1$ ppm) is consistent with the formation of a four-coordinate boron complex [cf. $\delta^{11}_{B} = 59.5$ ppm for $B(C_6F_5)_3$ in CD_2Cl_2].



1



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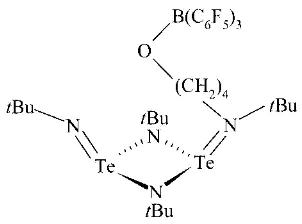

3

An X-ray structural determination of **2**, on crystals obtained from a saturated CH_2Cl_2 solution at −20 °C, confirmed the formation of a 1:1 adduct and revealed a *cis*(*endo*, *exo*) arrangement of the exocyclic NtBu groups (Figure 1).[13] This conformation is also found in **1**·HCl, whereas a *cis*(*endo*, *endo*) arrangement is observed for **1** in the solid state.[14] Pertinent bond lengths and bond angles for **2** are given in the caption to Figure 1. Coordination of **1** to $B(C_6F_5)_3$ lengthens one of the exocyclic Te−N bonds involving the coordinated nitrogen by ca. 0.10 Å, whereas the other exocyclic Te−N bond is unchanged. Concomitantly, the endocyclic Te−N bond lengths involving the tellurium atom connected to the three-coordinate nitrogen are elongated by ca. 0.04 Å. The Te_2N_2 ring is puckered, with a torsion angle N(2)−Te(1)−N(1)−Te(2) of −21.17(11)°, and the geometry at the bridging N atoms is distinctly non-planar $\Sigma\angle$N(1) = 344.8° and $\Sigma\angle$N(2) = 341.3°. The B−N bond length of 1.632(4) Å in **2** is identical to that in $(C_6F_5)_3B\cdot NH_2t$Bu.[15] As indicated in Figure 1 the tellurium atom Te(1) engages in weak Te···F interactions [3.136(2) and 3.112(2) Å; sum of van der Waals radii is 3.53 Å[16]] with one of the *ortho*-fluorine atoms of two C_6F_5 groups. Similar intramolecular M···F contacts have been observed in transition-metal complexes.[17]

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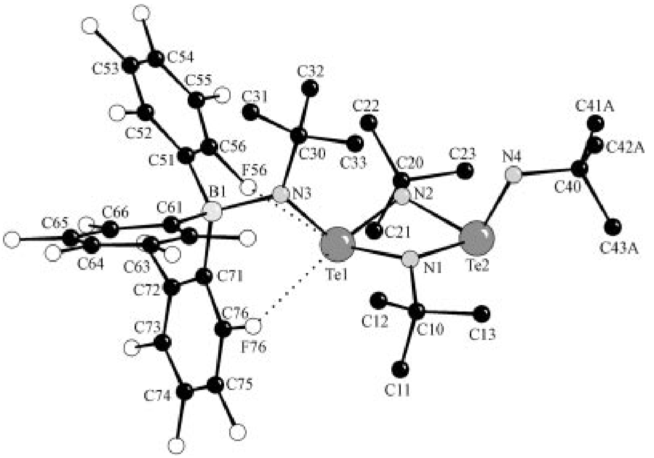


Figure 1. X-ray structure of **2** showing the weak intramolecular Te···F interactions; selected bond lengths (Å) and bond angles (deg): Te(1)−N(1) 2.035(2), Te(1)−N(2) 2.040(2), Te(1)−N(3) 1.970 (2), Te(2)−N(1) 2.061(3), Te(2)−N(2) 2.081(2), Te(2)−N(4) 1.875(3), B(1)−N(3) 1.632(4)

Surprisingly, an attempt to recrystallize **2** from THF/*n*-pentane (1:1) produced X-ray quality orange-yellow needles, within 20 min at 23 °C, of a complex identified as **3** by CHN analysis, multinuclear NMR spectroscopy and an X-ray structural analysis. The ^1H and ^{13}C NMR spectra of **3** in $[D_8]$THF show the characteristic ($CH_2CH_2CH_2CH_2O$) resonances of a ring-opened THF molecule[10d,11] in addition to resonances corresponding to the N*t*Bu groups. In the ^1H NMR spectrum two of these resonances are almost isochronous (δ = 1.479 and 1.477 ppm) and have a relative intensity corresponding to 27 H compared to 9 H for the third resonance at δ = 1.503 ppm. In the ^{13}C NMR spectrum three environments are readily distinguishable because of their well-separated chemical shifts. The ^{11}B NMR chemical shift of this product in $[D_8]$THF is δ = −3.6 ppm. Collectively, the NMR spectroscopic data suggest that complex **2** promotes THF ring-opening to give the adduct **3**, which is isolated in essentially quantitative yield. Subsequently, it was shown that **3** can also be obtained in high yield by addition of a THF solution of **1** to a solution of $B(C_6F_5)_3$ in THF at 23 °C.

X-ray crystallography[18] confirmed the molecular structure of **3** (Figure 2), with the ring-opened THF molecule linked to boron through the oxygen atom and to one of the terminal N*t*Bu groups via a carbon atom. In contrast to **2**, the $(CH_2)_4OB(C_6F_5)_3$ substituent occupies an *endo* position with respect to the Te_2N_2 ring while both terminal N*t*Bu groups are in *exo* configurations. The trends in Te−N bond lengths in **3** compared to those in **1**[14] are similar to, but less pronounced than, those described above for **2**. An interesting feature of the solid-state structure of **3** is the intermolecular Te···F interactions of 2.991(2) and 3.275(2) Å (Figure 2) that produce molecular strands parallel to the *b* axis. These strands are separated by THF solvent molecules. The shorter contact involves Te(1), which has a larger formal positive charge than Te(2) (Scheme 1). The Te_2N_2 ring in **3**, with a torsion angle of 14.0(1)°, is less puckered than that of **1** and **2**, and the geometry at the bridging nitrogen atoms is closer to planarity [$\Sigma\angle N(1) = 352.3°$ and $\Sigma\angle N(2) = 356.8°$]. The B−O bond length in **3** is 1.444(5) Å {cf. 1.480(11) Å in the anion $[HOB(C_6F_5)_3]^-$}.[19]

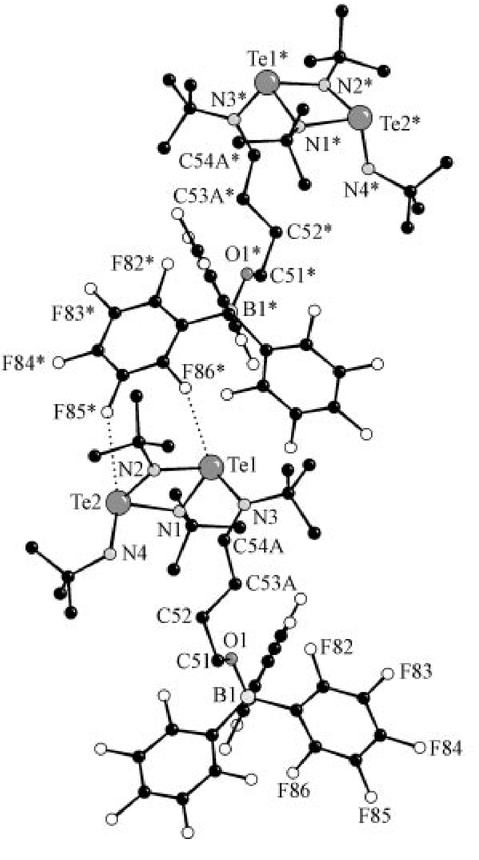
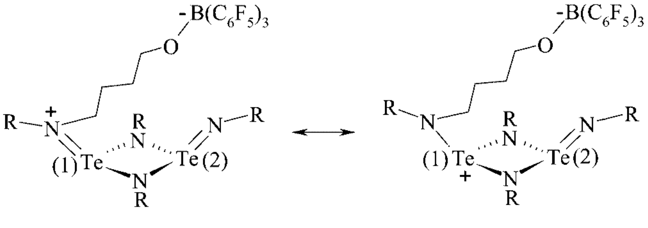


Figure 2. X-ray structure of **3** showing the weak intermolecular Te···F interactions; selected bond lengths (Å) and bond angles (deg): Te(1)−N(1) 2.020(3), Te(1)−N(2) 2.012(3), Te(1)−N(3) 1.922 (3), Te(2)−N(1) 2.036(3), Te(2)−N(2) 2.053(3), Te(2)−N(4) 1.905(3), B(1)−O(1) 1.444(5); the THF molecule in the lattice is not shown



Scheme 1

The NMR spectra for **3** in $[D_8]$THF at 23 °C indicate that the Te···F contacts are not maintained in solution. Thus, the ^{19}F NMR spectrum shows only one set of resonances at δ = 131.3, 163.8 and 166.7 ppm, corresponding to the *ortho*, *para* and *meta* fluorine atoms, respectively, of the three C_6F_5 groups. By contrast, the complex NMR spectra for **2** in CD_2Cl_2 at 23 °C indicate intramolecular Te···F interactions. Thus, the ^{19}F NMR spectrum exhibits multiple resonances in each of the regions characteristic of *ortho*, *meta* and *para*-fluorines of a C_6F_5 group. The ^{13}C NMR spectrum of **2** is especially difficult to assign due to numerous overlapping doublets. The ^1H NMR spectrum of **2** exhibits four equally intense singlets that are consistent with the inequivalence of the bridging N*t*Bu groups as well as the terminal N*t*Bu groups. Variable-temperature NMR studies indicated the presence of conformational isomers, but the spectra could not be unequivocally assigned.

The strong Lewis acid $B(C_6F_5)_3$ forms a complex with THF.[20] Over a few hours at room temperature, the THF is polymerized by $B(C_6F_5)_3$, as reported for some other Lewis acids, for example $AlCl_3$.[21] The addition of **1** to a freshly prepared solution of $B(C_6F_5)_3$ in THF preempts this polymerization and, instead, generates the ring-opened complex **3**. By analogy with transition-metal systems,[10] it is proposed that coordination of the THF oxygen atom to the electrophilic boron centre polarizes the C−O bond so that the α-carbon atom is susceptible to nucleophilic attack. As a result, and in contrast to the THF ring-opening mode observed for $PPh_3/TeBr_4$,[12] the carbon atom of the THF fragment is bonded to the nucleophilic centre in **3**.

Experimental Section

2: A solution of $B(C_6F_5)_3$ (0.285 g, 0.556 mmol) in *n*-pentane (20 mL) was added to an orange-red solution of sublimed [*t*BuNTe(μ-N*t*Bu)$_2$TeN*t*Bu][19] (0.300 g, 0.556 mmol) in *n*-pentane (20 mL) at −78 °C. After 3.5 h at 23 °C the solvent was removed from the reaction mixture under vacuum to give analytically pure [*t*BuNTe(μ-N*t*Bu)$_2$TeN(*t*Bu)B(C_6F_5)$_3$] (0.546 g, 0.519 mmol, 93%) as a yellow-orange solid. $C_{34}H_{36}BF_{15}N_4Te_2$ (1051.68): calcd. C 38.83, H 3.45, N 5.33; found C 38.13, H 3.24, N 4.93. All NMR spectroscopic data were recorded in CD_2Cl_2 solution at 23 °C. ^1H NMR: δ = 1.617 (s, 9 H, *t*Bu), 1.589 (s, 9 H, *t*Bu), 1.501 (s, 9 H, *t*Bu), 1.426 (s, 9 H, *t*Bu) ppm. ^{11}B NMR: δ = −6.06 (s) ppm. ^{19}F NMR: δ = −116.10 (m, *ortho*), −124.30 (m, *ortho*), −130.10 (m, *ortho*), −130.50 (m, *ortho*), −130.90 (m, *ortho*), −157.24 (m, *para*), −159.60 (m, *para*), −161.65 (m, *para*), −161.90 (m, *meta*), −164.56 (m, *meta*), −166.42 (m, *meta*), −166.88 (m, *meta*) ppm. ^{125}Te NMR: δ = 1552.9 (s) ppm.

3: A solution of **1** (0.300 g, 0.556 mmol) in THF (10 mL) was added to a solution of $B(C_6F_5)_3$ (0.285 g, 0.556 mmol) in THF (10 mL) at −78 °C. After 2 h at 23 °C the solvent was removed under vacuum to give **3**·THF (0.533 g, 0.474 mmol, 85%) as an orange solid. Analytical and spectroscopic data were obtained for crystals of **3**·THF obtained from the attempted recrystallization of **2** from THF/*n*-pentane (1:1). $C_{42}H_{52}BF_{15}N_4O_2Te_2$ (1195.89): calcd. C 42.18, H 4.38, N 4.68; found C 42.11, H 4.21, N 4.61. All NMR spectroscopic data were recorded in [D_8]THF at 23 °C. ^1H NMR: δ = 4.02 (t, 2 H, CH_2-CH_2-CH_2-C*H*$_2$-O), 3.61 (4 H, THF, CH_2-C*H*$_2$-O), 3.17 (t, 2 H, C*H*$_2$-CH_2-CH_2-CH_2-O), 1.96 (q, 2 H, CH_2-CH_2-C*H*$_2$-CH_2-O), 1.77 (4 H, THF, C*H*$_2$-CH_2-O), 1.59 (q, 2 H, CH_2-C*H*$_2$-CH_2-CH_2-O), 1.50 (s, 9 H, *t*Bu), 1.479 and 1.477 (both s, 27 H, *t*Bu) ppm. ^{11}B NMR: δ = −3.64 (s) ppm. ^{13}C NMR: δ = 149.09 [d, $^1J_{C,F}$ = 235.0 Hz, *ortho*], 138.91 [d, $^1J_{C,F}$ = 245.9 Hz, *para*], 137.20 [d, $^1J_{C,F}$ = 249.1 Hz, *meta*], 126.64 (br, *ipso*), 68.27 (THF, CH_2-*C*H$_2$-O), 66.44 (*C*Me$_3$), 64.03 (CH_2-CH_2-CH_2-*C*H$_2$-O), 63.23 (*C*Me$_3$), 60.23 (*C*Me$_3$), 44.83 (*C*H$_2$-CH_2-CH_2-CH_2-O), 36.83 (C*Me*$_3$), 35.75 (C*Me*$_3$), 34.32 (CH_2-*C*H$_2$-*C*H$_2$-CH_2-O), 32.79 (*C*Me$_3$), 30.85 (CH_2-*C*H$_2$-CH_2-CH_2-O), 26.43 (THF, *C*H$_2$-CH_2-O) ppm. ^{19}F NMR: δ = −131.34 (m, *ortho*), −163.84 (m, *para*), −166.71 (m, *meta*) ppm. ^{125}Te NMR: δ = 1395.7 (s) ppm.

X-ray data were collected on a Nonius Kappa CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 173 K. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and not refined.

Acknowledgments

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[13] Crystal data for **2**: crystal size 0.12 × 0.12 × 0.10 mm^3, monoclinic $P2_1/c$ (No. 14) a = 12.3660(2) Å, b = 18.3420(4) Å, c = 17.1050(3) Å, β = 98.3940(8)°, V = 838.15(12) Å^3, Z = 4. The three methyl carbon atoms [labelled C(41A), C(42A), C(43A), C(41B), C(42B) and C(43B)] of one of the *tert*-butyl groups were disordered over two positions with refined site-occupancy factors of 0.581(9) and 0.419(9), respectively. The final cycle of full-matrix least-squares refinement using F^2 was based on 8683 reflections [6763 reflections with $I > 2\sigma(I)$], 533 variable parameters and converged with R = 0.0338.

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[18] Crystal data for **3**·THF: crystal size $0.10 \times 0.10 \times 0.05$ mm^3, monoclinic $P2_1/c$ (No. 14), $a = 10.9920(1)$ Å, $b = 24.3640(3)$ Å, $c = 18.8900(2)$ Å, $\beta = 102.4600(7)°$, $V = 4939.76(9)$ Å^3, $Z = 4$. Two of the carbon atoms [labelled C(53A), C(54A) and C(53B), C(54B)] of the ring-opened THF molecule were disordered over two sites with refined site-occupancy factors of 0.647(6) and 0.353(6), respectively. Least-squares refinement on F^2 based on 10081 reflections and 614 variable parameters [7186 reflections with $I > 2\sigma(I)$] gave a final R_1 of 0.039. CCDC-211059 (**2**) and -208709 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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