parameters are collected in Table III. Corrections to the intesity data for absorption were applied empirically (ψ scan method, seven reflections, 252 data, six-parameter pseudoellipsoid model).

The direct methods routine SOLV successfully located the four Fe atoms, and the structure was completed from subsequent different maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized, updated contributions (d(H–H) = 0.96 Å).

All software is contained in the P3 and SHELXTL libraries (Nicolet Corp., Madison, WI). Additional crystallographic data are available as supplementary material.

$[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CHCH(CH_3)CO_2Et)$ (26). 17 (102 mg, 0.24 mmol) and lithium hexamethyldisilazide (44 mg, 0.26 mmol) were stirred in THF (30 mL) at –20 °C for 45 min. The solution was cooled to –78 °C, and CH_3I (0.028 atm, 530 mL, 0.65 mmol) was added. The solution was stirred at room temperatue for 1 h, solvent was removed, and diethyl ether (20 mL) was added. Filtration, evaporation of solvent, and flash chromatography (alumina, 2:1 CH_2Cl_2/hexane) gave 26 (87 mg, 83%): mp (open capillary) 155–156 °C dec; ^1H NMR (acetone-d_6 270 MHz) δ 11.27 (d, J = 11.8 Hz, μ-CH), 4.93 (s, C_5H_5), 4.80 (s, C_5H_5), 4.22 (dq, J = 3.8, 7.1 Hz, C*H*H), 4.21 (dq, J = 3.8, 7.1 Hz, CH*H*), 3.39 (dq, J = 6.5, 11.8 Hz, CH), 1.70 (d, J = 6.5 Hz, CH_3), 1.30 (t, J = 7.1 Hz, CH_3), ^{13}C NMR (acetone-d_6, 126 MHz, 0.07 M Cr(acac)$_3$) δ 271.5 (μ-CO), 214.1 (CO), 213.2 (CO), 177.0 (CO_2), 173.4 (d, J = 131 Hz, μ-CH), 88.5 (d, J = 181 Hz, C_5H_5), 88.3 (d, J = 179 Hz, C_5H_5), 63.7 (d, J = 136 Hz, CH), 60.3 (t, J = 148 Hz, CH_2), 25.0 (q, J = 132 Hz, CH_3), 14.7 (q, J = 117 Hz, CH_3); IR (CH_2Cl_2) 1987 (s), 1944 (m), 1782 (s), 1716 (m) cm^{-1}; HRMS calcd for M – CO, $C_{18}H_{20}O_4Fe$, 412.0060, found 412.0047.

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Registry No. **1**, 82660-14-8; **2**, 109864-35-9; **3**, 87858-04-6; **4**, 109956-78-7; **5**, 109864-36-0; **6E**, 109864-38-2; **6Z**, 109956-80-1; **7**, 109864-39-3; **8**, 109864-41-7; **9**, 87711-26-0; **10**, 67378-10-3; **11**, 99326-81-5; **12**, 87711-12-4; **13**, 109864-33-7; **14**, 109864-43-9; **16**, 109864-44-0; **17**, 109864-45-1; **18**, 82621-29-2; **19**, 99923-10-1; **22**, 99923-12-3; **24**, 87711-31-7; **25**, 109889-33-0; **26**, 109864-46-2; $CpFe(CO)_2I$, 12078-28-3; $[(C_5H_5)Fe(CO)_3]^+PF_6^-$, 38834-26-3; $Net_4^+[HFe(CO)_4]^-$, 25879-01-0; $[(C_5H_5)_2Fe]^+BF_4^-$, 1282-37-7; lithium diethyl malonate, 34727-00-9; ethyl diazoacetate, 623-73-4; methyl 2-diazopropionate, 34757-14-7; (trimethylsilyl)diazomethane, 18107-18-1; lithium hexamethyldisilazide, 4039-32-1.

Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a structure factor table (calculated vs. observed) (27 pages). Ordering information is given on any current masthead page.

X-ray Crystal Structures of Bis(dichlorophenyltelluro)methane and Bis(trichlorotelluro)methane

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X-ray crystal structures are reported for bis(dichlorophenyltelluro)methane (1) $[(C_6H_5TeCl_2)_2CH_2$; monoclinic; space group $C2/c$; a = 24.90 (1) Å, b = 5.464 (2) Å, c = 18.158 (4) Å, β = 138.37 (3)°; Z = 4; R_F = 0.017 for 1176 observed reflections, T = –75 °C] and for bis(trichlorotelluro)methane (2) $[(TeCl_3)_2CH_2$; monoclinic; space group $P2_1/c$; a = 9.025 (3) Å, b = 6.677 (4) Å, c = 17.480 (4) Å, β = 106.16 (2)°; Z = 4; R_F = 0.042 for 2042 observed reflections, T = –74 °C]. The Te–CH_2–Te linkage in these compounds favors intramolecular Te–Cl–Te bridging interactions, resulting in unimolecular rather than oligomeric structures. In 1 the CH_2 bridge is supported by a pair of asymmetric Te···Cl–Te contacts involving one of the two chlorine atoms on each Te atom. For 2, the interactions are stronger to the point of becoming a nearly symmetrical triple bridge. The unusual ^{125}Te quadrupole couplings, previously reported for these compounds, are attributed to the constraints imposed by these bridging systems.

Introduction

The large number of crystallographic structural studies of R_2TeX_2 and $RTeX_3$ compounds, where X is a halogen, have demonstrated the stereochemical preferences of Te(IV) in such systems. In the solid state, R_2TeX_2 molecules usually adopt the distorted ψ-trigonal-bipyramidal geometry predicted by VSEPR.[1] The halogen atoms occupy the axial positions while the organic groups and the nonbonding pair of electrons occupy the equatorial positions. These molecules are weakly interconnected by secondary bonds[2] between tellurium and halogen atoms of neighboring molecules.

The $RTeX_3$ compounds, in contrast, associate in the solid state through the formation of symmetrical Te–X–Te bridges to form dimers or polymers. Each Te atom is in an irregular square-pyramidal environment in which two terminal halogen atoms and two bridging halogen atoms occupy the basal plane. The apical organic group is presumably trans to the nonbonding pair of electrons while each terminal halogen is trans to one of the bridging halogen atoms.

The preferred stereochemistry in these compounds may be altered in a variety of ways. For example, where the organic groups of an R_2TeX_2 species are replaced by a single bidendate group,[3-10] this may place a restriction on the C–Te–C bond angle. Moreover, for either $RTeX_3$ or R_2TeX_2, donor atoms, included as part of the organic

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Table I. Crystal Data, Acquisition, and Refinement Details for Bis(dichlorophenyltelluro)methane

Crystal Data

formula $(C_6H_5TeCl_2)_2CH_2$
$Z = 4$
fw 563.3
$U = 1641.4$ Å^3
$\rho_{calcd} = 2.288$ g cm^{-1}
μ(Mo Kα) = 42.07 cm^{-1}
space group $C2/c$
$a = 24.90$ (1) Å
$b = 5.464$ (2) Å
$c = 18.158$ (4) Å
$\beta = 138.37$ (3)°
temp = −75 °C

Acquisition and Refinement Details

cryst dimens (mm): 0.09 × 0.18 × 0.17
radiatn: Mo Kα; graphite monochromator; 0.710 69 Å
transmissn factors: 0.6203–0.7290
scan mode: Ω–2θ
scan width:[a] 1.1° + 0.35 tan θ
scan speed: 0.92–3.30° min^{-1}
max 2θ: 50°
reflectns: 1446 unique,[b] 1176 ($I \geq 2.5\sigma(I)$)
refined parameters: 112
GOF = $[\sum w(|F_o| - |F_c|)^2]$/degrees of freedom = 1.01
$R_F = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.017$ for 1176 data[c]
$R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum(wF_o^2)]^{1/2} = 0.020$
weighting scheme: $w = [\sigma_F^2 + 0.0002F^2]^{-1}$

[a] Backgrounds of 25% of the scan width were measured on each side of the scan. [b] Merged from 2806 ($\pm h,k,\pm l$); $R = 0.027$. [c] $R_F = 0.027$ for 1446 data.

Table II. Fractional Atomic Coordinates and Isotropic Temperature Factors for $(C_6H_5TeCl_2)_2CH_2$ at −75 °C

atom	x	y	z	U_{iso},[a] Å^2
Te	0.900293 (12)	0.17454 (4)	0.186259 (18)	0.0210
Cl(1)	1.00857 (5)	−0.05242 (17)	0.36798 (7)	0.0312
Cl(2)	0.81801 (5)	0.43405 (20)	0.01736 (7)	0.0353
C(1)	1	0.3878 (9)	1/4	0.025
C(11)	0.8725 (2)	0.4005 (6)	0.2514 (3)	0.022
C(12)	0.9080 (3)	0.3530 (7)	0.3556 (3)	0.034
C(13)	0.8906 (3)	0.5037 (8)	0.3977 (3)	0.038
C(14)	0.8381 (3)	0.6980 (7)	0.3362 (3)	0.037
C(15)	0.8015 (3)	0.7385 (8)	0.2317 (3)	0.036
C(16)	0.8177 (3)	0.5916 (7)	0.1879 (3)	0.030
H(1)	1.018 (3)	0.471 (7)	0.311 (3)	0.034 (10)
H(12)	0.941 (3)	0.212 (9)	0.392 (4)	0.060 (14)
H(13)	0.918 (3)	0.464 (8)	0.472 (4)	0.044 (12)
H(14)	0.834 (3)	0.792 (8)	0.370 (4)	0.048 (13)
H(15)	0.763 (3)	0.868 (8)	0.183 (3)	0.037 (12)
H(16)	0.790 (3)	0.620 (7)	0.116 (3)	0.032 (12)

[a] U_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Crystal Data, Acquisition, and Refinement Details for Bis(trichlorotelluro)methane

Crystal Data

formula $(TeCl_3)_2CH_2$
$Z = 4$
fw 481.95
$U = 1011.7$ Å^3
$\rho_{calcd} = 3.164$ g cm^{-1}
μ(Mo Kα) = 73.1 cm^{-1}
space group $P2_1/c$
$a = 9.025$ (3) Å
$b = 6.677$ (4) Å
$c = 17.480$ (4) Å
$\beta = 106.16$ (2)°
temp = −74 °C

Acquisition and Refinement Details

crystl dimens (mm): 0.31 × 0.32 × 0.48
radiatn: Mo Kα; graphite monochromator; 0.710 69 Å
scan mode: Ω–2θ
scan width:[a] 1.1° + 0.35 tan θ
scan speed: 1.18–5.49° min^{-1}
max 2θ: 55°
reflectns: 2505 unique, 2042 ($I \geq 2.5\sigma(I)$)
refined parameters: 78
GOF = $(\sum w(|F_o| - |F_c|)^2)$/degrees of freedom = 1.17
$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.042$ (for 2042 data)
$R_2 = [\sum(|F_o| - |F_c|)^2/\sum(F_o^2]^{1/2} = 0.049$

[a] Backgrounds of 25% of the scan width were measured on each side of the scan.

ligand(s), may usurp the role of the bridging halogen, either intramolecularly[11–15] or intermolecularly.[9,16] In other cases intermolecular interactions not involving tellurium are energetically more favorable and thus preclude bridge bonding to tellurium entirely.[10,17,18] For example, in the structure of bis(4-hydroxy-3-methylphenyl)tellurium dichloride,[18] a hydrogen bond, Cl···H–O, occurs to the exclusion of any significant secondary Te···Cl–Te bonding. Ionic modifications of R_2TeX_2, such as $[R_3Te]^+[RTeI_4]^-$,[19] are structurally and chemically different from the covalent species and will not be discussed further here.

Incorporation of two, or more, Te functionalities in the same organic molecule[20] such that they are in close proximity to one another will impose spatial and geometric restrictions on the stereochemistry about tellurium. The present study presents two such examples: $(C_6H_5TeCl_2)_2CH_2$ (1) and $(TeCl_3)_2CH_2$ (2). Tellurium-125 Mössbauer spectroscopy of these compounds[21] indicates the presence of a smaller electric field gradient than that typically observed for R_2TeCl_2 or $RTeCl_3$. This suggested that the stereochemistries about the tellurium atoms may be significantly different for 1 and 2 compared to those for $(C_6H_5)_2TeCl_2$ or $C_6H_5TeCl_3$, respectively, thus providing the motivation for the present work.

Experimental Section

The preparation and characterization of the title compounds have been described previously.[21] Crystals of $(C_6H_5TeCl_2)_2CH_2$ (1) were obtained from toluene solution by slow evaporation of solvent at reduced pressure. Crystals of $(TeCl_3)_2CH_2$ (2) were grown similarly from trichloroethylene solvent. The chemical integrity of crystals of 1 was confirmed by microanalysis. (Calcd: C, 27.62; H, 2.14. Found: C, 27.83; H, 2.13.) Crystals of 2 were analysed by mass spectrometry and were found to yield a spectrum identical with that of the compound reported and analysed previously.[21] Both samples are colorless crystalline solids, although 2 becomes, in time, slightly discolored.

All X-ray diffraction data were acquired by using an Enraf-Nonius CAD-4F diffractometer with an extensively modified low-temperature attachment and monochromatized Mo Kα radiation. Intensity standards were measured every 40 (1) or 60 (2) min of aquisition time. In addition to the normal fluctuations these intensities declined systematically by 10% (1) and 18% (2) during data collection. Accurate cell dimensions were determined, for 1, from 24 reflections (θ = 15–25°) and, for 2, from 25 reflections (θ = 17–27.5°). Diffraction symbols were determined from the diffractometer data and, in the case of 2, were checked against precession and Weissenberg photographs. Lorentz and polarization corrections, scaling, and analytical absorption corrections[22] were applied in each case. The structures were both solved by Patterson and Fourier methods. 1 was refined using programs from the NRC VAX[23] package. The refinement of 2 was performed with the system CRYSTALS.[24] Atomic scattering

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Table IV. Fractional Atomic Coordinates and Isotropic Temperature Factors for $(TeCl_3)_2CH_2$ at -74 °C

atom	x	y	z	U_{iso} or U_{equiv},[a] Å^2
Te(1)	0.01534 (7)	0.1879 (1)	0.15847 (4)	0.0206
Te(2)	0.39495 (7)	0.1618 (1)	0.16129 (4)	0.0194
Cl(1)	0.2499 (3)	-0.0148 (4)	0.2664 (1)	0.0257
Cl(2)	0.2221 (4)	0.4914 (4)	0.1803 (2)	0.0314
Cl(11)	-0.1434 (3)	0.3523 (4)	0.0460 (2)	0.0344
Cl(12)	-0.1237 (3)	-0.1159 (4)	0.1261 (2)	0.0321
Cl(21)	0.4803 (3)	-0.1514 (4)	0.1302 (2)	0.0299
Cl(22)	0.4527 (3)	0.3176 (5)	0.0536 (2)	0.0338
C(1)	0.1673 (11)	0.0997 (8)	0.0914 (6)	0.0200 (18)
H(1)	0.1446	0.1755	0.0414	0.06 (3)
H(2)	0.1558	-0.0438	0.0795	0.06 (3)

[a] Anisotropic thermal parameters refined for Te(1)–Cl(22). $U_{equiv} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

factors, including anomalous dispersion,[25] were used.

For 1, the final full-matrix least-squares refinement included fractional coordinates for all atoms, anisotropic temperature factors for all non-hydrogen atoms, isotropic temperature factors for the hydrogen atoms and the refined extinction parameter[26] ($g = 2.2$ (2) $\times 10^{-7}$). The weighting scheme (see Table I) was chosen so that the average $w(|F_o| - |F_c|)^2$ was constant for ranges of $|F|$ and $(\sin\theta)/\lambda$. The highest peak (0.45 (9) e Å^{-3}) and lowest trough (-0.47 (9) e Å^{-3}) in the final difference map were 0.92 and 1.01 Å from Te, respectively. Details of the data aquisition and structure refinement are given in Table I. Final positional parameters and equivalent isotropic thermal parameters are listed in Table II. Anisotropic temperature factors as well as a listing of observed and calculated structure factors have been deposited as supplementary material.

Data pertinent to the structure analysis of 2 are listed in Table III. In the data set for this structure some of the presumed systematically absent reflections ($h0l$, $l = 2n + 1$) appeared to be weakly observed (31 out of 194 were greater than $3\sigma(\mathbf{I})$; maximum $35\sigma(\mathbf{I})$). Disregarding this initially, the structural solution in $P2_1/c$ refined to $R_1 = 0.079$ with isotropic thermal parameters and including only the non-hydrogen atoms. Inclusion of anisotropic thermal parameters for all tellurium and chlorine atoms resulted in refinement to $R_1 = 0.048$; however, the thermal ellipsoids obtained were physically unreasonable. Attempted refinement of numerous models, some obtained by direct methods, in the space group $P2_1$, including the weak $h0l$, l odd, data yielded no significant improvement in the thermal parameters nor in the agreement of the isotropic refinement. While the data clearly suffer from a systematic effect, the good agreement between the analytically calculated absorption and the measured ψ-scan data indicated that absorption was not a likely cause of this effect. Photographic examination of crystals from several samples revealed them to be of low quality (broad diffraction maxima), and twinning was a common feature. We doubt, however, that better material could be obtained. The possibility that the crystal used to acquire the data was twinned was examined at some length; however, no satisfactory model was developed. In these unfortunate circumstances the uncorrected data were adjusted by using the empirical DIFABS correction of Walker and Stuart[27] based upon the isotropic solution at $R_1 = 0.079$. The resulting corrections ranged from 0.821 to 1.182, and after further refinement with the same variables the residual dropped to $R_1 = 0.063$.

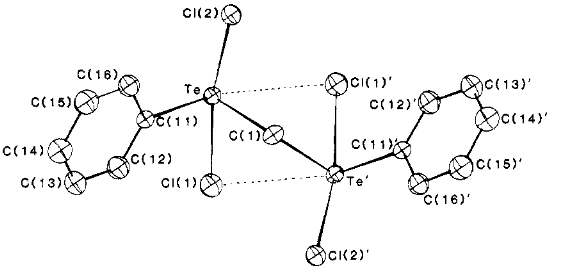

Figure 1. Molecular structure of $(C_6H_5TeCl_2)_2CH_2$.

Table V. Interatomic[a,b] Distances (Å) and Bond Angles (deg) for $(C_6H_5TeCl_2)_2CH_2$ (1) at -75 °C

Distances			
Te···Te	3.583 (3)	C(11)–C(12)	1.387 (6)
Te–Cl(1)	2.529 (3)	C(11)–C(16)	1.389 (6)
Te–Cl(2)	2.494 (3)	C(12)–C(13)	1.395 (6)
Te–C(1)	2.137 (3)	C(13)–C(14)	1.379 (6)
Te–C(11)	2.152 (4)	C(14)–C(15)	1.376 (6)
Te···Cl(1)′	3.317 (2)	C(15)–C(16)	1.386 (6)
Te···Cl(2)″	3.678 (5)		
Bond Angles			
Cl(1)–Te–Cl(2)	167.94 (3)		
Cl(1)–Te–C(1)	83.49 (11)	Cl(2)–Te–C(1)	84.84 (11)
Cl(1)–Te–C(11)	91.80 (10)	Cl(2)–Te–C(11)	92.51 (10)
Cl(1)–Te–Cl(1)′	84.56 (4)	Cl(2)–Te–Cl(1)′	87.88 (5)
Cl(1)–Te–Cl(2)″	124.46 (7)	Cl(2)–Te–Cl(2)″	67.49 (8)
C(11)–Te–Cl(1)′	161.98 (9)	C(1)–Te–C(11)	96.37 (13)
C(11)–Te–Cl(2)″	78.68 (9)	C(1)–Te–Cl(1)′	65.71 (9)
		C(1)–Te–Cl(2)″	151.45 (9)
Cl(1)′–Te–Cl(2)″	117.81 (4)		
		Te–Cl(2)–Te″	112.51 (8)
Te–C(1)–Te′	113.9 (3)	Te–Cl(1)–Te′	74.22 (5)

[a] Singly primed atoms are related to the unprimed by $(2 - x, y, {}^1/_2 - z)$. [b] Doubly primed atoms are related to the unprimed by $({}^3/_2 - x, {}^1/_2 - y, -z)$.

Final refinement of 78 parameters, including anisotropic thermal parameters for the tellurium and chlorine atoms, yielded $R_1 = 0.042$ for 2042 observed reflections. The hydrogen atoms were constrained to calculated positions with a single refined isotropic thermal parameter. As the averaged $(|F_o|)^2$ varied very little as function of $\langle|F|\rangle$, or $(\sin\theta)/\lambda$, unit weights were used in the final refinement. The largest peak in the final difference map was 2.24 (5) e Å^{-3}, situated 0.93 Å from Te(2). Final positional parameters for 2 are given in Table IV. Anisotropic thermal parameters and observed and calculated structure factors are contained in supplementary material. Diagrams were generated with the program SNOOPI.[28]

Discussion

Figure 1 shows the molecular structure of 1, viewed down the twofold axis which bisects the molecule at the methylene carbon atom. Selected interatomic distances and bond angles for 1 are listed in Table V. The primary bonds to tellurium are arranged in the expected ψ-trigonal bipyramid with the chlorine atoms axial and the phenyl and methylene groups in equatorial positions. The primary bondlengths to tellurium fall within the range found for other R_2TeCl_2 compounds,[3,5,11,16,18,29-36] although the Te–C bonds (2.137 (3) and 2.152 (4) Å) are at the upper end of

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Table VI. Comparative Angles (deg) for R_2TeCl_2 Compounds (Labeling Corresponds to 1)

	1	3	4
	$(C_6H_5TeCl_2)_2CH_2$	$(C_6H_5)_2TeCl_2{}^a$	$(CH_3)_2TeCl_2{}^b$
C(1)–Te–C(11)	96.37 (13)	99.0 (3)	96.63 (6)
C(1)–Te–Cl(1)	83.49 (11)	88.4 (2)	86.61 (5)
C(1)–Te–Cl(2)	84.84 (11)	88.1 (2)	89.29 (5)
C(1)–Te···Cl(1)′	65.71 (9)	...	72.80 (4)
C(1)–Te···Cl(2)″	151.45 (9)	164.1 (2)	161.37 (5)
C(11)–Te–Cl(1)	91.80 (10)	88.6 (2)	86.50 (4)
C(11)–Te–Cl(2)	92.51 (10)	89.2 (2)	87.66 (4)
C(11)–Te···Cl(1)′	161.98 (9)	...	169.35 (4)
C(11)–Te···Cl(2)″	78.68 (9)	95.5 (2)	81.27 (4)
Cl(1)–Te–Cl(2)	167.94 (3)	175.54 (7)	172.44 (1)
Cl(1)–Te···Cl(1)′	84.56 (4)	...	91.47 (1)
Cl(1)–Te···Cl(2)″	124.46 (7)	85.47 (6)	74.80 (1)
Cl(2)–Te···Cl(1)′	87.88 (5)	...	93.39 (1)
Cl(2)–Te···Cl(2)″	67.49 (8)	98.63 (6)	109.04 (1)
Cl(1)···Te···Cl(2)″	117.81 (4)	...	108.30 (1)

^{a}From ref 29. ^{b}From ref 30.

their range. The usual distortion from ideal trigonal-bipyramidal geometry, in which the ligands are bent away from the presumed site of the nonbonding pair of electrons, is observed. The C–Te–C bond angle (96.37 (13)°) falls in the range for R_2TeCl_2 structures (90.06 (8)°[3]–99.2(2)°[18]). The Cl–Te–Cl angle (167.94 (3)°), however, is the smallest yet reported for a R_2TeCl_2 species (previous range 169.1[36]–178.8 (1)°,[34] average 175°). It is interesting to note that these axial chlorine atoms incline toward the methylene carbon (Cl(1)–Te–C(1) = 83.49 (11)°; Cl(2)–Te–C(1) = 84.84 (11)°) and away from the phenyl ligand (Cl(1)–Te–C(11) = 91.80 (10)°; Cl(2)–Te–C(11) = 92.51 (10)°).

An intramolecular secondary bond between Te and Cl(1)′ (3.317 (2) Å) occurs roughly trans to the phenyl ligand and in the equatorial plane of Te (see Table V for angles). This interaction, though weak (bond valence 0.075),[37] is stronger than any previously reported secondary interaction in an R_2TeCl_2 species. The apparent elongation of the Te–C(11) bond, which is trans to this secondary Te···Cl interaction, is consistent with the theory of secondary bonding.[2] However, no correlation between Te–C bond lengths and trans Te···Cl secondary interactions can be discerned in the literature data for R_2TeCl_2 structures. This may be largely a consequence of the magnitude of the errors in the reported Te–C bond lengths and systematic errors in the different studies. The shortest intermolecular contact is a very weak secondary interaction (Te···Cl(2)″ = 3.678 (5) Å; bond valence 0.028),[37] roughly trans to C(1) (C(1)–Te···Cl(2)″ = 151.45 (9)°). Pairs of these contacts, situated about a crystallographic center of symmetry, link adjacent molecules into infinite chains parallel to [1,0,1]. The chlorine atom having the shorter secondary contact also has the longer primary Te–Cl bond length, as expected from bond valence summation ideas. This is generally a recognizable feature in R_2TeCl_2 structures.

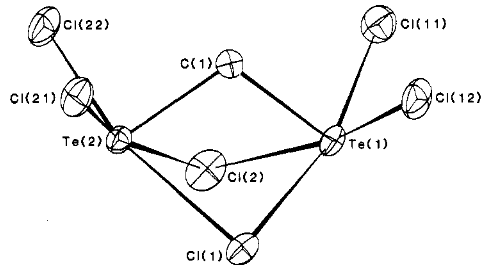

Figure 2. Molecular structure of $(TeCl_3)_2Ch_2$.

Table VII. Interatomic Distances (Å) and Bond Angles (deg) for $(TeCl_3)_2CH_2$ at –74 °C

Bond Distances			
Te(1)–Cl(1)	2.766 (3)	Te(2)–Cl(1)	2.796 (3)
Te(1)–Cl(2)	2.708 (3)	Te(2)–Cl(2)	2.771 (3)
Te(1)–Cl(11)	2.357 (3)	Te(2)–Cl(21)	2.344 (3)
Te(1)–Cl(12)	2.370 (3)	Te(2)–Cl(22)	2.334 (3)
Te(1)–C(1)	2.121 (9)	Te(2)–C(1)	2.119 (9)
Bond Angles			
Cl(1)–Te(1)–Cl(2)	84.46 (8)	Cl(1)–Te(2)–Cl(2)	82.74 (8)
Cl(1)–Te(1)–Cl(11)	165.71 (9)	Cl(1)–Te(2)–Cl(21)	91.17 (9)
Cl(1)–Te(1)–Cl(12)	89.87 (9)	Cl(1)–Te(2)–Cl(22)	165.64 (9)
Cl(1)–Te(1)–C(1)	75.6 (2)	Cl(1)–Te(2)–C(1)	75.0 (2)
Cl(2)–Te(1)–Cl(11)	90.2 (1)	Cl(2)–Te(2)–Cl(21)	165.65 (9)
Cl(2)–Te(1)–Cl(12)	166.5 (1)	Cl(2)–Te(2)–Cl(22)	90.1 (1)
Cl(2)–Te(1)–C(1)	76.1 (2)	Cl(2)–Te(2)–C(1)	74.7 (2)
Cl(11)–Te(1)–Cl(12)	92.3 (1)	Cl(21)–Te(2)–Cl(22)	92.8 (1)
Cl(11)–Te(1)–C(1)	90.2 (2)	Cl(21)–Te(2)–C(1)	91.2 (2)
Cl(12)–Te(1)–C(1)	90.6 (2)	Cl(22)–Te(2)–C(1)	91.2 (2)
Te(1)–Cl(1)–Te(2)	75.81 (6)	Te(1)–C(1)–Te(2)	107.4 (4)
Te(1)–Cl(2)–Te(2)	77.15 (7)		

The intramolecular nonbonding Te···Te distance of 3.583 (3) Å is considerably shorter than twice the accepted van der Waals radius for tellurium (4.12 Å)[38] The Te–Te bond is 2.86 (2) Å in Te metal and 2.702 (10) Å in $(p\text{-}ClC_6H_4Te)_2$.[39] The Te–C–Te angle (113.9 (3)°) is larger than the ideal tetrahedral angle, suggesting a repulsive Te···Te interaction. For R_2TeCl_2, separations between Te atoms bridged via secondary bonds alone are invariably greater than twice the van der Waals radius of tellurium (4.12 Å).[38] The shortest such distance reported is 4.459 (2) Å in $(C_6H_5)(p\text{-}BrC_6H_4)TeCl_2$.[31] In 1 the intermolecular Te···Te distance is 5.207 (3) Å.

Table VI compares selected bond angles about Te in 1 with those for $(C_6H_5)_2TeCl_2$[29] (3) and $(CH_3)_2TeCl_2$[30] (4). In 3 only one very weak Te···Cl secondary bond (3.677 (2) Å; bond valence 0.028)[37] occurs and is trans to one phenyl group. In 4 two relatively stronger Te···Cl secondary bonds [3.478 (1) (bond valence 0.049) and 3.412 (1) Å (bond valence 0.058)][37] are situated roughly trans to each of the two methyl groups. In 1 there is one relatively strong intramolecular secondary bond, one weak intermolecular secondary bond, and the nonbonding Te···Te contact (see above). It is probable that the difference in the ^{125}Te Mössbauer quadrupole splittings for these compounds (1, 8.4 (1) mm s^{-1}; 3, 9.2 (1) mm s^{-1}; 4, 9.4 (1) mm s^{-1})[21,40] arise from these subtle stereochemical differences. Certainly, the stereochemical environment about tellurium in 1 is somewhat more crowded than that in 3 or 4, and this is consistent with a reduced quadrupole coupling constant. The present lack of an adequate model to estimate electric field gradients and asymmetry parameters from structural data in such systems precludes a more quantitative correlation with the Mössbauer data. Close inspection of reported structural parameters of R_2TeCl_2 compounds[3,5,29,30,34] along with their ^{125}Te Mössbauer parameters[40–42] reveals no systematic relationship between them.

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(37) Bond valences were calculated by using the empirical method proposed by Brown and Altermatt. Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect B: Struct. Sci.* **1985**, *B41*, 244. with this method, a Te(IV)···Cl separation of 3.81 Å (the sum of the van der Waals radii) corresponds to a bond valence of 0.020.

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Table VIII. Selected Comparative Bond Angles (deg) at Tellurium for Some $RTeCl_3$ Structures[a]

	2	5[b]	6[c]	7[d]
$C-Te-Cl_{term.}$	90.2 (2)	92.3 (2)	91.8 (5)	92.7 (2)
	90.6 (2)	90.5 (2)	90.2 (7)	91.6 (2)
	91.2 (2)	92.3 (2)		91.5 (2)
	91.2 (2)	91.4 (2)		91.9 (2)
$C-Te-Cl_{bridging}$	76.1 (2)	84.9 (2)	86.8 (5)	84.7 (2)
	75.6 (2)	86.4 (1)	89.6 (7)	91.3 (2)
	74.7 (2)	85.9 (2)		87.4 (2)
	75.0 (2)	85.0 (2)		89.4 (2)
$Cl_{term.}-Te-Cl_{term.}$	92.3 (1)	95.64 (6)	92.4 (2)	92.3 (1)
	92.8 (1)	94.49 (6)	92.8 (2)	91.7 (1)
$Cl_{term.}-Te-Cl_{bridge,cis}$	90.2 (1)	88.20 (5)	90.3 (2)	93.6 (1)
	89.9 (1)	90.68 (6)	92.1 (2)	90.0 (1)
	90.1 (1)	90.92 (6)		92.6 (1)
	91.2 (1)	89.10 (6)		90.3 (1)
$Cl_{term.}-Te-Cl_{bridge,trans}$	166.5 (1)	173.56 (5)	177.0 (2)	173.1 (1)
	165.71 (9)	174.09 (7)	175.1 (2)	175.2 (1)
	165.65 (9)	174.33 (8)		177.8 (1)
	165.64 (9)	175.08 (9)		175.6 (1)
$Cl_{bridge}-Te-Cl_{bridge}$	84.46 (8)	85.40 (5)	87.0 (2)	84.3 (1)
	82.74 (8)	85.40 (5)	83.0 (2)	85.4 (1)

[a] See text for chemical formulas. [b] See ref 43. [c] See ref 44. [d] See ref 46.

The molecular structure of **2** is shown in Figure 2. Interatomic distances and bond angles are given in Table VII. It can be seen that the two tellurium atoms in the molecule have the square-pyramidal stereochemistry typical of $RTeX_3$, except that, in this case, tellurium obtains five-coordination via intramolecular bridge bonds rather than intermolecular bridges. One structure, named by the author as di-μ-bromo-μ-1,2-cyclohexylenetetrabromoditellurium, $Te_2Br_6C_6H_{10}$,[20] is the only reported structure of an $(TeX_3)-R-(TeX_3)$ molecule and displays similar intramolecular bridging halogen atoms. Other $RTeCl_3$ compounds either have a μ-Cl linked chain polymer structure[29,43-45] or form dimers with two μ-Cl bridges.[46] In cases where another donor atom can coordinate to Te via chelation, monomers are formed.[12-15]

The tellurium atoms of **2** are roughly equally disposed with respect to the bridging chlorine atoms (Te(1)–Cl(1) = 2.766 (3) Å; Te(2)–Cl(1) = 2.796 (3) Å; Te(1)–Cl(2) = 2.708 (3) Å; Te(2)–Cl(2) = 2.771 (3) Å). These bond lengths are typical of $Te-Cl_{bridging}$ for $RTeCl_3$; previous range is 2.722 (2)[43]–2.798 (2)[46] Å. However, the bond lengths between tellurium and the terminal chlorine atoms in **2** (range 2.334 (3)–2.370 (3) Å) are, on the average, shorter than the previously reported values for the same $RTeCl_3$ compounds,[29,43-45] ranging from 2.363 (2)[46] to 2.397 (6)[44] Å. In **2**, there is a negative correlation between the lengths of Te–Cl bonds which are trans to one another. The Te–C bond lengths (2.121 (9) and 2.119 (9) Å) are not significantly different from the average of literature values for $RTeCl_3$ (2.13 Å).[12-15,29,43-45]

The shorter $Te-Cl_{term.}$ (term. = terminal) bonds in **2** can, perhaps, be understood in light of the distortions caused by the $-CH_2-$ linkage. Whereas $RTeCl_3$ compounds generally display bond angles about tellurium that are close to 90°, the bridging chlorine atoms of **2** make angles at Te ranging between 74.7 (2) and 76.1 (2)° with respect to the methylene carbon. Consequently, they are not as precisely trans to the terminal chlorine atoms as they might be in the absence of the $-CH_2-$ link (average $Cl_{term.}-Te-Cl_{bridging}$ angle = 165.9°). Considering the complementary variations in trans bond lengths, it is reasonable to expect that deviations from 180° disposition of these bonds would permit a shortening of the Te–Cl terminal bonds. Bond angles about tellurium for **2** are compared, in Table VIII, with analogous angles for $(C_6H_5TeCl_3)_n$[43] (**5**) and $(p\text{-}C_2H_5OC_6H_4TeCl_3)_n$[44] (**6**), both of which have μ-Cl-bridged chain structures, and $(p\text{-}C_6H_5OC_6H_4TeCl_3)_2$[46] (**7**), which is a di-μ-Cl-bridged dimer.

The combination of the methylene linkage and the two μ-Cl bridges, in **2**, results in an intramolecular Te···Te contact of 3.417 (1) Å, as compared to 3.585 (3) Å in **1**, where the Cl bridges are highly asymmetric, and 4.073 (2) Å in **7**, where there are only Cl bridges joining the two tellurium atoms. Further evidence for the strength of these bridging Te–Cl bonds, in **2**, is found in the Te(1)–C(1)–Te(2) bond angle (107.4 (4)°), which is smaller than the ideal tetrahedral angle (109.5°). Note that in **1** the corresponding angle was 113.8 (2)°.

In **2** there are three intermolecular contacts, Te···Cl, less than the sum of the van der Waals radii (3.81 Å),[38] which are located approximately over the presumed position of the nonbonding pair of electrons on one or other of the tellurium atoms (Te(1)···Cl(1)′ = 3.625 (3) Å, C(1)–Te(1)···Cl(1)′ = 161.1 (2)°; Te(2)···Cl(21)″ = 3.718 (3) Å, C(1)–Te(2)···Cl(21)″ = 127.7 (3)°; Te(2)···Cl(1)″ = 3.779 (3) Å, C(1)–Te(2)···Cl(1)″ = 154.3 (2)°).[47] These long interactions correspond to very small bond valences, 0.033, 0.025, and 0.022, respectively.[37]

2 displays the unusually small ^{125}Te quadrupole coupling, as measured by Mössbauer spectroscopy,[21] of 7.61 (1) mm s^{-1}, as compared to a previous range of 8.0–9.4(1) mm s^{-1},[40-42] for $RTeCl_3$ species. The quadrupole splitting[40] for **6**, whose bond angles[44] are included in Table VIII, is 9.4 (1) mm s^{-1}. In these square-pyramidal environments, one would expect the largest component of the electric field gradient tensor, V_{zz}, at Te, to lie along the axis defined by the carbon atom and the nonbonding pair of electrons. The angular distortions at Te, in **2**, resulting from the intramolecular bridging interactions, deviate further from this pseudoaxial symmetry, thus reducing the electric field gradient and resulting in the smaller quadrupole splitting.

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Supplementary Material Available: Tables of thermal parameters for **1** and **2** (2 pages); listings of structure factor amplitudes for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

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