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Structure of Dichloro[(*Z*)-2-chloro-2-*p*-tolylvinyl](*p*-methoxyphenyl)tellurium(IV)

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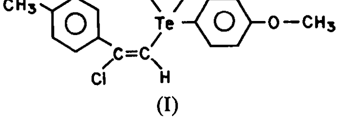
Abstract. $[TeCl_2(C_9H_8Cl)(C_7H_7O)]$, $M_r = 457·26$, orthorhombic, $Pbcn$, $a = 18·829$ (3), $b = 8·809$ (3), $c = 20·969$ (3) Å, $V = 3478$ (2) Å^3, $Z = 8$, $D_x = 1·747$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 21·75$ cm^{-1}, $F(000) = 1776$, $T = 296$ K, final $R = 0·034$ for 1958 independent observed reflections. The Te^{IV} ion is in a trigonal bipyramidal configuration with the lone pair of electrons at one of the equatorial positions. Distances and angles are: Te—Cl = 2·478 (2), 2·521 (2); Te—C = 2·085 (6), 2·117 (5) (aryl) Å; Cl—Te—Cl = 177·65 (6); Cl—Te—C = 90·8 (2), 90·2 (1), 86·8 (2), 90·1 (1); C—Te—C = 94·1 (2)°.

Introduction. Vinylic tellurides are emerging as important intermediates in the synthesis of vinyllithium compounds (Barros, Comasseto & Berriel, 1989) which are, in turn, important intermediates in organic synthesis, either as nucleophiles leading to products of chain elongation by reaction with many electrophiles or as precursors of the widely used vinyl cuprate compounds (Lipshutz, 1989; Comasseto & Berriel, 1990).

The crystal structure determination of compound (I) was undertaken because the knowledge of its stereochemistry is needed, both to predict successive reaction pathways (it is supposed that transformations occur with retention of the olefin geometry) and to postulate the structure of the intermediate compound in its synthesis.



(I)

Experimental. The synthesis of the title compound is being published elsewhere (Comasseto, Stefani & Chieffi, 1990).

A single colorless crystal with approximate dimensions 0·20 × 0·40 × 0·45 mm was used for data collection and cell determination on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the θ range 9 to 19°. Intensity data were collected in the ω–2θ scan mode up to $\theta_{max} = 25°$; 3173 reflections were measured, of which 2789 were independent ($R_{int} = 0·025$, $0 \le h \le 22$, $0 \le k \le 10$, $0 \le l \le 24$), and 1958 with $I > 3\sigma(I)$ were employed in the refinement procedure (191 parameters refined). Data were corrected for Lp and absorption, max. and min. transmission factors 1·16, 0·76 (Walker & Stuart, 1983). The intensities of two standard reflections (0,0,16, 0,16,0) were essentially constant throughout the experiment.

The structure was solved using the heavy-atom method and difference Fourier techniques. In the final cycles of least-squares refinement on F, all non-H atoms were treated anisotropically. H atoms were included as fixed contributors at positions found in a difference synthesis, slightly modified when possible on stereochemical grounds, all with a common isotropic temperature factor that refined to $U = 0·086$ Å^2. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + 0·0005F_o^2$ resulting in $R = 0·034$, $wR = 0·036$ and $S = 1·34$. Maximum shift-to-e.s.d. ratio was 0·001 and the maximum and minimum electron densities in the final difference map were 0·77 and −0·74 e Å^{-3}, respectively. Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970); for H atoms from Stewart, Davidson & Simpson (1965). Programs used: *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. Final atomic parameters for non-H atoms are given in Table 1,* interatomic distances

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* Lists of H-atom positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53713 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	B_{eq}
Te	0·6878 (1)	0·1080 (1)	0·4049 (1)	4·01 (1)
Cl(1)	0·5674 (1)	0·1862 (2)	0·4395 (1)	5·66 (6)
Cl(2)	0·8080 (1)	0·0215 (2)	0·3663 (1)	5·85 (6)
Cl(3)	0·6163 (2)	0·1922 (2)	0·2667 (1)	9·2 (1)
O(1)	0·6866 (2)	−0·3582 (5)	0·6282 (2)	5·3 (2)
C(1)	0·6445 (3)	−0·0420 (6)	0·3385 (3)	4·2 (2)
C(2)	0·6185 (3)	0·0000 (6)	0·2825 (3)	4·1 (2)
C(3)	0·5918 (3)	−0·0987 (7)	0·2327 (2)	3·9 (2)
C(4)	0·5652 (3)	−0·0449 (7)	0·1761 (3)	4·4 (2)
C(5)	0·5423 (3)	−0·1469 (8)	0·1293 (3)	5·1 (2)
C(6)	0·5445 (3)	−0·3004 (8)	0·1377 (3)	4·8 (2)
C(7)	0·5716 (3)	−0·3552 (7)	0·1941 (3)	5·1 (2)
C(8)	0·5958 (3)	−0·2573 (7)	0·2410 (3)	4·7 (2)
C(9)	0·5167 (4)	−0·4094 (9)	0·0879 (3)	7·1 (3)
C(10)	0·6913 (3)	−0·0553 (6)	0·4789 (2)	3·8 (2)
C(11)	0·7542 (3)	−0·0882 (6)	0·5092 (3)	4·3 (2)
C(12)	0·7550 (3)	−0·1922 (7)	0·5600 (3)	4·5 (2)
C(13)	0·6927 (3)	−0·2596 (7)	0·5795 (3)	4·1 (2)
C(14)	0·6303 (3)	−0·2284 (7)	0·5476 (3)	4·8 (2)
C(15)	0·6292 (3)	−0·1264 (7)	0·4974 (3)	4·4 (2)
C(16)	0·7481 (3)	−0·3861 (8)	0·6664 (3)	6·6 (3)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Te—Cl(1)	2·478 (2)	Te—Cl(2)	2·521 (2)
Te—C(1)	2·085 (6)	Te—C(10)	2·117 (5)
Cl(3)—C(2)	1·726 (6)	O(1)—C(13)	1·345 (7)
O(1)—C(16)	1·429 (8)	C(1)—C(2)	1·325 (8)
C(2)—C(3)	1·449 (8)	C(3)—C(4)	1·373 (8)
C(3)—C(8)	1·410 (9)	C(4)—C(5)	1·399 (9)
C(5)—C(6)	1·36 (1)	C(6)—C(7)	1·375 (9)
C(6)—C(9)	1·51 (1)	C(7)—C(8)	1·385 (9)
C(10)—C(11)	1·375 (7)	C(10)—C(15)	1·382 (7)
C(11)—C(12)	1·405 (8)	C(12)—C(13)	1·377 (8)
C(13)—C(14)	1·379 (8)	C(14)—C(15)	1·384 (8)

Cl(1)—Te—Cl(2)	177·65 (6)	Cl(1)—Te—C(1)	90·8 (2)
Cl(1)—Te—C(10)	90·2 (1)	Cl(2)—Te—C(1)	86·8 (2)
Cl(2)—Te—C(10)	90·1 (1)	C(1)—Te—C(10)	94·1 (2)
C(13)—O(1)—C(16)	117·9 (5)	Te—C(1)—C(2)	124·0 (4)
Cl(3)—C(2)—C(1)	116·9 (4)	Cl(3)—C(2)—C(3)	116·2 (4)
C(1)—C(2)—C(3)	126·8 (5)	C(2)—C(3)—C(4)	122·9 (5)
C(2)—C(3)—C(8)	119·2 (5)	C(4)—C(3)—C(8)	117·9 (5)
C(3)—C(4)—C(5)	119·8 (5)	C(4)—C(5)—C(6)	122·5 (6)
C(5)—C(6)—C(7)	118·0 (6)	C(5)—C(6)—C(9)	122·0 (6)
C(7)—C(6)—C(9)	120·0 (6)	C(6)—C(7)—C(8)	120·9 (6)
C(3)—C(8)—C(7)	120·8 (5)	Te—C(10)—C(11)	120·6 (4)
Te—C(10)—C(15)	119·2 (4)	C(11)—C(10)—C(15)	120·2 (5)
C(10)—C(11)—C(12)	119·8 (5)	C(11)—C(12)—C(13)	119·8 (5)
O(1)—C(13)—C(12)	125·2 (5)	O(1)—C(13)—C(14)	115·1 (5)
C(12)—C(13)—C(14)	119·7 (5)	C(13)—C(14)—C(15)	120·7 (5)
C(10)—C(15)—C(14)	119·7 (5)		

and angles are in Table 2. Fig. 1 is a projection of the molecule showing the atom numbering.

The Te^{IV} ion presents a typical trigonal bipyramidal configuration formed from four bonds to the ligands (two Cl and two C atoms) and one lone pair of electrons. The lone pair invariably occupies one of the equatorial sites, together with C(1) and C(10) in this compound, while the Cl atoms occupy the axial positions. This configuration is in complete agreement with the valence-shell electron-pair-repulsion model (VSEPR) (Gillespie, 1972). The quadruple average angle of the lone pair, α_4^E, is 112·1° and is a typical value found in TeX_4E configurations (Hargittai & Rozsondai, 1986). The Te—Cl bond lengths of 2·478 (2) and 2·521 (2) Å and the Cl—Te—Cl angle of 177·65 (6)° are in good agreement, within experimental accuracy, with the values found in other $TeCl_2RR'$ compounds (Castellano, Zukerman-Schpector, Ferreira & Comasseto, 1986; Zukerman-Schpector, Castellano, Comasseto & Stefani, 1988) and, as expected for trigonal bipyramidal coordination, the axial bonds are 0·12 and 0·16 Å longer than the sum of the normal covalent radii, 2·36 Å (Ziolo & Troup, 1983). On the other hand, the C—Te—C angle of 94·1 (2)° is smaller than the average value of 99° found in the these species. The Te—C(10) bond of 2·117 (5) Å is in good agreement with the values found for most Te^{IV}—C(aryl) bonds (Zukerman-Schpector, Castellano, Comasseto & Stefani, 1988, and references therein). Using the empirical value proposed by Lide (1962) for the radius of the trigonal C atom and the Pauling (1960) radius for the Te atom, the predicted Te—C distance is (0·74 + 1·37) = 2·11 Å, in good agreement with the values observed, Te—C(1) = 2·085 (6), Te—C(10) = 2·117 (5) Å.

Both phenyl rings are planar to within experimental accuracy [σ_{av} defined as $(\sum_i d_i^2/N-3)^{1/2}$ are σ_{av}C(3)–C(8) = 0·009 and σ_{av}C(10)–C(15) = 0·012]; the average C—C distance, uncorrected for thermal motion, is 1·384 (3) Å, which is in good agreement with the values found elsewhere (Domenicano, Murray-Rust & Vaciago, 1983). The dihedral angle between the planes defined by atoms O(1), C(13), C(13), C(16) and C(10)–C(15) inclusive is 5 (1)°. The C(1)—C(2) double-bond distance, 1·325 (8) Å, is in the expected range. The distances C(2)—C(3) = 1·449 (8) and O(1)—C(13) = 1·345 (7) Å are both shorter than the sum of the corresponding single-bond radii (Pauling, 1960), presumably due to conjugation with the phenyl rings to which they are attached.

The C(1)···C(3) distance of 2·481 (7) Å is in good agreement with the value of 2·50 Å predicted from the 1···3 non-bonded radius, also called the 'one angle' atomic radius, for C atoms of 1·25 Å (O'Keeffe & Hyde, 1981). From the Te···C(2) distance of 3·035 (5) Å, the non-bonded radius for

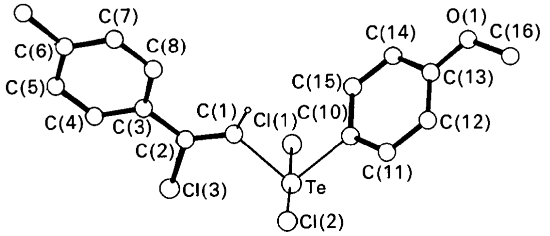
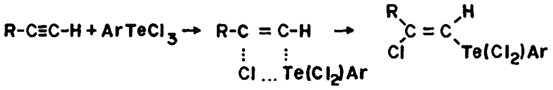


Fig. 1. Perspective view of the molecule showing the atom labelling.

Te may be estimated to be 1·79 Å; a value of 1·78 Å is found in $TeCl_2(C_7H_7O)(C_7H_{11}O_2)$ (Castellano, Zukerman-Schpector, Ferreira & Comasseto, 1986).

The fact that the title compound is in a *Z* configuration is consistent with a four-member transition state (II) and not with a telluronium intermediate which should lead to the *E* isomer.


(II)

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Structure of Wolffram's Salt Analogues [M(−chxn)$_2$Br]Br$_2$ [M = Pd, Pt; −chxn = (−)-1,2-cyclohexanediamine]

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Abstract. *trans*-Dibromobis[(−)-1(*R*),2(*R*)-cyclohexanediamine]palladium(IV)–bis[(−)-1(*R*),2(*R*)-cyclohexanediamine]palladium(II) tetrabromide, $[Pd(C_6H_{14}N_2)_2Br_2][Pd(C_6H_{14}N_2)_2]Br_4$, M_r = 936·2, MDO1: monoclinic, a = 24·464 (3), b = 7·073 (1), c = 10·586 (2) Å, β = 102·504 (6)°, V = 1788·4 (4) Å^3, Z = 2; superposition structure: orthorhombic, $I222$, a = 23·884 (3), b = 7·073 (1), c = 5·293 (1) Å, V = 894·2 (2) Å^3, Z = 1, D_x = 1·783 g cm^{-3}, $F(000)$ = 558, Ag $K\alpha$ (λ = 0·56087 Å), μ = 36·3 cm^{-1}, T = 295 K, $R(F)$ = 0·032 for 1390 observed unique reflexions [$I > 3\sigma(I)$]. *trans*-Dibromobis[(−)-1(*R*),2(*R*)-cyclohexanediamine]platinum(IV)–bis[(−)-1(*R*),2(*R*)-cyclohexanediamine]platinum(II) tetrabromide, $[Pt(C_6H_{14}N_2)_2Br_2][Pt(C_6H_{14}N_2)_2]Br_4$, M_r = 1326·4, MDO1: monoclinic, a = 24·478 (3), b = 7·022 (1), c = 10·747 (1) Å, β = 102·668 (7)°, V = 1802·4 (3) Å^3, Z = 2; superposition structure: orthorhombic, $I222$, a = 23·884 (3), b = 7·022 (1), c = 5·374 (1) Å, V = 901·3 (2) Å^3, Z = 1, D_x = 2·443 g cm^{-3}, $F(000)$ = 622, Mo $K\alpha$ (λ = 0·71073 Å), μ = 144·5 cm^{-1}, T = 295 K, $R(F)$ = 0·036 for 2697 reflexions [$I > 3\sigma(I)$]. $[Pt(C_6H_{14}N_2)_2Cl_2][Pt(C_6H_{14}N_2)_2]Cl_4$, M_r = 1059·6, MDO1: monoclinic, a = 24·810 (4), b = 6·820 (1), c = 10·316 (2) Å, β = 101·999 (3)°, V = 853·7 (3) Å^3, Z = 2. The superposition structures are isomorphous with the platinum chloride compound [Larsen & Toftlund (1977). *Acta Chem. Scand. Ser. A*, **31**, 182–186]. They are built up of M^{IV}—$X\cdots M^{II}$ chains parallel to the c axis, but with two half-weight halide ions indicating disorder. Pd^{IV}—Br = 2·521 (4), Pd^{II}—Br = 2·782 (4) and Pd—N = 2·058 (3) Å. PdN$_4$ is tetrahedrally distorted with N—Pd—N = 177·6 (8)°. Pt^{IV}—Br =

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