Isolation and Structure of Bis(2,2′-biphenylylene)dichloropertellurane, [12-Te-6(C4Cl2)] (λ^6-Tellane)

Soichi Sato, Takahiro Yamashita, Ernst Horn, and Naomichi Furukawa*

Tsukuba Advanced Research Alliance Center and Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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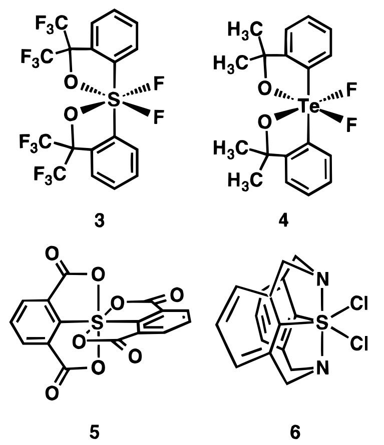
*Summary: Bis(2,2′-biphenylylene)tellurane (**1**; λ^4-tellane) reacts with sulfuryl chloride to give bis(2,2′-biphenylylene)dichloropertellurane, [12-Te-6(C4Cl2)] (**2**; λ^6-tellane) in high yield. The structure of the pertellurane **2** was determined by single-crystal X-ray crystallographic analysis, revealing that it has a distorted-octahedral geometry and a cis configuration with respect to the coordinated chlorine atoms.*

Chart 1



There are only a few hexavalent organic compounds among the hypervalent heteroatom species, and tetra- and pentavalent compounds which often exhibit a trigonal-bipyramidal structure are more common.[1] The first hexavalent organochalcogen(VI) species (λ^6-tellane) [12-X-6(C2O2F2)] (X = S (**3**), Te (**4**)) and [12-S-6(C2O4) (**5**)] have been reported by Martin et al.[2] as shown in Chart 1. Both **3** and **4** have been generated by the oxidative addition of the corresponding tetravalent chalcogenurane [10-X-4(C2O2)] with BrF_3. These structures were determined to be octahedral with *cis* configurations by X-ray crystallographic analysis. We reported that the organopersulfurane [12-S-6(C2N2Cl2)] (**6**) has been synthesized from the reaction of the diaza[3.3]metacyclophane 1,11-(methanoaminomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]thiazocin with *t*-BuOCl or *N*-chlorobenzotriazole.[3] However, its detailed structure could not be determined. The synthesis of hexamethylpertellurane, [12-Te-6(C6)], and tetramethyldifluoropertellurane, [12-Te-6(C4F2)], has been reported by Morrison et al., as have the molecular structure analysis of $(CH_3)_6Te$ by gas-phase electron diffraction[2] and its theoretical MO calculation by Schaefer et al.[4] However, synthesis of $(CH_3)_4F_2Te$ required XeF_2, which is an expensive reagent, and no structural details of the two compounds have been reported until recently. Hellwinkel et al. reported that bis(2,2′-biphenylylene)tellurane (**1**) on treatment with 1 equiv of Br_2 or I_2 gave only the corresponding telluronium bromide or iodide, and they did not obtain the corresponding pertellurane.[5] On the other hand, we have investigated the reactions of tetraaryltellurane [10-Te-4(C4)] with various reagents in order to synthesize new tetravalent telluranes containing oxygen or sulfur atoms as the ligands.[6] Furthermore, we undertook the reaction of bis(2,2′-biphenylylene)tellurane (**1**) with sulfuryl chloride and obtained the new pertellurane **2**. Here we describe the first isolation of bis(2,2′-biphenylylene)dichloropertellurane, [12-Te-6(C4Cl2)] (**2**; λ^6-tellane), and its crystal and molecular structure.

The tellurane **1** was reacted with 1 molar equiv of sulfuryl chloride in dry THF at −78 °C. After the removal of the solvent at room temperature, the corresponding tetraaryldichloropertellurane (**2**) was isolated as stable yellow crystals in 50% yield, as shown in Scheme 1. The product **2** was identified by ^{1}H, ^{13}C, and ^{125}Te NMR, mass spectroscopy, and elemental analysis.[6]

In the case of [12-Te-6(X4Y2)] having X and Y ligands (where Y is a more electronegative ligand than X), it has been reported that the corresponding pertelluranes in the *cis* configuration tend to be more stable than the corresponding *trans* configuration and the results of various NMR spectra indicate that the two X ligands on the Y−Te−Y plane are not equivalent to the other two X ligands.[2,3] Examination of the ^{1}H and ^{13}C NMR spectra of the compound **2** reveals that two biphenylylene groups are in nonequivalent states[7] with 4 doublet and 4 triplet peaks by ^{1}H NMR and 12 peaks by ^{13}C NMR. Furthermore, only the ^{1}H NMR chemical shift of the 3′-position in the *cis*-pertellurane(VI) **2**,

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(6) (a) Sato, S.; Kondo, N.; Furukawa, N. *Organometallics* **1994**, *13*, 3393−3395. (b) Sato, S.; Kondo, N.; Furukawa, N. *Organometallics* **1995**, *14*, 5393−5398.

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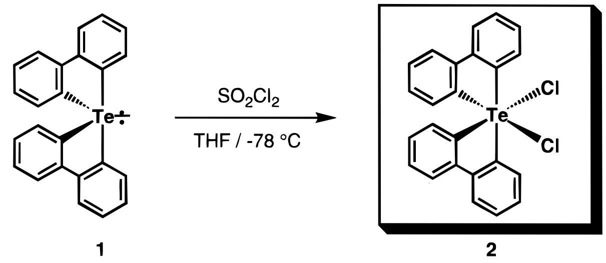
Scheme 1



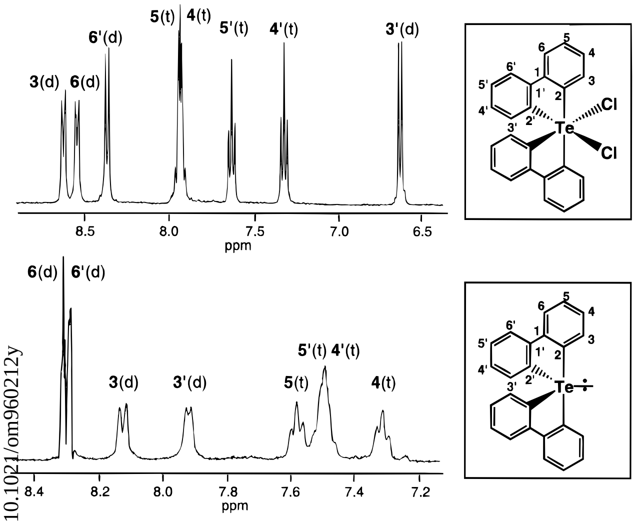


Figure 1. ^{1}H NMR spectrum of **2** at room temperature (upper) and that of **1** at −105 °C (lower),[8] along with the atom numbering of each.

having two biphenylylene groups, appears at an unusually high field compared with those of bis(2,2′-biphenylylene)selenurane or -tellurane **1** if the pseudorotation is slower than the time scale of NMR at low temperature,[8] as shown in Figure 1. This result indicates that the 3′-proton is shielded by the aromatic ring of the neighboring biphenylylene group. On the basis of these results we can conclude that compound **2** is a hexacoordinated organopertellurane having a *cis* configuration with respect to the two chlorine atoms and the inter- or intramolecular permutation of the ligands in Te(VI) is slower than the NMR time scale or is nonexistent. Furthermore, we have succeeded in determining the structure of the product **2** by X-ray crystallographic analysis.

Single crystals of **2** were formed by recrystallization from a dry THF/CH$_2$Cl$_2$ solution. A transparent light yellow crystal of dimensions 0.20 × 0.30 × 0.70 mm was analyzed on an Enraf-Nonius CAD4 four-circle diffractometer at 296 K. The crystallographic data and numerical details for the compound **2** are given in ref 9. The structure was solved by direct methods. The initial E map revealed the Te atom on the respective symmetry site (0.5, y', 0.25) with one unique chlorine atom bonded to it. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. Hydrogen atoms were added at calculated positions (C−H = 0.97, 1.08 Å for carbons with tetrahedral and planar geometries, respectively) but not refined. The neutral atom scattering factors used in the refinements were taken from Cromer and Waber[10] and corrected for anomalous dispersion.[11] Only the 1916 reflections with $I > 3.00\sigma(I)$ were used in the refinements. The final cycle of refinement included 137 variable parameters and converged with $R = 0.025$ and $R_w = 0.032$. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.44 and −0.36 e/Å^3, respectively, with the maximum located at a distance of 1.07 Å from the tellurium atom.

The molecular structure of **2** and the adopted numbering scheme for one enantiomer are illustrated by an ORTEP plot in Figure 2, together with a selected list of bond distances and angles.

The unit cell consists of four molecules of [Te(C$_{12}$H$_8$)$_2$Cl$_2$] and four CH$_2$Cl$_2$ molecules, each on a crystallographic 2-fold axis of symmetry. The racemic compound contains two types of tellurium centers, each having two biphenylylene ligands and two chloride atoms in their coordination sphere in both the Δ and Λ configurations, respectively. The central tellurium atoms have a distorted-octahedral coordination geometry with the two chloride atoms *cis* to each other. The Te−Cl bond distance exhibited is 2.530(1) Å, which is longer than the Te−Cl single covalent bond (2.31 Å)[12] and the Te−Cl bond (2.33 ± 0.02 Å)[13] of TeCl$_4$ but is similar to the apical bond lengths (2.511 and 2.528 Å) found in (CH$_3$)$_2$Cl$_2$Te and *trans*-TeCl$_4$(SC(N(CH$_3$)$_2$)$_2$)$_2$.[14] The average Te−C bond distance exhibited is 2.123(4) Å, which is similar to the Te−C single covalent bond (2.101 Å) and slightly shorter than the Te−C apical bond (2.24 Å) of bis(2,2′-biphenylylene)tellurane (**1**). A comparison of Te−C bond distances in the corresponding di-, tetra-, and hexavalent tellurium species shows that the variation of bond distances with increasing valency is irregular. The Te−C bond distances become

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(7) **2**: mp 214−216 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ 6.63 (d, J = 7.5 Hz, 2H, 3′-Ar H), 7.32 (t, J = 7.4 Hz, 2H, 4′-Ar H), 7.62 (t, J = 7.5 Hz, 2H, 5′-Ar H), 7.92 (t, J = 6.7 Hz, 2H, 4-Ar H), 7.94 (t, J = 6.7 Hz, 2H, 5-Ar H), 8.36 (d, J = 7.6 Hz, 2H, 6′-Ar H), 8.53 (d, J = 6.7 Hz, 2H, 6-Ar H), 8.61 (d, J = 6.7 Hz, 2H, 3-Ar H); ^{13}C NMR (67.8 MHz, DMSO-d_6, room temperature) δ 124.4, 125.0, 125.3, 126.7, 130.7, 131.4, 132.5, 132.6, 133.0, 133.6, 137.1, 147.7; ^{125}Te NMR (85.2 MHz, DMSO, room temperature) δ 569.0; MS (m/z) 504 (M$^+$), 469 (M$^+$ − 35), 433 (M$^+$ − 71), 282 (M$^+$ − 222). Anal. Calcd for C$_{24}$H$_{16}$Cl$_2$Te: C, 51.08; H, 3.09. Found: C, 51.11; H, 3.01. Each chemical shift was determined by two-dimensional shift correlation (^{1}H−^{1}H and ^{13}C−^{1}H COSY) spectra. All NMR spectra were recorded on a JEOL EX-270 and Bruker ARX-400.

(8) Ogawa, S.; Sato, S.; Erata, T.; Furukawa, N. *Tetrahedron Lett.* **1992**, *33*, 1915−1918.

(9) Crystallographic data for compound **2**: [C$_{24}$H$_{12}$Cl$_2$Te]·CH$_2$Cl$_2$, M_r = 587.83, monoclinic, space group $C2/c$ (No. 15), a = 15.626(2) Å, b = 11.650(1) Å, c = 13.865(2) Å, β = 112.14(1)°, V = 2337.9(5) Å^3, d_{calcd} = 1.67 g/cm^3, Z = 4, $F(000)$ = 1152.00, μ = 17.4 cm^{-1}. The data collection was carried out on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) using the $\omega/2\theta$ scan technique. A total of 2259 reflections was collected in the range $2.8 < 2\theta < 50°$. The data were corrected for decomposition (2.9%), crystal absorption (maximum and minimum transmission factors equal to 1.00 and 0.73, respectively), and Lorentz and polarization effects. The final cycle of refinement included 137 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.025$ and $R_w = \sum(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2}$ = 0.032. All calculations were performed on an Indy workstation using the teXsan crystallographic software package from Molecular Structure Corp. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

(10) Cromer, D. T.; Mann, B. J. *Acta Crystallogr.* **1968**, *A24*, 321.

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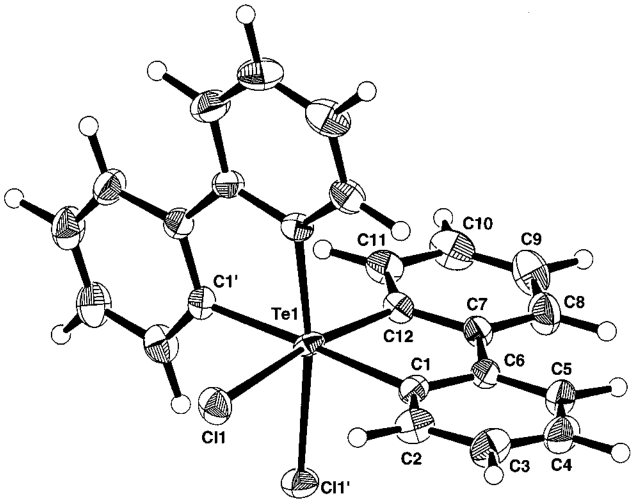

Figure 2. ORTEP view of **2** (Λ). Bond distances (Å) and angles (deg) of the non-hydrogen atoms of this enantiomer are given below (esd's in parenthesis). The primed atoms refer to the equivalent position $(1 - x, y, 0.5 - z)$ with respect to the unique asymmetric unit at (x, y, z). Bond distances: Te(1)−Cl(1), 2.530(1); Te(1)−C(1), 2.130(3); Te(1)−C(12), 2.116(4); C(1)−C(2), 1.378(5); C(1)−C(6), 1.400(5); C(2)−C(3), 1.390(6); C(3)−C(4), 1.369(7); C(4)−C(5), 1.377(6); C(5)−C(6), 1.398(5); C(6)−C(7), 1.471(5); C(7)−C(8), 1.396(6); C(7)−C(12), 1.404(5); C(8)−C(9), 1.385(7); C(9)−C(10), 1.377(7); C(10)−C(11), 1.398(6); C(11)−C(12), 1.381(5). Bond angles: Cl(1)−Te(1)−Cl(1)′, 86.48(5); Cl(1)−Te(1)−C(1), 90.3(1); Cl(1)−Te(1)−C(1)′, 87.8(1); Cl(1)−Te(1)−C(12), 171.3(1); Cl(1)−Te(1)−C(12)′, 88.1(1); C(1)−Te(1)−C(1)′, 177.3(2); C(1)−Te(1)−C(12), 99.0(1); C(1)−Te(1)−C(12)′, 82.7(1); C(12)−Te(1)−C(12)′, 98.1(2); Te(1)−C(1)−C(2), 126.6(3); Te(1)−C(1)−C(6), 109.8(3); C(2)−C(1)−C(6), 123.5(4); C(1)−C(2)−C(3), 118.0(4); C(2)−C(3)−C(4), 119.8(4); C(3)−C(4)−C(5), 121.9(4); C(4)−C(5)−C(6), 120.1(4); C(1)−C(6)−C(5), 116.7(4); C(1)−C(6)−C(7), 118.9(3); C(5)−C(6)−C(7), 124.4(4); C(6)−C(7)−C(8), 124.4(4); C(6)−C(7)−C(12), 117.9(3); C(8)−C(7)−C(12), 117.7(4); C(7)−C(8)−C(9), 120.1(4); C(8)−C(9)−C(10), 121.1(4); C(9)−C(10)−C(11), 120.5(4); C(10)−C(11)−C(12), 117.9(4); C(7)−C(12)−C(11), 122.8(4).

longer in the order dibenzotellurophene(II) (2.087 Å),[15] the pertellurane(VI) **2**, and the tellurane(IV) **1**. These results identify the order of Te−C bond distances of $(CH_3)_x$Te $(x = 2, 4, 6)$.[16]

Furthermore, the bond angle of C(1)−Te(1)−C(12) is 99.0(1)°, which is smaller than that of equatorial carbons and a tellurium(IV) atom (108.2(2)°),[5a] and the hydrogen atoms at the 3′-position of *cis*-pertellurane(VI) **2** are located nearer to the aromatic ring in the other biphenylylene group compared with the structure of bis(2,2′-biphenylylene)tellurane (**1**). The space-filling view of **2** (Λ) is shown in Figure 3. This result indicates the magnetic behavior of the hydrogen atoms at the 3′-position of **2**, as described above.

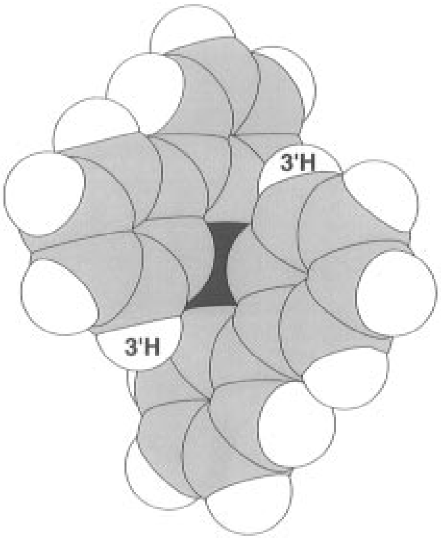

Figure 3. Space-filling illustration of **2** (Λ).

The present results provide a new procedure for the synthesis of organopertellurane (λ^6-tellane), further work on which is currently underway in our laboratory.

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Supporting Information Available: A textual presentation of experimental data and tables of crystal data, positional parameters, thermal parameters, root mean-square amplitudes, and bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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