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New cyclic tellurides. Synthesis, reaction and ligand properties of 2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane ($C_6H_{16}OSi_2Te$). X-Ray structure determination of $C_6H_{16}OSi_2TeI_2$

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Abstract

A new tellurium-containing heterocyclic compound, 2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane ($C_6H_{16}OSi_2Te$) (**1**), has been prepared by treatment of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane with sodium telluride. Mononuclear and dinuclear palladium complexes of this telluride have been prepared by the reaction of **1** with $PdCl_2(PhCN)_2$ and Na_2PdCl_4, respectively. The following new derivatives of **1** have also been produced: $C_6H_{16}OSi_2TeI_2$ (**2**), $C_6H_{16}OSi_2TeBr_2$, $C_6H_{16}OSi_2TeCl_2$, $C_6H_{16}OSi_2Te(CH_3)I$, and $C_6H_{16}OSi_2Te(CH_2Ph)Br$. IR, ^1H and ^{13}C NMR and mass spectral data of these new compounds are reported and discussed. ^1H NMR studies revealed that in $CDCl_3$ solution both telluronium salts reductively eliminate alkyl halide. The crystal structure of compound **2** has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group, $P2_1/c$, with four molecules in a unit cell of dimensions a 12.960(3), b 8.846(2), c 13.754(4) Å, β 92.44(2)°, $R = 0.049$, and $R_w = 0.067$ for 3599 unique reflections with $|F_0| > 3\sigma(F_0)$. The compound forms a six-membered ring of a slightly displaced boat type. The geometry about the Te atom is pseudo-octahedral, with two carbon atoms (Te–C = 2.156(7) and 2.137(6) Å) and two iodine atoms of the neighbouring molecules (weak intermolecular bonds, Te $\cdots$ I = 3.769 and 3.806 Å) in the equatorial positions and two iodine atoms (Te–I = 2.909(1) and 2.913(1) Å) in the axial positions.

Introduction

The organic chemistry of selenium and tellurium heterocycles has been the subject of extensive investigations [1], yet study of tellurium heterocycles is consid-

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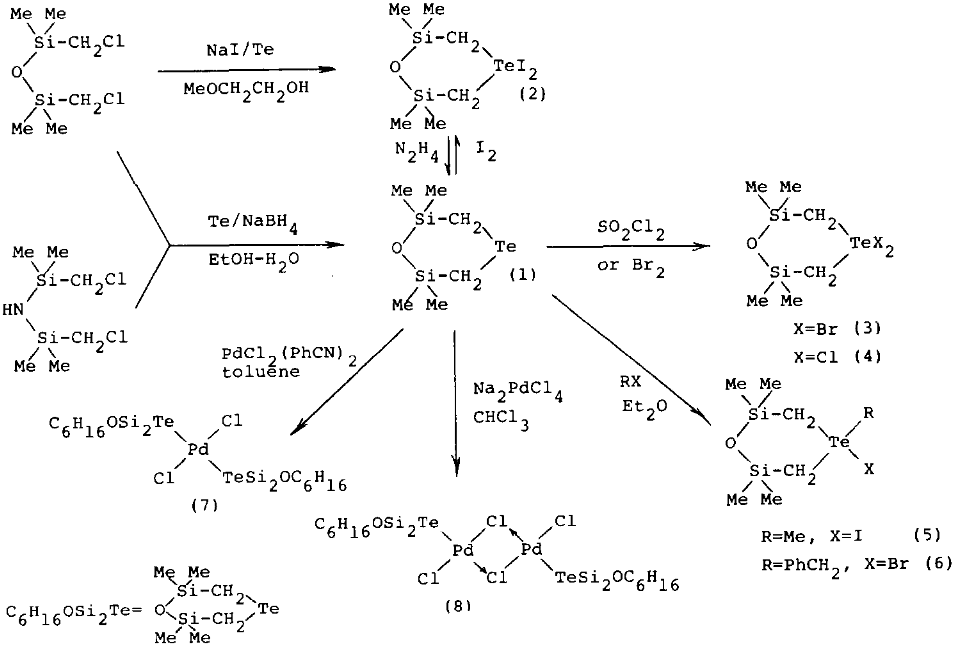
erably less advanced than that of selenium heterocycles. So far we have been interested in the synthesis of heterocyclic selenium [2] and tellurium [3] compounds and their use as donors in charge-transfer complexes [4] or as ligands for various transition metal ions [5]. In the present work, we report the synthesis, reaction and ligand properties as well as spectroscopic and X-ray structural studies of new cyclic tellurium compounds containing both oxygen and silicon atoms in the same ring, namely, 1-oxa-4-tellura-2,6-disilacyclohexane derivatives. It is worth noting that corresponding selenium analogue have long been known [6].

Results and discussion

The new heterocyclic tellurium compound, 2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane (**1**) was prepared by reacting 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane with sodium telluride, prepared *in situ* from tellurium powder and sodium borohydride in aqueous ethanol. Compound **1** was also prepared by reducing its diiodide (**2**) which, in turn, can be obtained directly by treatment of the disiloxane with tellurium powder and sodium iodide [3a]. Compound **1** is insoluble in water and not sensitive to hydrolysis. It reacts with halogen or SO_2Cl_2 to afford 4,4-diiodo (**2**), 4,4-dibromo (**3**), and 4,4-dichloro compounds (**4**), and with methyl iodide and benzyl bromide to produce the corresponding methyltelluronium (**5**) and benzyltelluronium (**6**) salts respectively. Just like diphenyl telluride [7], it also acts as a ligand for mononuclear (**7**) and dinuclear (**8**) palladium complexes. Preparative methods of all these new compounds are shown in Scheme 1. Isolated yields,



Scheme 1. Methods of preparation of new cyclic telluride and its derivatives.

Table 1

Isolated yield and some analytical data for compounds **1**–**8**

Compound	Isolated yield [a] (%)	Melting point (°C)	Colour	Found (calc.) (%)	
				C	H
1	40 [b], 61 [c]	oil	yellow	25.19 (25.03)	5.83 (5.60)
2	45 [b]	189–190	dark orange	13.44 (13.30)	3.26 (2.98)
3	88	156–158	white	15.90 (16.09)	3.51 (3.60)
4	86	147–149	white	19.33 (20.08)	4.33 (4.49)
5	95	204–206 (dec)	white	18.84 (19.56)	4.43 (4.45)
6	92	110–112	white	34.26 (34.02)	4.83 (5.05)
7	72	169–170	orange	19.81 (19.14)	4.14 (4.28)
8	57	171–173 (dec)	brownish yellow	15.29 (15.49)	3.38 (3.47)

[a] Based on compound **1** charged. [b] Based on disiloxane charged. [c] Produced by reduction of compound **2**.

melting points, colour, and C,H analytical data for all compounds are shown in Table 1.

The IR spectra of these compounds display characteristic bands at certain frequencies. All compounds showed medium to strong bands due to C–H asymmetric and symmetric stretching (ν_{as} and ν_s) and symmetric deformation (δ_s) of methyl group ($Si-CH_3$) in the range of 2960–2900 and 1260–1250 cm^{-1}, respectively. The spectra showed weak bands near 1400 cm^{-1} due to $\delta_{as}(Si-CH_3)$ and $\delta_s(Si-CH_2)$ and a strong band in the range of 1040–1015 cm^{-1} due to ν(Si–O). There are also three medium to strong bands at 900–790 cm^{-1} which may be attributed to the $Si-CH_3$ group, and in fact the starting disiloxane showed three strong bands at 850, 820, and 800 cm^{-1} together with strong bands at 1260 and 1075 cm^{-1}. Two weak to medium bands due to ν_{as}(C–Te) and ν_s(C–Te) generally appeared at the range of 560–505 cm^{-1} [8], while two bands around 360–320 cm^{-1} might be assignable to stretching of Te–X and/or Pd–Cl bonds, though the assignment is obscure. All IR data and some assignments are summarized in Table 2.

The ^1H NMR spectra of compounds **1**, **2**, **3**, and **4** show two singlets due to methyl ($Si-CH_3$) and methylene ($Te-CH_2$) protons. The methylene signals were flanked by satellites arising from coupling with ^{125}Te. The value of $^2J(^{125}Te-CH_2)$ depends on the oxidation state of the tellurium atom in these compounds. It is 33.6 Hz for **1** and around 56 Hz for **2**, **3**, and **4** (see Table 3). In compounds **5**, **6**, **7**, and **8**, each of methylene protons had different chemical shift and the spectrum appeared as two doublets of a simple AB pattern. Similar coupling patterns have been observed previously with some telluronium salts [9]. It is now shown that methylene protons also become non-equivalent by coordination of the telluride ligand to palladium. In compounds **6** and **8**, even methyl protons of the CH_3-Si group show different chemical shifts.

Table 2.

IR data for compounds 1–8 (KBr discs) and representative assignments

1 [a]	**2**	**3**	**4**	**5**	**6**	**7**	**8**	Assignments
					3050w			phenyl
					3020w			phenyl
2960m	2955w	2960w	2955m	2950m	2960m	2960m	2960m	$\nu_{as}(CH_3)$
2900w	2900w	2910w	2910w	2900w	2900w	2910w	2910w	$\nu_s(CH_3)$
					1600w			phenyl
					1490m			
					1455m			
1410w	1400w	1400w	1400w	1410w	1410w	1400w	1400w	$\delta_{as}(Si-CH_3)$, $\delta_s(Si-CH_2)$
1365w	1355sh	1355sh	1360sh	1370w	1360w	1365w	1370w	
	1350m	1350m	1350w					
1250s	1255s	1260s	1255s	1260s	1255s	1255s	1255s	$\delta_s(Si-CH_3)$
					1150w			
	1100m	1105m	1100m					
				1070sh	1065w	1060m	1060m	
1050sh					1050m		1050sh	
1030s								
1015s	1040s	1040s	1035s	1020s	1015s	1020s	1025s	$\nu(Si-O)$
						1010sh		
955w						970w	970w	
870m	870w	870m	870m	870m	870m	870m	870m	$Si-CH_3$
840s	835s	835s	835s	840s	840s	840s	840s	
790s	800s	805s	800s	805s	800s	800s	800s	
740w					760m			phenyl
710m	710m	710m	710m	710m	720w	715m	715m	
					695m			phenyl
640w	650w	650w	645w					
	625w	630w	625w		600w			
555w	560w	560w	560w	560sh	570w	560w	560sh	$\nu_{as}(C-Te)$
520w	505w	515w	520w	540m	540m	530w	535m	$\nu_s(C-Te)$
	355w	355w	355m	350w	350w	350w	350w	Te–X, Pd–Cl(?)
	320w	325w	320m	325w	325w	325w	330m	

[a] Neat.

The ^1H NMR spectrum of compound **5** in $CDCl_3$ shows signals due to methyl (CH_3–Si), methylene (CH_2–Te), and methyl (CH_3–Te) at δ(ppm) 0.31, 2.34, and 2.74, respectively, but as time passes (24 h) the spectrum completely collapses and a new dominant singlet appears at around δ 2.5. This may be due to reductive elimination or dissociation of **5** giving CH_3I as observed in similar telluronium salts [10]. The ^1H NMR spectrum of **6** immediately after solution in $CDCl_3$ shows one unidentified small singlet at δ 4.49 in addition to signals attributable to **6** such as two doublets ($SiCH_2Te$, δ 1.17 and 2.08) and one singlet ($PhCH_2Te$, δ 4.92). The chemical shift of this singlet is quite close to that of benzyl bromide (δ 4.50). As time passes (36 h) the signals at δ 1.17, 2.08, and 4.92 all disappear and a new singlet appears at δ 2.05 together with two singlets at δ 4.49 and 4.50. Although the results cannot yet be explained, they do show the facility of the dissociation of compound **6** to benzyl bromide and some other species [10].

The mass spectra of compounds **1**, **2**, **5**, and **6** were determined. All compounds except **6** showed the molecular ion peak at 100% to 0.2% relative abundance (Table 4).

Table 3

Selected ^{1}H and ^{13}C NMR data for compounds **1**–**8** [a]

Compound	^{1}H NMR (δ)	^{13}C NMR (δ)
1	0.33 (s, 12H)	
	1.49 (s, 4H, J(TeH) = 33.6)	
2	0.44 (s, 12H)	4.0, 14.7
	2.75 (s, 4H, J(TeH) = 56.0)	
3	0.45 (s, 12H)	3.8, 17.8
	2.65 (s, 4H, J(TeH) = 56.2)	
4	0.41 (s, 12H)	
	2.41 (s, 4H, J(TeH) = 56.0)	
5	0.31 (s, 12H)	4.1, 6.5, 9.8
	2.34 (4H) [b]	
	2.74 (s, 3H, J(TeH) = 27.8)	
6	0.11 (s, 6H)	
	0.34 (s, 6H)	
	1.17 (d, 2H, J(HH) = 12.4)	
	2.08 (d, 2H, J(HH) = 12.4)	
	4.92 (s, 2H, J(TeH) = 47.0)	
	7.25–7.45 (m, 5H) [c]	
7	0.28 (s, 24H)	
	1.58 (d, 4H)	
	2.35 (d, 4H, J(HH) = 14.4)	
8	0.25 (s, 12H)	
	0.31 (s, 12H)	
	1.84 (d, 4H, J(HH) = 13.9)	
	2.35 (d, 4H, J(HH) = 13.9)	

[a] J(TeH) denotes $^2J(^{125}Te{-}H)$ in Hz. [b] Two doublets of AB pattern, centred at 2.34. [c] Other signals (unidentified): 4.49(s).

Table 4

Some representative mass spectral data of new compounds

m/e	Relative intensity				Possible ion
	1	**2**	**5**	**6**	
544		0.2			$C_6H_{16}OSi_2TeI_2^+$
529		0.7			$C_5H_{13}OSi_2TeI_2^+$
432			2		$C_6H_{16}OSi_2Te(CH_3)I^+$
417		31			$C_6H_{16}OSi_2TeI^+$
305			7		$C_6H_{16}OSi_2TeCH_3^+$
290	100	100	37	52	$C_6H_{16}OSi_2Te^+$
275	87	100	41	54	$C_5H_{13}OSi_2Te^+$
254		100			I_2^+
247	60	97	31	39	$C_5H_{13}OSiTe^+$
172				19	$PhCH_2Br^+$
142			100		CH_3I^+
131	83	100	55	62	TeH^+
91				100	$PhCH_2^+$
73		65	19	13	$CH_3Si(CH_2)O^+$ (?)
65				22	$C_5H_5^+$
59	12	70	21	13	CH_3SiO^+ (?)
44	10	10	35		SiO^+ (?)
43	19	30	10		CH_3Si^+ (?)

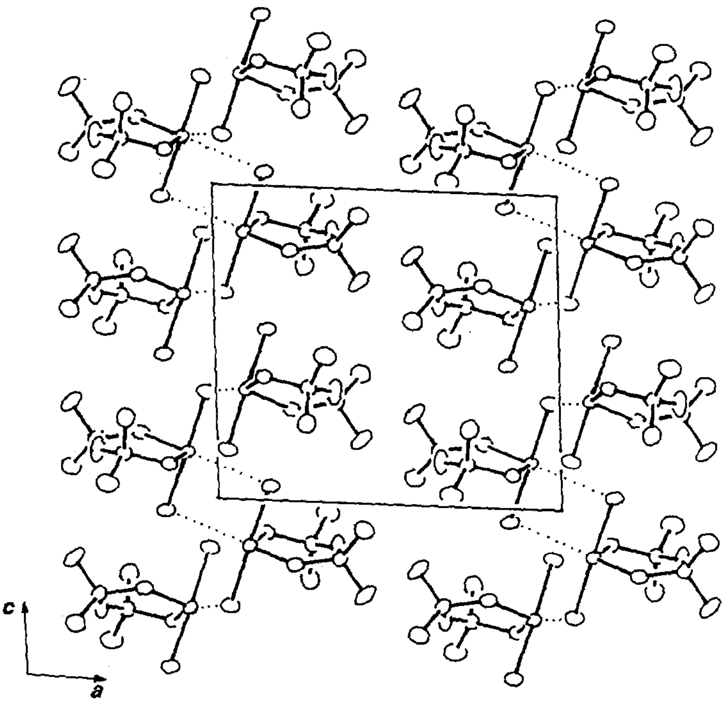


Fig. 1. ORTEP drawing of the crystal structure of compound **2** viewed down the *b* axis. The thermal ellipsoids in this and the following figures are drawn at the 50% probability level.

The telluride **1** reacted readily with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) to form a shiny black-green solid, whose solid-state ESR data showed a single line of *g* factor 2.0025 (±0.0002). This value is almost the same as those reported for some other telluride-TCNQ complexes [11] and is very close to the free-electron value suggesting that the signal arises from unpaired electron density on TCNQ. More detailed studies on this complex will be reported elsewhere.

The reaction of sodium telluride with one equivalent of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane, $(ClCH_2Si(Me)_2)_2NH$, would be an obvious route to the synthesis of $HN(Si(Me)_2CH_2)_2Te$. However, when sodium telluride, generated (like **1**) in an aqueous ethanolic solution was allowed to interact with the silazane in ethanol either at ambient temperature or under reflux, compound **1** was isolated unexpectedly in 13% yield in addition to elemental tellurium after the same work up procedure as that used to obtain **1**. This result can be explained by the easy hydrolysis of the starting silazane and of the resulting nitrogen-containing cyclic telluride where the Si–N bond may readily be converted to an Si–O bond. Strictly dry conditions should be necessary to obtain the expected telluride.

Compound **2** has been identified by crystal structure determination as containing four $C_6H_{16}OSi_2TeI_2$ molecules in a unit cell, and the crystal structure down the *b* axis is given in Fig. 1. The final positional and isotropic temperature factors of the non-hydrogen atoms are listed in Table 5. The coordination about the Te atom and the structure of the six-membered ring are shown in Figs. 2 and 3, respectively. Important interatomic distances and angles are listed in Table 6.

Table 5

Positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms

Atom	x	y	z	B_{eq} (Å^2)
Te	0.08808(3)	0.03101(4)	0.35291(3)	3.9
I(1)	0.15194(4)	0.14592(7)	0.54430(4)	6.1
I(2)	0.02903(4)	−0.07908(6)	0.15885(4)	5.8
Si(1)	0.3536(2)	0.0620(2)	0.3209(2)	5.4
Si(2)	0.2711(2)	−0.2560(2)	0.3642(2)	4.9
O(1)	0.3472(4)	−0.1110(7)	0.3559(6)	8.8
C(1)	0.2213(6)	0.1403(8)	0.2956(5)	5.0
C(2)	0.1398(5)	−0.1896(7)	0.3953(5)	4.4
C(3)	0.4240(8)	0.1728(13)	0.4148(7)	8.3
C(4)	0.4226(9)	0.0719(17)	0.2062(9)	11.5
C(5)	0.2638(8)	−0.3649(13)	0.2503(7)	8.6
C(6)	0.3197(9)	−0.3794(12)	0.4657(7)	8.6

Although the bonding about the Te atom in this established structure might appear to be four-coordinated with two carbon atoms and two unshared lone pairs of electrons at the equatorial positions and two iodine atoms at axial positions, it is probably best described as pseudo-octahedral. There are two normal covalent bonds to carbon atoms with distances of 2.156(7) and 2.137(6) Å. Two axial bonds, approximately perpendicular to the C–Te–C plane, are formed with iodine atoms at 2.909(1) and 2.913(1) Å making an angle of 178.3(2)° with each other. The distances are in the range 2.851–2.985 Å as observed in earlier studies [12–14]. The octahedron is completed by intermolecular coordination of two iodine atoms of two different neighbouring molecules at 3.769(1) and 3.806(1) Å. The distances are apparently longer than the sum of the normal single bond radii for Te and I (2.70 Å), whereas they are significantly shorter than the sum of the van der Waals radii (4.35 Å) [15]. The geometrical parameters about the Te atoms are also given in Table 6.

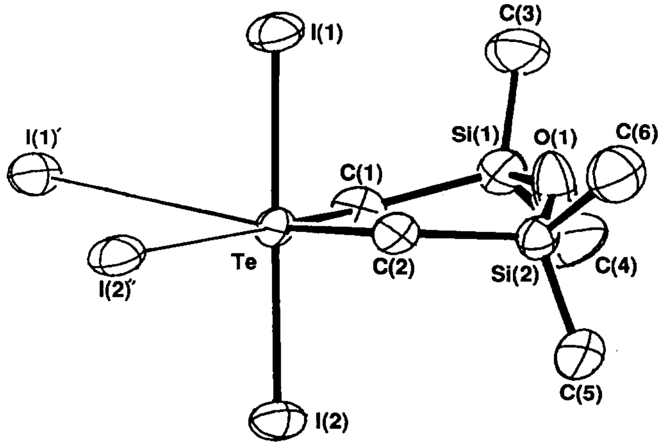


Fig. 2. Molecular structure of compound 2. The coordination geometry about the tellurium atom is also shown. The primed and double-primed atoms are iodine atoms of two different neighbouring molecules.

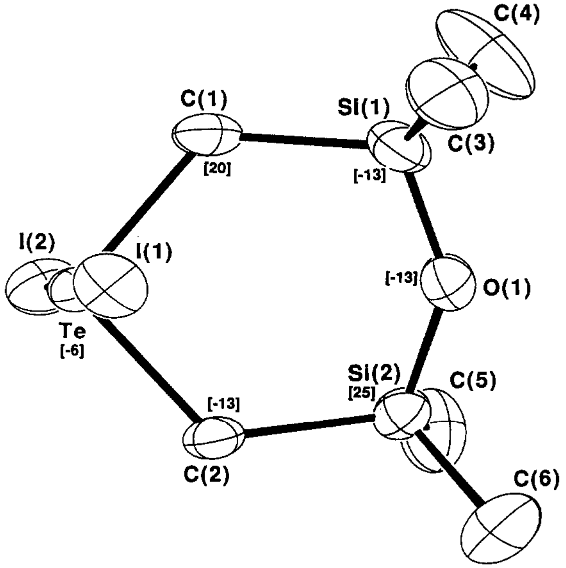


Fig. 3. View of compound 2 normal to the mean plane of six-membered ring. The number in brackets shows the perpendicular displacements of the atoms, in units of 0.01 Å, from the mean plane of the ring.

Table 6

Important interatomic distances (Å) and angles (deg) [a]

Te–I(1)	2.909(1)	Te–I(2)	2.913(1)
Te–C(1)	2.156(7)	Te–C(2)	2.137(6)
Si(1)–O(1)	1.608(6)	Si(1)–C(1)	1.869(7)
Si(1)–C(3)	1.833(6)	Si(1)–C(4)	1.848(12)
Si(2)–O(1)	1.625(6)	Si(2)–C(2)	1.868(7)
Si(2)–C(5)	1.837(10)	Si(2)–C(6)	1.861(10)
Te ··· I(1)′	3.806(1)	Te ··· I(2)″	3.769(1)
I(1)–Te–I(2)	178.32(2)	I(1)–Te–C(1)	88.4(2)
I(1)–Te–C(2)	89.9(2)	I(2)–Te–C(1)	89.9(2)
I(2)–Te–C(2)	90.7(2)	C(1)–Te–C(2)	105.2(3)
O(1)–Si(1)–C(1)	110.5(3)	O(1)–Si(1)–C(3)	109.2(4)
O(1)–Si(1)–C(4)	109.5(5)	C(1)–Si(1)–C(3)	111.0(4)
C(1)–Si(1)–C(4)	107.3(5)	C(3)–Si(1)–C(4)	109.4(5)
O(1)–Si(2)–C(2)	109.2(3)	O(1)–Si(2)–C(5)	111.3(5)
O(1)–Si(2)–C(6)	109.2(4)	C(2)–Si(2)–C(5)	110.2(4)
C(2)–Si(2)–C(6)	107.1(4)	C(5)–Si(2)–C(6)	109.6(5)
Si(1)–O(1)–Si(2)	144.3(4)	Te–C(1)–Si(1)	120.6(4)
Te–C(2)–Si(2)	120.2(3)		
I(1)–Te ··· I(1)′	90.75(2)	I(1)–Te ··· I(2)″	79.48(2)
I(2)–Te ··· I(1)′	90.91(2)	I(2)–Te ··· I(2)″	100.21(1)
I(1)′ ··· Te ··· I(2)″	93.34(2)	I(1)′ ··· Te–C(1)	177.6(2)
I(1)′ ··· Te–C(2)	77.0(2)	I(2)″ ··· Te–C(1)	84.3(2)
I(2)″ ··· Te–C(2)	165.6(2)		

[a] Unprimed atoms are in the $C_6H_{16}OSi_2TeI_2$ molecule. Primed and double-primed atoms are in relation to a centre of symmetry and a 2_1 screw axis symmetry with unprimed atom, respectively.

The stronger intermolecular bondings between Te and I are indicated by the dotted lines in Fig. 1. The connected molecules are infinitely extended along the *b* and *c* crystallographic axes. Such coordination and structure have also been observed in the compounds $C_4H_8OTeI_2$ [14] and $C_4H_8STeI_2$ [12].

As shown in Fig. 3, the six-membered ring formed by Te, two C, two Si, and O atoms is in the boat form, with slight deviations from the mean plane defined by the Te, Si(1), O(1), and C(2) atoms (within 0.01 Å). The deviations of the C(1) and Si(2) atoms from the mean plane are 0.28 and 0.40 A, respectively. This abnormal boat form with only small deviations may be produced by a large Si–O–Si angle, 144.3(4)°, which is generally found in compounds with the Si–O–Si bond [16,17].

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 (200 MHz) spectrometer as solution in $CDCl_3$ unless otherwise indicated. IR spectra of solid (KBr) and paraffin film were recorded on a Perkin–Elmer 521 infrared spectrophotometer. Mass spectra were determined on a JEOL JMS-DX 300 mass spectrometer, equipped with a JAM-3500 data processing system. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected.

Dichlorobis(benzonitrile)palladium was prepared by a published method [18], while all other materials including sodium chloropalladate (Mitsuwa Pure Chemicals), 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane and disilazane (Shin-etsu Silicon Chemicals) were purchased from commercial sources and used without further purification.

2,2,6,6-Tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane (1)

This compound was prepared by two methods:

Method A. To a suspension of tellurium powder (2.55 g, 20 mmol) in a mixture of ethanol–water (60/10 ml) was added sodium borohydride (2.01 g, 53 mmol). The reaction mixture was then heated to reflux, whereupon a vigorous evolution of hydrogen started. All tellurium was consumed within 20 min, producing a faintly red solution. 1,3-Bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane, $(ClCH_2Si(CH_3)_2)_2O$, (4.63 g, 20 mmol) was then added in one portion to the solution at room temperature. After the mixture was refluxed for 3 h, it was diluted with saturated NaCl solution (150 ml) and air was passed through it for 12 h to remove the unreacted Te^{2-} anion. The mixture was extracted with ether (3 × 50 ml). The extract was washed with water, dried over $MgSO_4$ and evaporated under reduced pressure to leave compound **1** as a yellow oil with an unpleasant odour. It was purified by column chromatography on silica gel using hexane–ethyl acetate (10 : 1) as eluant to give 2.32 g (8.06 mmol; 40.3%) of pure **1** which is stable to both air and water.

Method B. Hydrazine hydrate was added dropwise to a boiling ethanolic solution of 2,2,6,6-tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane (**2**) (1.08 g, 2 mmol) until the orange colour disappeared. The solution was filtered, poured into water (500 ml) and extracted with ether (3 × 50 ml). The solvent was removed under reduced pressure to leave compound **1** which was purified by column chromatography as described in Method A; 0.35 g, 1.22 mmol, 60.8%.

2,2,6,6-Tetramethyl-1-oxa-4,4-diiodo-4-tellura-2,6-disilacyclohexane (2)

A mixture of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane (4.63 g, 20 mmol), tellurium powder (2.55 g, 20 mmol) and sodium iodide (12 g, 80 mmol) in 2-methoxyethanol (150 ml) was stirred under reflux for 8 h, during which some orange precipitates appeared. Deionized water (600 ml) was added to complete the precipitation, and the precipitates were filtered off, washed with water, rinsed with acetone, and air dried. These were purified by column chromatography on silica gel using hexane-ethyl acetate (10 : 1) as eluant to give pure compound **2** as a dark orange solid (4.9 g, 9.04 mmol, 45.2%).

2,2,6,6-Tetramethyl-1-oxa-4,4-dibromo-4-tellura-2,6-disilacyclohexane (3)

To a solution of **1** (0.58 g, 2 mmol) in 25 ml of ether was added drop by drop a solution of bromine in 25 ml of ether. A fine pale yellow precipitate was formed immediately and soon settled to give a clear and almost colourless solution. Bromine was added in this way until a permanent colour of bromine resulted when an additional drop of bromine was added. When the solvent was allowed to evaporate, pale yellow crystals of compound **3** were obtained. The product was recrystallized from ethanol to give white crystals of pure **3**; 0.79 g, 1.76 mmol, 88%.

2,2,6,6-Tetramethyl-1-oxa-4,4-dichloro-4-tellura-2,6-disilacyclohexane (4)

Excess of thionyl chloride in ether (30 ml) was added to a well-stirred solution of compound **1** (0.58 g, 2 mmol) in the same solvent (50 ml) at room temperature and the mixture was stirred for 1 h. The solvent was distilled off under reduced pressure to leave white solids of compound **4** which were collected and recrystallized from ethanol. The yield was 0.62 g (1.73 mmol, 86.4%).

2,2,4,6,6-Pentamethyl-1-oxa-4-iodo-4-tellura-2,6-disilacyclohexane (5)

Excess of iodomethane (5 ml) was added to a solution of compound **1** (0.58 g, 2 mmol) in 30 ml of ether. A white precipitate was formed immediately; the excess of iodomethane and ether were allowed to evaporate. Recrystallization from ethanol–water (10 : 2) gave compound **5** as a pure white solid (0.82 g, 1.91 mmol, 95.4%).

2,2,6,6-Tetramethyl-1-oxa-4-benzyl-4-bromo-4-tellura-2,6-disilacyclohexane (6)

This compound was prepared in the same way as compound **5** using excess benzyl bromide as white crystals; 0.84 g, 1.83 mmol, 91.5%.

Bis(2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane)dichloropalladium(II) (7)

A benzonitrile-$PdCl_2$ complex, $PdCl_2(PhCN)_2$, (0.192 g, 0.5 mmol) was dissolved in anhydrous toluene (50 ml) and a small amount of insoluble material was filtered off. To the resulting red-brown solution was added compound **1** (0.288 g, 1 mmol), and the solution was stirred for 24 h at room temperature. Evaporation of toluene yielded an orange solid which was removed and washed with hexane until no yellow colour appeared in the washings, and dried *in vacuo* to give an orange powder of compound **7** in 71.8% yield (0.270 g, 0.359 mmol).

Bis(2,2,6,6-tetramethyl-1-oxa-4-tellura-2,6-disilacyclohexane)dichloro-μ,μ′-dipalladium(II) (8)

To a solution of Na_2PdCl_4 (0.294 g, 1 mmol) in $CHCl_3$ (20 ml) was added a solution of compound **1** (0.288 g, 1 mmol) in $CHCl_3$ (10 ml) and the mixture was stirred at room temperature for 24 h under nitrogen atmosphere. Evaporation of two-thirds of the solution gave a brown-yellow solid which was removed by filtration, washed with ethanol and dried under vacuum. The solid was dissolved in hot $CHCl_3$ (500 ml) and the solution was filtered. Addition of hexane (1000 ml) to the filtrate afforded a brownish yellow precipitate of compound **8** which was collected and dried under vacuum; 0.267 g, 0.287 mmol, 57.4%.

Reaction of 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane with Na_2Te

Sodium telluride was prepared from elemental tellurium (2.55 g, 20 mmol) and sodium borohydride (2.01 g, 53 mmol) in ethanol–water (60/10 ml) as described for the preparation of **1**. To the Na_2Te solution was added 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane, $(ClCH_2Si(CH_3)_2)_2NH$, (4.61 g, 20 mmol). The resultant solution was either stirred for 3 h at room temperature or heated under reflux for 3 h. Work-up as compound **1** yielded 0.75 g (2.61 mmol, 13%) of the telluride **1** and elemental tellurium. Diiodo and dibromo derivatives of this telluride were also prepared and confirmed to be compounds **2** and **3**, respectively. None of the expected cyclic telluride with N in the cycle was obtained under these conditions.

X-Ray structure determination of compound 2

Single crystals suitable for X-ray diffraction were obtained from a methyl ethyl ether solution. An orange plate-like crystal with dimensions of 0.2 × 0.2 × 0.07 mm was used for collection of intensity data. Diffraction data were collected at 295 K with an Enraf Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.71073 Å). The unit cell parameters were derived from least-squares refinement of 25 well-centred reflections ($20° < 2\theta < 30°$).

Crystal data. $TeI_2Si_2OC_6H_{16}$, $M = 541.77$, monoclinic, $P2_1/c$, a 12.960(3), b 8.846(2), c 13.754(4) Å, β 92.44(2)°, U 1575.4 Å^3, $Z = 4$, D_c 2.284 g/cm^3, $F(000) = 984$, μ(Mo-K_α) 58.9 cm^{-1}.

Intensity data were collected by the ω–2θ scan technique in the range $1° < 2\theta < 60°$. The intensities of three standard reflections measured every 2 hours showed no significant variations. Lorentz and polarization corrections and an empirical absorption correction were applied to the 4849 reflections measured. For the determination and refinements of the structure, 3599 independent reflections with $|F_o| > 3\sigma(F_o)$ were used. The structure was solved by the heavy-atom method and refined by full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were visible in difference Fourier maps and were included as isotropic in the structure factor calculations at the final stage of refinement. Refinement with the weighting scheme $w^{-1} = (\sigma^2(F_o) + (0.015F_o)^2)$ converged at $R = 0.049$ and $R_w = 0.067$. The final electron density maps showed no residual peaks > 1.4 e Å^{-3} close to the I atoms. Atomic scattering factors and anomalous dispersion terms were taken from ref. 19. All calculations were carried out on a HITAC M-680H computer at the Data Processing Center of the Institute for Molecular Science by using the program system UNICS III [20].

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References

1 M. Renson, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, Vol. 1, John Wiley & Sons, Chichester, 1986, ch. 13.
2 A. Toshimitsu, S. Uemura and M. Okano, J. Chem. Soc., Perkin Trans. I, (1979) 1206.
3 (a) A.Z. Al-Rubaie, H.H. Al-Shirayda and A.I. Auoub, Inorg. Chim. Acta, 134 (1987) 139; (b) A.Z. Al-Rubaie and E.A. Al-Masoudi, Heteroatom Chem., in press.
4 A.Z. Al-Rubaie and E.A. Al-Masoudi, Polyhedron, 9 (1990) 847.
5 A.Z. Al-Rubaie, Y.N. Al-Obaidi and L.Z. Yousif, Polyhedron, 9 (1990) 1141.
6 M. Schmidt and M. Wieber, Chem. Ber., 94 (1961) 1426.
7 K. Ohe, H. Takahashi, S. Uemura and N. Sugita, J. Organomet. Chem., 326 (1987) 35.
8 O.H. Ellestad, P. Klaboe and G. Hagen, Spectrochim. Acta, 29A (1973) 1247.
9 A.Z. Al-Rubaie, W.R. McWhinnie, P. Granfer and S. Chapelle, J. Organomet. Chem., 234 (1982) 287.
10 N.S. Dance, W.R. McWhinnie, J. Mallaski and Z.M. Mirzai, J. Organomet. Chem., 198 (1980) 131.
11 H.B. Singh, W.R. McWhinnie, R.F. Ziolo and C.H.W. Jones, J. Chem. Soc., Dalton Trans., (1984) 1267.
12 C. Knobler, J.D. McCullough and H. Hope, Inorg. Chem., 9 (1970) 797.
13 G.Y. Chao and J.D. McCullough, Acta Crystallogr., 15 (1962) 887.
14 H. Hope, C. Knobler and J.D. McCullough, Inorg. Chem., 12 (1973) 2665.
15 L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, NY, 1960, pp. 224, 260.
16 H. Steinfink, B. Post and I. Fankuchen, Acta Crystallogr., 8 (1955) 420.
17 D. Carlström and G. Falkenberg, Acta Chem. Scand., 27 (1973) 1203.
18 J.R. Doyle, P.E. Slade and H.B. Jonassen, Inorg. Synth., 6 (1960) 218.
19 J.A. Ibers and W.C. Hamilton (Eds.), International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
20 T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Houkoku, 55 (1979) 69.