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## Structure of the telluroketone TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub> coordinated to an Li<sub>8</sub>O<sub>6</sub> cluster

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ABSTRACT

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# The reaction of Li<sub>2</sub>[C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] with elemental tellurium in THF was carried out in an attempt to generate the tellurocarbonyl dianion [TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> as the dilithium derivative. This thermally unstable tridentate ligand was characterized by <sup>31</sup>P and <sup>7</sup>Li NMR spectroscopy. Attempted recrystallization gave yellow crystals, which were shown by X-ray crystallography to be a neutral, centrosymmetric complex comprised of two molecules of the novel telluroketone [TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] stabilized by *N*,*Te*,*N* coordination to LiOLi units of the rhombic dodecahedral cluster [Li<sub>8</sub>( $\mu$ <sub>5</sub>-O)<sub>2</sub>( $\mu$ <sub>5</sub>-OH)<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>].

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#### 1. Introduction

Recently Davies et al. reported the synthesis of the bis(ditellurophosphinate)  $[PhP(Te)_2CH_2P(Te)_2Ph]^{2-}$  as its dilithium derivative [1]. Attempted recrystallization of this extremely airand moisture-sensitive product produced a small amount of yellow crystals that were identified by X-ray crystallography. The composition was established to consist of the dianion  $[PhP(Te)_2CH_2CH_2 P(Te)_2Ph]^{2-}$  and the dication  $[Li_8(OH)_6(THF)_8]^{2+}$  (1) (Fig. 1), which exhibits a rhombic dodecahedral cluster arrangement of Li and O atoms [1]. However, discussion of the structural parameters of this interesting complex were prevented by the inferior quality of the X-ray data ( $R_1 = 12.55\%$ ).

In recent work we have synthesized dilithium salts of the chacogenocarbonyl dianions  $[EC(PPh_2S)_2]^{2-}$  (E = S, Se) by the reactions of Li<sub>2</sub>[C(PPh\_2S)<sub>2</sub>] with elemental chalcogens in the presence of tetramethylethylenediamine (TMEDA) [2]. The solid-state structure of the selenium derivative **2** was shown to be bicyclic with the Li<sup>+</sup> cations bis-*S*,*Se*-chelated by the dianionic ligand. Two-electron oxidation of this dianion with I<sub>2</sub> yielded the neutral selone stabilized as a complex with lithium iodide {[Li(TMEDA)][I(Se)C(PPh\_2S)<sub>2</sub>]}(**3**); the attempted removal of LiI from **3** resulted in decomposition of the selone [2].



In contrast to the reactions with sulfur or selenium, the treatment of Li<sub>2</sub>[C(PPh<sub>2</sub>S)<sub>2</sub>] with tellurium does not proceed cleanly to give a single product [3]. Consequently, we turned our attention to the reaction of the well-known methanediide Li<sub>2</sub>[C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] [4–6] with tellurium to determine whether the presence of bulky SiMe<sub>3</sub> substituents on the ligating nitrogen atoms might have a stabilizing influence on the C-Te functionality. In this contribution we describe the formation and X-ray structure of a dimeric complex that incorporates two molecules of the neutral ligand  $TeC(PPh_2NSiMe_3)_2$  (4), a rare example of a telluroketone (tellone) [7], which is stabilized by N,Te,N-coordination to LiOLi units of the neutral rhombic dodecahedral cluster  $Li_8(\mu_5-O)_2(\mu_5-OH)_4(C_4H_8O)_4$  (vide infra). The latter is related to the dicationic  $Li_8O_6$  cluster illustrated in Fig. 1 [1] by the removal of two protons. Previously, the structural characterization of telluroketones had been limited to 2-telluroimidazoline (5) [8] and the tungsten pentacarbonyl complex of 1,1,3,3-indantellone **(6) [9]**.





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**Fig. 1.** The Li<sub>8</sub>O<sub>6</sub> rhombic dodecahedron in  $[Li_8(OH)_6(THF)_8]^{2+}(1)$  [1].

 $(THF)_8]^{2^+}$  are now taken up by nitrogen donor atoms of the two telluroketone ligands **4.** As was the case with the polyhedral dication  $[Li_8(OH)_6(THF)_8]^{2^+}$  [1], the neutral cluster  $Li_8(\mu_5-O)_2(\mu_5-OH)_4-(C_4H_8O)_4$  is likely formed by the interaction of lithium cations with small amounts of moisture that were absorbed by the glass vessel during the prolonged recrystallization of **7.** The dication  $[Li_8(OH)_6-(THF)_8]^{2^+}$  is viewed to be comprised of a hexameric (LiOH)\_6 aggregate which is bi-capped by two Li<sup>+</sup> cations [1] based on the well-known propensity of lithium alkoxides to form hexameric (LiOR)\_6 clusters [11]. The formation of  $Li_2O$  from the hydrolytic degradation of highly moisture-sensitive lithium reagents by adventitious moisture is a well-established phenomenon. Some recent examples include the sandwich complexes { $Li_1^mBuC(N^t-$ 



#### 2. Results and discussion

The reaction of Li<sub>2</sub>[C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] with tellurium powder in THF initially produced a green solution which became dark purple after several hours at 23 °C. The <sup>31</sup>P NMR spectrum of the reaction mixture showed two major resonances at  $\delta$  17.1 and 34.2, both of which were singlets, together with a minor resonance at  $\delta$  –4.9, which is attributable to the neutral precursor H<sub>2</sub>C[PPh<sub>2</sub>(NSiMe<sub>3</sub>)]<sub>2</sub>, cf. lit value: -3.0 ppm in CDCl<sub>3</sub> [10]. When the reaction was monitored by <sup>31</sup>P NMR spectroscopy the major peak observed was the singlet at  $\delta$ 17.1, but a substantial amount of unreacted  $Li_2[C(PPh_2NSiMe_3)_2]$ remained after 1 h, in addition to the resonance at  $\delta$  –4.9 for H<sub>2-</sub>  $C[PPh_2(NSiMe_3)]_2$  and some minor resonances in the  $\delta$  32–34 region. Removal of the solvent from a reaction mixture that had been stirred for ca. 24 h gave an extremely air- and moisture-sensitive sticky black residue, which was extracted with heptane to give a yellow solution. This solution exhibited only the resonances at  $\delta$  17.1 and -4.9 in the <sup>31</sup>P NMR spectrum; the <sup>7</sup>Li NMR spectrum showed a singlet at  $\delta$  1.06, but attempts to record the <sup>125</sup>Te NMR spectrum resulted in decomposition as manifested by the formation of elemental tellurium on the sides of the NMR tube. These observations suggest that the <sup>31</sup>P NMR resonance at  $\delta$  17.1 can be attributed to the expected product [Li(THF)]<sub>2</sub>[TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>](7)(Scheme 1); the resonance observed at  $\delta$  34.2 after longer reactions times is likely due to a decomposition product resulting from the thermal lability of the C-Te bond.

Attempts to grow crystals of  $[\text{Li}(\text{THF})]_2[\text{TeC}(\text{PPh}_2\text{NSiMe}_3)_2]$  (7) were unsuccessful, presumably owing to thermal instability. However, storage of the yellow heptane solution in an argon-filled glove box for 1 week yielded a few yellow crystals that were identified by X-ray crystallography as {[TeC(PPh}\_2\text{NSiMe}\_3)\_2] [Li\_4(\mu\_5-O)(\mu\_5-OH)\_2(C\_4H\_8O)\_2]\cdot C\_7H\_{16}]\_2 [8(C<sub>7</sub>H<sub>16</sub>)<sub>2</sub>] (Scheme 1 and Fig. 2a).

Complex **8** is a centrosymmetric dimer comprised of two molecules of the telluroketone TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub> (**4**) *N*,*Te*,*N*-coordinated to two LiOLi units of the dimeric Li<sub>8</sub>O<sub>6</sub> cluster Li<sub>8</sub>( $\mu_5$ -O)<sub>2</sub>( $\mu_5$ -OH)<sub>4</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub> (Fig. 2). As can be seen from a comparison of Figs. 1 and 2b, this neutral cluster is derived from the dication [Li<sub>8</sub>(OH)<sub>6</sub>(THF)<sub>8</sub>]<sup>2+</sup> [1] through the replacement of two hydroxyl (OH<sup>-</sup>) groups by two oxide (O<sup>2-</sup>) ligands; additionally, four of the coordination sites occupied by THF ligands in [Li<sub>8</sub>(OH)<sub>6</sub>

Bu)<sub>2</sub>}<sub>4</sub>·Li<sub>2</sub>O [12] and [3-furyl-C(NTMS)<sub>2</sub>Li]<sub>4</sub>·Li<sub>2</sub>O [13], [2-FC<sub>6</sub>H<sub>4</sub>-C(NTMS)<sub>2</sub>Li]<sub>4</sub>·Li<sub>2</sub>O [14]. Earlier representatives can be found in Refs. [15–19]. While hydrolysis is the likely source of LiOH in **8**, the formation of Li<sub>2</sub>O could also result from reduction of adventitious O<sub>2</sub> by the highly reducing dianion [(Te)C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>]<sup>2–</sup> in **7**, which would also explain the formation of the telluroketone **4**.

The quality of the X-ray structure of **8** ( $R_1 = 8.54\%$ ) is sufficient to allow a detailed discussion of the structural parameters, which are summarized in Table 1. The central carbon in the telluroketone TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub> is essentially planar ( $\Sigma \angle C13 \sim 357.8^{\circ}$ ), consistent with a three-coordinate carbon centre. The P–C (1.729(8) Å)and P–N (1.583(7)Å) bond distances are shorter and longer. respectively, than those in [CH<sub>2</sub>(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] (P-C 1.825(1) and P-N 1.536(2)Å) [20] suggesting electron delocalization within the NPCPN backbone of the tellone 4. The C-Te bond length of 2.065(7) Å in 8 is comparable with reported values of 2.087(4) Å for the 2-telluroimidazolines 5 [8] and 2.04-2.05 Å in telluroamides [21], but significantly longer than the distance 1.987(5) Å found for the metal complex 6 in which the telluroketone ligand is weakly coordinated to tungsten [9]. The calculated carbontellurium double bond distance in Me<sub>2</sub>C=Te is 1.968 Å [22], while C-single bond values is 2.158 Å [23].

The Te–O distance of 1.9456(5) Å falls within single and double bond values. A Te=O distance of 1.829(1) Å has been reported recently for a monomeric telluroxane [24], cf. a calculated value of 1.814 Å for Ph<sub>2</sub>Te=O [25], while the mean Te–O single-bond value in the polymer [(4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeO]<sub>n</sub> is 2.063 Å [26]. Thus the tellurium center is bonded quite strongly to the Li<sub>8</sub>O<sub>6</sub> cluster in **8.** The O–Te–C bond angle is 97.1(3)°.

The Li–O distances within the Li<sub>8</sub>O<sub>6</sub> cluster fall within the range 1.894(15)–2.049(14) Å. All Li atoms in this cage structure are fourcoordinate, but there are two different lithium environments. Each Li atom in the central lithium core (Li1, Li2, Li1\*, Li2\*) is connected to an oxide, two hydroxides and a THF molecule. By contrast, the THF molecule is replaced by an imino nitrogen donor from the (Te)C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub> ligand for each of the other four lithium atoms (Li3, Li4, Li3\*, Li4\*). The Li–O distances for the latter quartet of lithium atoms (1.937(16)–2.049 (14) Å are significantly longer than those exhibited by Li1, Li2, Li1\* and Li2\* (1.894(15)–1.959 (15) Å). The Li–N distances of 2.049(14) and 2.057(14) Å are



Scheme 1. Synthesis of Li<sub>2</sub>[TeC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>] (7) and subsequent formation of 8.

slightly shorter than the values of 2.108(9) and 2.128(9) Å reported for Li<sub>2</sub>[C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>], which also adopts a dimeric structure [27].

#### 3. Experimental

#### 3.1. General procedures

All reactions and manipulations of reagents and products were carried out under an argon atmosphere by using standard Schlenk or glove-box techniques. Solvents were dried over and then distilled from Na/benzophenone (THF, benzene and heptane). <sup>t</sup>BuLi (1.7 M in pentane), tellurium powder, azidotrimethylsilane and Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> were purchased from Aldrich Chemical Co. and used without further purification. <sup>31</sup>P NMR spectra were recorded on

Bruker 400 spectrometers. The  ${}^{1}$ H,  ${}^{31}$ P and  ${}^{7}$ Li chemical shifts are given relative to TMS, 85% H<sub>3</sub>PO<sub>4</sub> and aqueous LiCl, respectively.

 $H_2C(PPh_2NSiMe_3)_2$  was obtained in 87% yield by the reaction of  $Ph_2PCH_2PPh_2$  with an excess of neat trimethylsilyl azide at 130 °C according to the literature procedure [10]. The reagent Li<sub>2</sub>[C(PPh<sub>2</sub>-NSiMe<sub>3</sub>)<sub>2</sub>] was prepared by the treatment of  $CH_2[PPh_2(NSiMe_3)]_2$  with two equivalents of *tert*-butyllithium in benzene [28]. Yield: 60%. <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  14.6 (s), cf. lit value: 14.4 ppm [4]; <sup>7</sup>Li NMR (155.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  2.98 (s).

#### 3.1.1. Reaction of $Li_2[C\{PPh_2(NSiMe_3)\}_2]$ with tellurium

A mixture of  $Li_2[C(PPh_2NSiMe_3)_2]$  (0.33 g, 0.58 mmol) and tellurium powder (0.074 g, 0.58 mmol) in a 100 mL flask was cooled to -78 °C. Tetrahydrofuran (15 mL) was slowly added to the flask and the reaction mixture was stirred for 15 min to give a green solution



Fig. 2. (a) Molecular structure of 8(C<sub>7</sub>H<sub>16</sub>)<sub>2</sub>. Solvent heptane molecule is not shown. Hydrogen atoms of phenyl, methyl and hydroxyl groups have been omitted for clarity (b) the Li<sub>8</sub>O<sub>6</sub> cluster in 8.

Table 1	
Selected bond lengths (Å) and bond angles (°) for 8	

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Te1-01	1.946(5)	Li2-03	1.937(16)	Li4-03	2.049(14)	P2-C20	1.816(8)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Te1-C13	2.065(7)	Li2-02	1.951(15)	Li4–N2	2.142(14)	P2-C14	1.838(8)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Li1-01	1.919(13)	Li3-01	1.937(16)	P1-N1	1.589(7)	Si1-N1	1.694(7)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Li1-03	1.925(15)	Li3-02	2.009(15)	P1-C13	1.730(8)	Si2-N2	1.700(7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Li1-02	1.959(15)	Li3-03	2.018(14)	P1-C7	1.813(8)	N2-Li4	2.142(14)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Li1-05	1.961(14)	Li3-N1	2.057(14)	P1-C1	1.816(8)	01-Li4	2.043(16)
Li2-04       1.923(17)       Li4-01       2.043(16)       P2-C13       1.728(8)       O3-Li2       1.937(16)         O1-Te1-C13       97.1(3)       N1-Si1-C27       110.1(4)         N1-P1-C13       117.7(4)       C26-Si1-C27       106.0(5)	Li2-01	1.894(15)	Li4-02	1.997(15)	P2-N2	1.577(7)	02-Li3	2.009(15)
O1-Te1-C13     97.1(3)     N1-Si1-C27     110.1(4)       N1-P1-C13     117.7(4)     C26-Si1-C27     106.0(5)	Li2-04	1.923(17)	Li4-01	2.043(16)	P2-C13	1.728(8)	03-Li2	1.937(16)
N1-P1-C13 117.7(4) C26-Si1-C27 106.0(5)	01-Te1-C13		97.1(3)		N1-Si1-C27		110.1(4)	
	N1-P1-C13		117.7(4)		C26-Si1-C27		106.0(5)	
N1-P1-C7 108.1(4) N1-Si1-C28 116.3(4)	N1-P1-C7		108.1(4)		N1-Si1-C28		116.3(4)	
C13-P1-C7 109.5(4) C26-Si1-C28 106.7(4)	C13-P1-C7		109.5(4)		C26-Si1-C28		106.7(4)	
N1-P1-C1 110.4(4) C27-Si1-C28 106.2(4)	N1-P1-C1		110.4(4)		C27-Si1-C28		106.2(4)	
C13-P1-C1 103.8(4) N2-Si2-C30 116.5(4)	C13-P1-C1		103.8(4)		N2-Si2-C30		116.5(4)	
C7-P1-C1 106.9(4) N2-Si2-C31 111.1(4)	C7-P1-C1		106.9(4)		N2-Si2-C31		111.1(4)	
N2-P2-C13 116.1(4) C30-Si2-C31 105.2(4)	N2-P2-C13		116.1(4)		C30-Si2-C31		105.2(4)	
N2-P2-C20 111.8(4) N2-Si2-C29 108.6(4)	N2-P2-C20		111.8(4)		N2-Si2-C29		108.6(4)	
C13-P2-C20 104.8(4) C30-Si2-C29 109.3(4)	C13-P2-C20		104.8(4)		C30-Si2-C29		109.3(4)	
N2-P2-C14 112.5(4) C31-Si2-C29 105.5(5)	N2-P2-C14		112.5(4)		C31-Si2-C29		105.5(5)	
C13-P2-C14 109.7(4) P2-C13-P1 133.6(5)	C13-P2-C14		109.7(4)		P2-C13-P1		133.6(5)	
C20-P2-C14 100.6(4) P2-C13-Te1 114.1(4)	C20-P2-C14		100.6(4)		P2-C13-Te1		114.1(4)	
N1-Si1-C26 111.0(4) P1-C13-Te1 110.1(4)	N1-Si1-C26		111.0(4)		P1-C13-Te1		110.1(4)	

Table 2
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Crystallographic data for **8**(C<sub>7</sub>H<sub>16</sub>)<sub>2</sub>.

	8
Empirical formula	C <sub>92</sub> H <sub>144</sub> P <sub>4</sub> N <sub>4</sub> Si <sub>4</sub> Li <sub>8</sub> O <sub>10</sub> Te <sub>2</sub>
Formula weight	2013.07
T (K)	120(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	ΡĪ
a (Å)	12.233(2)
b (Å)	14.883(3)
c (Å)	15.788(3)
α (°)	74.70(3)
β (°)	68.57(3)
γ (°)	87.34(3)
$V(Å^3)$	2576.8(9)
Ζ	1
$D_{\text{calc}} (\text{mg m}^{-3})$	1.297
Absorption coefficient (mm <sup>-1</sup> )	0.728
F(000)	1048
Crystal size (mm <sup>3</sup> )	$0.19 \times 0.13 \times 0.09$
θ (°)	2.27-25.05
Limiting indices	$-14\leqslant h\leqslant 14$ ,
	$-17 \leqslant k \leqslant 17$ ,
	$-18 \leqslant l \leqslant 18$
Reflections collected/unique (R <sub>int</sub> )	16871/9040 (0.0910)
Completeness to theta	98.8%
Max. and min. transmission	0.9373 and 0.8740
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	9040/0/567
Goodness-of-fit (GOF) on $F^2$	1.138
Final R indices	
$R_1$ , $wR_2$ $[I > 2\sigma(I)]$	0.0869, 0.1608
$R_1$ , $wR_2$ (all data)	0.1234, 0.1809
Largest difference in peak and hole ( $e Å^{-3}$ )	0.882 and -0.689

and then it was allowed to warm to room temperature and stirred for a further 24 h to produce a dark purple solution. NMR data for the THF solution: <sup>31</sup>P NMR (162 MHz, 25 °C:  $\delta$  –4.9 (s), 17.1 (s), 34.2 (s).

Removal of solvent from the reaction mixture under vacuum gave a dark (black) sticky solid, which was extracted with heptane to give a yellow solution: <sup>31</sup>P NMR (162 MHz, 25 °C) –4.9 (s), 17.1 (s); <sup>7</sup>Li NMR (155.5 MHz, 25 °C):  $\delta$  1.06 (s). After ca. 1 week in an argon-filled glove box at room temperature, a few pale yellow crystals were formed and identified as **8** by X-ray crystallography.

#### 4. X-ray crystallography

Crystallographic data for  $\mathbf{8}(C_7H_{16})_2$  are given in Table 2. Data were collected with a Nonius Kappa CCD diffractometer with use of monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 120 K. The structure was solved by direct methods using the program SHELXS-97 and refined with SHELXL-97 [29] and by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms of hydroxy groups (O2 and O3) were not located in Fourier maps for **8**. Hydrogen atoms were included in calculated positions and were refined by riding mode.

#### 5. Conclusions

In addition to providing a rare example of a structurally characterized telluroketone, the title compound embodies a neutral  $Li_8O_2(OH)_4$  cluster that is related by the removal of two protons to the dicationic cluster  $[Li_8(OH)_6]^{2+}$  reported recently by Davies et al. [1]. In contrast to that precedent, the structural determination in the present instance is sufficiently precise to allow a meaningful discussion of geometrical parameters.

#### Acknowledgment

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#### Appendix Supplementary. material

CCDC 906326 contains the supplementary crystallographic data for complex **8**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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