Preparation and Structure of $(Bu^tNTeNPPh_2NSiMe_3)_2$, a Tellurium Diimide Dimer

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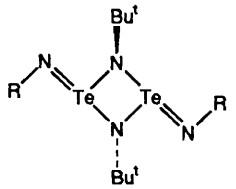
The reaction of $Ph_2P(NSiMe_3)_2Te(Cl)$=NR (R = PPh_2NSiMe_3) with Bu^tNHLi in toluene at −78 °C produces the tellurium diimide dimer $(Bu^tNTeNR)_2$, which is shown by X-ray crystallography to consist of a planar four-membered Te_2N_2 ring with short exocyclic tellurium–nitrogen bonds.

The structures, reactivity and physical properties of sulfur(IV) diimides (RN=S=NR) have been thoroughly investigated[1,2] since the discovery of the first example (R = Bu^t) nearly forty years ago.[3] An associated (dimeric) structure has been invoked to explain the skeletal scrambling reactions of sulfur(IV) diimides,[4] but these compounds are invariably monomers in the solid state. A planar *cis, trans* conformation **1a** is usually preferred,[5] however exceptions have been reported.[6–8] Selenium(IV) diimides RN=Se=NR, which have been known since 1976, are thermally unstable when R = Bu^t, $SiMe_3$.[9,10] No solid-state structures have been determined, but recent NMR studies indicate the *cis, trans* structure **1b** in solution.[11]

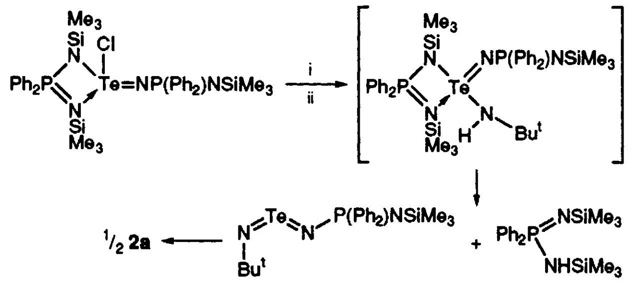
1a, E = S
1b, E = Se



2a (R = PPh_2NSiMe_3)

The only claim to tellurium(IV) diimides involves the preparation of the poorly characterized derivatives RNTeNR (R = COMe, SO_2Ar) from $TeCl_4$ and $(Me_3Si)_2NR$.[12] However, the properties of these 'tellurium diimides' (high melting points, low solubilities) suggest associated structures. We describe here a novel synthesis and the first structural determination of a tellurium(IV) diimide, which is shown to be the dimer **2a**.

The slow addition of a solution of Bu^tNHLi (0.585 mmol) in toluene (5 ml) to an equimolar amount of $Ph_2P(NSiMe_3)_2TeCl(=NPPh_2NSiMe_3)$, prepared from $TeCl_4$ and two molar equivalents of $Li[Ph_2P(NSiMe_3)_2]$,[13] in toluene (30 ml) at −78 °C, followed by warming to 23 °C for 2 hours, produced an orange solution which exhibited three $^{31}P\{^1H\}$ NMR resonances at δ 14.4 [$J(^{31}P–^{125}Te)$ = 124.6 Hz], 12.5 [$J(^{31}P–^{125}Te)$ = 112.0 Hz] and −0.03. The latter resonance is attributed to $Ph_2P(NHSiMe_3)(NSiMe_3)$ [*cf.* lit.: $\delta^{31}P$ ($CDCl_3$) 0.2].[14] The intensity of this resonance was equal to the sum of the intensities of the two resonances at δ 14.4 and 12.5, which were approximately of equal intensity. Thermally stable, and extremely moisture-sensitive, orange crystals of $(Bu^tNTeNPPh_2NSiMe_3)_2$ **2a**† were isolated in 92% yield upon removal of toluene under vacuum followed by washing with cold hexanes (−78 °C, 2 × 10 ml). The dimeric structure of **2a** was established by an X-ray structural determination. Thus, as indicated in Scheme 1, this reaction provides a novel route to a tellurium diimide which, in a *cis, trans* conformation, can readily dimerize to give the observed structure.



Scheme 1 *Reagents*: i, Bu^tNHLi; ii, −LiCl

X-ray quality crystals of **2a** were obtained from a hexane solution at room temperature.‡ As indicated in Fig. 1, the centrosymmetric structure of **2a** consists of a planar four-membered Te_2N_2 ring (cyclroditelluradiazetidine) with bond lengths of 2.005(5) and 2.013(5) Å close to the expected value for a Te^{IV}–N single bond.[15] By contrast, the Te_2N_2 ring in $(Ph_3P{=}NTeCl_3)_2$ exhibits markedly unequal Te–N distances of 1.996(4) and 2.282(5) Å.[16] The exocyclic Te(1)–N(2) distance of 1.900(5) Å is among the shortest reported for Te–N compounds,[17] but somewhat longer than the predicted value

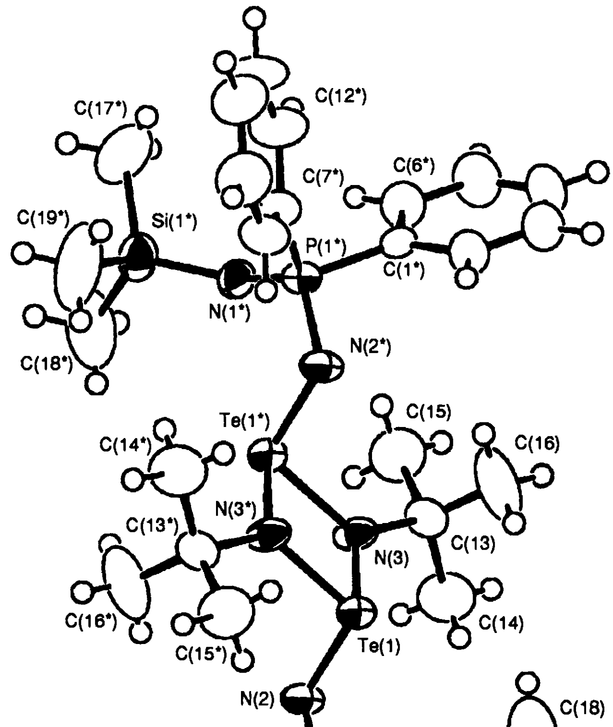


Fig. 1 ORTEP diagram of $(Bu^tNTeNPPh_2NSiMe_3)_2$ **2a** showing the atomic numbering scheme. Selected bond distances (Å) and bond angles (°): Si(1)–N(1) 1.682(6), N(1)–P(1) 1.556(5), P(1)–N(2) 1.647(2), N(2)–Te(1) 1.900(5), Te(1)–N(3) 2.005(5), Te(1)–N(3)* 2.013(5); Si(1)–N(1)–P(1) 138.1(4); N(1)–P(1)–N(2) 116.3(3); P(1)–N(2)–Te(1) 111.9(3); N(2)–Te(1)–N(3) 104.8(2); N(2)–Te(1)–N(3)* 97.8(2); N(3)–Te(1)–N(3)* 76.5(2); Te(1)–N(3)–Te(1)* 103.5(2). The asterisks indicate symmetry-related atoms.

of 1.83 Å for a Te–N double bond, suggesting some dipolar character. The endocyclic bond angle at nitrogen in **2a** is 103.5(2)° and the geometry at the ring nitrogen atoms is almost planar ($\Sigma\ \hat{N}(3) = 354.8°$) with the two Bu^t groups on opposite sides of the Te_2N_2 ring. The endocyclic bond angle at tellurium is 76.5(2)° and the exocyclic NTeN bond angles are 97.8(2) and 104.8(2)°. Thus the geometry at tellurium is distorted *pseudo*-tetrahedral with a lone pair occupying the vacant site. The $Me_3SiNPPh_2N$ groups are on opposite sides of the Te_2N_2 ring. The transannular Te–Te separation is 3.156(1) Å.

When solutions of **2a** (δ ^{31}P 14.4) in toluene, THF or CH_2Cl_2 are kept at 23 °C a second species **2b** (δ ^{31}P 12.5), which was also present in the original reaction mixture (*vide supra*), is produced. In view of the close similarity between the NMR data for **2a** and **2b**,† it is suggested that they are conformational isomers.

In summary, we have established that, unlike other chalcogen diimides, tellurium(IV) diimides may exist as dimers, as exemplified by **2a**. This dimerization is undoubtedly related to a combination of the weak π-character ($5p_\pi$–$2p_\pi$) and relatively high polarity of tellurium–nitrogen bonds.[15] The synthetic route described here provides a new avenue for investigations of the unexplored chemistry of tellurium diimides.

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Footnotes

† *Spectroscopic data*: **2a**, $^{31}P\{^1H\}$ NMR (THF, D_2O insert): δ 14.4 [s, $^2J(^{31}P–^{125}Te) = 124.6$ Hz]; ^{125}Te NMR (THF, D_2O insert): δ 1808.2 [d, $^2J(^{31}P–^{125}Te) = 131.2$ Hz]; ^1H NMR (C_6D_6): δ 7.9–8.1 and 7.0–7.2 (m, 10H, C_6H_5), 1.069 (s, 9H, CMe_3), 0.277 (s, 9H, $SiMe_3$). **2b**, $^{31}P(^1H)$ NMR (THF, D_2O insert): δ 12.5 [s, $^2J(^{31}P–^{125}Te) = 112.0$ Hz]; ^{125}Te NMR (THF, D_2O insert): δ 1632.4 [d, $^2J(^{31}P–^{125}Te) = 109.8$ Hz], ^1H NMR (C_6D_6): δ 7.9–8.1 and 7.0–7.2 (m, C_6H_5), 1.073 (s, CMe_3), 0.369 (s, $SiMe_3$).

‡ Orange prisms of **2a** were obtained by recrystallization from hexanes at 23 °C. Crystal dimensions were 0.20 × 0.30 × 0.55 mm. *Crystal data* for $C_{19}H_{28}N_3PTeSi$: $M = 485.11$, monoclinic, space group $P2_1/n$ (No. 14), $a = 8.822(3)$, $b = 15.849(2)$, $c = 16.791(2)$ Å, $\beta = 98.48(1)°$, $V = 2322.0(7)$ Å^3, $D_c = 1.388$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 14.08 cm^{-1}, $F(000) = 976$. Data were collected on a Rigaku AFC6S diffractometer operating in the $\omega = 2\theta$ mode at 23 °C. Of the 4288 unique reflections collected (Mo-Kα radiation, 0.71069 Å, graphite monochromator) 2383 were judged as observed using the criterion $I > 3\sigma I$. The structure was solved by heavy-atom methods and was refined by full-matrix least-squares calculations with anisotropic thermal parameters for non-hydrogen atoms. Refinement converged at $R = 3.4\%$, $R_w = 3.3\%$. An absorption correction and allowance for anomalous dispersion and secondary extinction were made. The data were corrected for Lorentz and polarization effects.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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