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Synthesis and Structure of Group 14 Element Derivatives of Carbotelluroates

Kazuyasu Tani, Ryo Yamada, Takahiro Kanda, Masahiro Suzuki,
Shinzi Kato,* and Toshiaki Murai*

Department of Chemistry, Faculty of Engineering, Gifu University,
1-1 Yanagido, Gifu 501-1193, Japan

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Group 14 element derivatives of carbotelluroates, RCOTeMPh$_3$ (M = Ge, Sn, Pb), were synthesized as stable compounds by reacting sodium carbotelluroates with Ph$_3$MCl and were characterized by IR and ^{13}C and ^{125}Te NMR spectra. Their molecular structures were revealed by X-ray molecular analysis. The C=O···Sn distance in RCOTeSnPh$_3$ was found to be shorter than the C=O···Ge distance in RCOTeGePh$_3$, despite the fact that the atomic radius of Sn is larger than that of Ge. A similar shortening of the nonbonding distance was observed for the corresponding selenium derivatives. Molecular orbital calculations of model compounds, i.e., CH$_3$COEM(CH$_3$)$_3$ (E = Se, Te; M = Ge, Sn, Pb), at the B3LYP/LANL2DZ+p level also supported this shortening of the C=O···Sn distance. NBO (natural bond orbital) analyses of the model compounds showed that two types of orbital interactions, $n_O \rightarrow \sigma^*_{ME}$ and $n_O \rightarrow \sigma^*_{MC}$ (E = S, Se, Te; M = Ge, Sn, Pb), are important in these carbochalcogenoates. Furthermore, the former interaction has a greater role in the case of carbothioates, whereas the latter is dominant in carbotelluroates.

Introduction

Organometallic compounds with bonds between the heavier group 14 elements, such as Ge, Sn, and Pb, and tellurium have attracted considerable interest due to their potential as single-source precursors in electronics-related applications.[1,2] Several organometallic compounds containing Ge−Te,[3,4] Sn−Te,[2,4−9] and Pb−Te bond(s)[4,7−9] have been reported, and in all cases alkyl and aryl groups are attached to the tellurium atom. In contrast, no derivatives bearing acyl groups have been synthesized. This is in part because of the lower stability of organotellurium compounds. For example, black tellurium readily deposits from *Te*-alkyl and *Te*-aryl carbotelluroates RCOTeR′ unless they are handled under an atmosphere of inert gas. Moreover, the appropriate starting materials that lead to group 14 element derivatives of carbotelluroates have not been developed.[10] Recently, we successfully synthesized and characterized solvent and metal halide free sodium carbotelluroates.[11] We also obtained group 14 element derivatives of carboselenoate as stable compounds.[12] We report here the first synthesis and the molecular and electronic structures of group 14 element derivatives of carbotelluroates. In addition, we compared their properties with those of carbothioates and carboselenoates.

Results and Discussion

Synthesis. Group 14 element derivatives of carbotelluroates, RCOTeMPh$_3$ (M = Ge, Sn, Pb), were ob-

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Table 1. Synthesis of Group 14 Element Derivatives of Carbotelluroates 2−4

R	M	compd	% yield[a]
1-adamantyl	Ge	**2a**	15
4-$CH_3C_6H_4$	Ge	**2b**	62
4-ClC_6H_4	Ge	**2c**	39
1-adamantyl	Sn	**3a**	25
4-$CH_3C_6H_4$	Sn	**3b**	41
4-ClC_6H_4	Sn	**3c**	55
1-adamantyl	Pb	**4a**	39
4-$CH_3C_6H_4$	Pb	**4b**	61
4-ClC_6H_4	Pb	**4c**	40

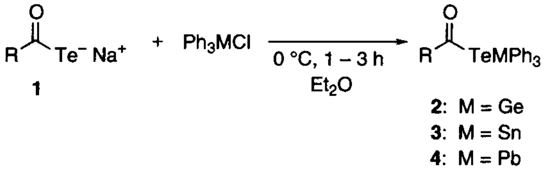
[a] Isolated yields.

Table 2. Spectroscopic Data for Group 14 Element Derivatives of Carbotelluroates 2−4

compd	IR ν(C═O)[a] (cm^{-1})	^{13}C NMR[b] δ(C═O)	^{125}Te NMR[b] δ
2a	1701	207.4	276.7
2b	1676	190.0	350.2
2c	1670	189.4	370.4
3a	1693	207.4	204.5
3b	1654	189.8	288.2
3c	1652	189.2	304.8
4a	1692	207.1	338.2
4b	1655	189.8	409.4
4c	1654	189.3	420.6

[a] As KBr disk. [b] In $CDCl_3$.

tained by reacting sodium carbotelluroates **1** with Ph_3MCl (eq 1, Table 1). For example, to a degassed Et_2O



(1)

suspension of the sodium salts **1** was added Ph_3GeCl (0.94−1.00 equiv) at 0 °C. The mixture changed from yellow to pale yellow, together with the precipitation of a small amount of black tellurium. After the mixture was stirred at the same temperature for 1−3 h, the resulting insoluble parts (black tellurium and NaCl) were filtered in vacuo. The solution was concentrated to half its original volume, and filtration of the resulting precipitates gave the corresponding *Te*-germyl carbotelluroates **2** as pale yellow microfine crystals in isolated yields of 15−62%. Under similar conditions, the reaction of **1** with Ph_3SnCl and Ph_3PbCl gave the corresponding *Te*-stannyl and *Te*-plumbyl carbotelluroates **3** and **4** as colorless and pale yellow microfine crystals in isolated yields of 25−55% and 39−61%, respectively. Compounds **2**−**4** are more stable than *Te*-alkyl carbotelluroates. No liberation of black tellurium was observed, even when **2**−**4** were exposed to the air for at least 1 day. On the other hand, when compounds **2**−**4** were dissolved in a solvent such as CH_2Cl_2 or $CHCl_3$, black tellurium was liberated even at −20 °C, leading to a complex mixture containing $(Ph_3M)_2Te$ (M = Ge,[7] Sn,[8] Pb[8]) within 6 h. This instability of **2**−**4** in solution is in marked contrast to the stability of group 14 element derivatives of carboselenoates.[12]

Table 3. Spectroscopic Data for 4-$CH_3C_6H_4COEMPh_3$

M	compd	E	IR ν(C═O)[a] (cm^{-1})	^{13}C NMR[b] δ(C═O)
Ge		S[c]	1651	191.7
	6	Se[d]	1654	192.2
	2b	Te	1676	190.0
Sn		S[c]	1621	196.0
	7	Se[e]	1644	194.9
	3b	Te	1654	189.8
Pb		Sc[c]	1618	196.4
	8	Se[f]	1641	195.4
	4b	Te	1655	189.8

[a] As KBr disk. [b] In $CDCl_3$. [c] Reference 14. [d] Reference 12c. [e] Reference 12a. [f] Reference 12b.

Spectroscopic data for group 14 element derivatives of carbotelluroates **2**−**4** are shown in Table 2. The ν(C═O) bands in Ge derivatives **2** are nearly the same as those of the corresponding *Te*-methyl carbotelluroates RCOTeMe (**5**),[11] whereas those in the Sn and Pb derivatives **3** and **4** show wavenumbers that are lower by 10−40 cm^{-1}. In ^{13}C NMR spectra, the signals due to the carbonyl carbon atom were observed at higher fields (by 5 ppm) compared to those of the *Te*-methyl carbotelluroates RCOTeMe (**5**). The Te signals in the ^{125}Te NMR spectra of carbotelluroates **2**−**4** are at higher fields (by 200 ppm) than those of *Te*-methyl carbotelluroates RCOTeMe (**5**) and at lower fields than those of Ph_3MTePh and $(Ph_3M)_2Te$.[13] The coupling constants between the Sn or Pb and Te atoms are 500 and 700 Hz, which are smaller than those for the M^{IV}−Te single bonds in Ph_3MTePh and $(Ph_3M)_2Te$ (M = Sn, ca. 3200 Hz; M = Pb, ca. 4000 Hz).[7,8] These results imply that the Sn−Te and Pb−Te bonds in **3** and **4** are weaker than those in Ph_3MTePh and $(Ph_3M)_2Te$.

Some of the IR and ^{13}C NMR spectroscopic data of group 14 element derivatives of carbochalcogenoates are given in Table 3. The C═O stretching absorption shifted to a higher frequency upon going from S to Se and Te. The signals due to the carbonyl carbon atoms in the ^{13}C NMR spectra also shifted to higher fields in the same order, except for Ge derivatives. These results suggest that the C═O bonds in Te derivatives may be stronger than those in S and Se derivatives. This tendency may depend on the degree of intramolecular coordination of the oxygen atom with the group 14 elements.

X-ray Crystallography. Suitable crystals for X-ray analysis were obtained by the recrystallization of **2b**, **3b**, and **4b** from mixed solvents of Et_2O/CH_2Cl_2/hexane, Et_2O/hexane, and Et_2O/AcOEt/hexane at −20 °C, respectively. Although the crystals of these compounds are not isomorphous, their forms are quite similar and resemble that of the corresponding sulfur homologue 4-$CH_3C_6H_4COSPbPh_3$.[14] The structure of **4b** is shown in Figure 1, and some important structural data are listed in Table 4.

This is the first X-ray molecular structure analysis of compounds bearing a Pb^{IV}−Te bond.[15] The lengths of the C(11)−O(11) and C(11)−Te(11) bonds in RCOTe-MPh_3 (M = Ge, Sn, Pb) are comparable to those in *Te*-methyl carbotelluroate,[11] diacyl telluride,[16a] carbotelluroato platinum complex,[16b] and diacyl ditelluride,[16c] indicating the existence of C═O double and C−Te single bonds, respectively. The average sums of the bond angles around group 14 elements are all 328°, which is

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(13) The ^{125}Te signals are as follows. Ph_3MTePh: M = Ge, −11.0 ppm; M = Sn, −205.8 ppm; M = Pb, −50.7 ppm.[4] $(Ph_3M)_2Te$: M = Ge, −832 ppm; M = Sn, −1290 ppm; M = Pb, −1079 ppm.[7,8]

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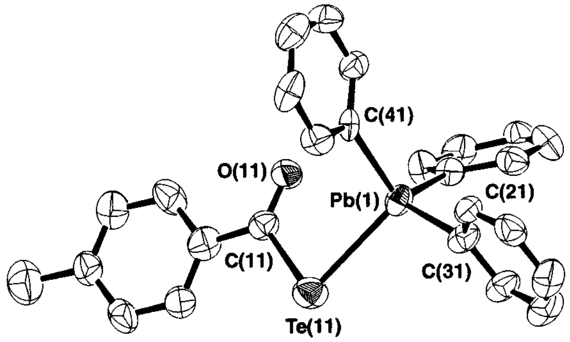

Figure 1. ORTEP drawing of 4-$CH_3C_6H_4COTePbPh_3$ (**4b**). Hydrogen atoms have been omitted for clarity.

Table 4. Bond Lengths (Å) and Angles (deg) of Group 14 Element Derivatives 2b−4b

	2b	3b	4b
M(1)···O(11)	3.332(2)	3.093(6)	3.159(9)
M(1)−Te(11)	2.5742(3)	2.745(1)	2.815(1)
Te(11)−C(11)	2.181(3)	2.189(9)	2.18(1)
O(11)−C(11)	1.204(3)	1.19(1)	1.22(1)
M(1)−C(21)	1.944(2)	2.147(9)	2.22(1)
M(1)−C(31)	1.951(3)	2.131(8)	2.20(1)
M(1)−C(41)	1.945(3)	2.140(8)	2.24(1)
M(1)−Te(11)−C(11)	93.76(7)	86.5(2)	87.5(3)
O(11)···M(1)−C(31)	158.28(8)	166.5(3)	166.5(4)

similar to the ideal tetrahedral value. The Ge(1)−Te(11) and Sn(1)−Te(11) bond distances are also close to those of cyclic and noncyclic compounds with Ge−Te[3] and Sn−Te single bonds.[5] The Pb(1)−Te(11) bond distance (2.815(1) Å) is in good agreement with the sum of the tellurium covalent radius (1.32 Å)[17] and the Pb(IV) metallic radius (1.50 Å),[18] which suggests a single bond between Pb(IV) and Te.

In **2b**, **3b**, and **4b**, the M···O (M = Ge, Sn, Pb) distances are shorter than the sum of the van der Waals radii of both atoms,[17] which suggests that a nonbonding intramolecular interaction is present between the nonbonding orbital on the carbonyl oxygen atom (n_O) and the σ^*_{MC31} orbital (∠O(11)···M(1)−C(31) = 160°) and/or the σ^*_{MTe} orbital, similar to the case for the corresponding carbothioate derivatives.[14] Interestingly, even though the atomic radius of Sn is greater than that of Ge, the C═O···Sn distance in **3b** is shorter than the C═O···Ge distance in **2b** by about 0.1 Å.

For comparison, an X-ray structural analysis of the selenium homologues, i.e., 4-$CH_3C_6H_4COSeMPh_3$ (**6**, M = Ge; **7**, M = Sn; **8**, M = Pb), was carried out. An ORTEP drawing of **8** is shown in Figure 2. Selected bond distances and angles are listed in Table 5.

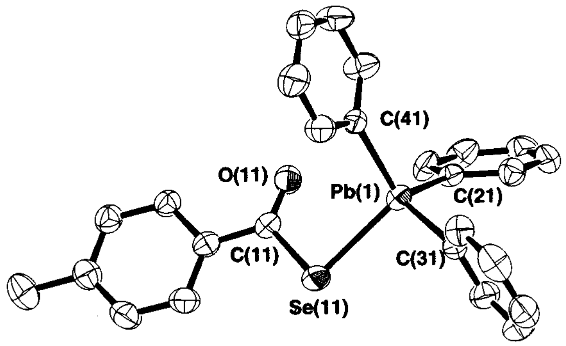

Figure 2. ORTEP drawing of 4-$CH_3C_6H_4COSePbPh_3$ (**8**). Hydrogen atoms have been omitted for clarity.

Table 5. Bond Lengths (Å) and Angles (deg) of 4-$CH_3C_6H_4COSeMPh_3$ (M = Ge, Sn, Pb)

	6	7	8
M(1)···O(11)	3.131(2)	3.068(4)	3.130(4)
M(1)−Se(11)	2.3760(4)	2.5515(7)	2.6365(5)
Se(11)−C(11)	1.953(3)	1.934(5)	1.941(4)
O(11)−C(11)	1.210(3)	1.199(6)	1.205(6)
M(1)-C(21)	1.944(3)	2.121(5)	2.198(4)
M(1)−C(31)	1.944(3)	2.145(5)	2.209(4)
M(1)−C(41)	1.942(2)	2.128(5)	2.202(4)
M(1)−Te(11)−C(11)	96.33(8)	92.4(2)	92.6(1)
O(11)···M(1)−C(31)	157.04(8)	156.5(2)	154.5(1)

The molecular forms are comparable to those of the carbotelluroate derivatives and carbothioate derivatives.[14] The C−O, C−Se, and Se−M (M = Ge, Sn, Pb) bond lengths of the carboselenoate derivatives show C═O double and C−Se and Se−M single bonds, respectively.[18,19] As expected, the distances between the carbonyl oxygen and the central group 14 elements are significantly shorter than the sum of the van der Waals radii of both atoms,[17] and the C═O···Sn distance in **7** is about 0.1 Å shorter than the C═O···Ge distance in **6**, similar to the case of carbotelluroates **2b** and **3b**.

Calculation. To explain the unusual shortening of the C═O···Sn distance, which is probably caused by nonbonding intramolecular interaction, ab initio MO calculations at the B3LYP/LANL2DZ+p level[20] were performed with the Gaussian 98 program[21] on the model compounds trimethylgermyl, trimethylstannyl, and trimethylplumbyl ethanechalcogenoates, $CH_3COEM(CH_3)_3$ (E = Se, M = Ge (**9**), Sn (**10**), Pb (**11**); E = Te: M = Ge (**12**), Sn (**13**), Pb (**14**)). Selected bond distances and angles are listed in Table 6.

The M···O distances in the optimized structures for carboselenoates and carbotelluroates were similar to those obtained by X-ray analysis; i.e., the Ge···O distances are longer than those with Sn and Pb. To obtain further information regarding the electronic structures, NBO (natural bond orbital) analyses were carried out.[21]

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(20) The Becke-style three-parameter density functional theory using the Lee−Yang−Parr correlation functional (B3LYP) was applied in our calculations. The effective core potentials (ECPs) LANL2DZ+p were used for C, O, Se, Te, Ge, Sn, and Pb. The d polarization function for the ECP basis set of all atoms, except for H, are taken from: Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, Y.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations;* Elsevier: Amsterdam, 1984.

Table 6. Calculated Geometrical Parameters (Bond Distances in Å and Angles in deg) for $CH_3COEM(CH_3)_3$ (E = Se, Te; M = Ge, Sn, Pb) at the B3LYP/LANL2DZ+p Level

	$CH_3COSeM(CH_3)_3$		
	M = Ge (**9**)	M = Sn (**10**)	M = Pb (**11**)
M(1)···O(3)	3.254	3.203	3.235
M(1)−Se(2)	2.442	2.616	2.681
Se(2)−C(4)	1.214	1.216	1.217
O(3)−C(4)	1.967	1.963	1.959
M(1)−C(6)	1.967	2.142	2.198
M(1)−C(7)	1.973	2.149	2.208
M(1)−C(8)	1.967	2.142	2.198
M(1)−Se(2)−C(4)	96.89	93.65	93.45

	$CH_3COTeM(CH_3)_3$		
	M = Ge (**12**)	M = Sn (**13**)	M = Pb (**14**)
M(1)···O(3)	3.409	3.332	3.348
M(1)−Te(2)	2.638	2.808	2.863
Te(2)−C(4)	1.212	1.214	1.214
O(3)−C(4)	2.185	2.183	2.181
M(1)−C(6)	1.970	2.145	2.203
M(1)−C(7)	1.076	2.151	2.211
M(1)−C(8)	1.970	2.145	2.203
M(1)−Te(2)−C(4)	93.56	89.86	89.49

Table 7. Orbital Energy and Contributions of Atomic Orbitals for $CH_3COEM(CH_3)_3$ (E = Se, Te; M = Ge, Sn, Pb) at the B3LYP/LANL2DZ+p Level

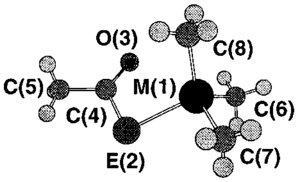
	$CH_3COSeM(CH_3)_3$		
	M = Ge (**9**)	M = Sn (**11**)	M = Pb (**11**)
orbital energy (au)			
$n_O(1)^a$	−0.67480	−0.67742	−0.67336
$n_O(2)^b$	−0.27414	−0.27631	−0.27205
σ^*_{MSe}	0.10997	0.07814	0.05593
σ^*_{MC7}	0.26792	0.19951	0.14229
σ^*_{MSe} (%)			
M	70.36	74.88	74.96
Se	29.64	25.12	25.06
σ^*_{MC7} (%)			
M	72.49	75.70	73.31
C7	27.51	24.30	26.69

	$CH_3COTeM(CH_3)_3$		
	M = Ge (**12**)	M = Sn (**13**)	M = Pb (**14**)
orbital energy (au)			
$n_O(1)^a$	−0.67637	−0.67909	−0.67650
$n_O(2)^b$	−0.28023	−0.28221	−0.27957
σ^*_{MTe}	0.08469	0.06247	0.04650
σ^*_{MC7}	0.25843	0.19099	0.13618
σ^*_{MTe} (%)			
M	64.52	69.88	70.05
Te	35.48	30.12	29.95
σ^*_{MC7} (%)			
M	72.23	75.52	73.19
C7	27.77	24.48	26.81

[a] The $sp^{0.7}$ hybridized lone pair of the carbonyl oxygen. [b] The p-type lone pair of the carbonyl oxygen.

The results regarding orbital energies and the magnitude of the contribution of atomic orbitals to σ^*_{ME} and σ^*_{MC7} are listed in Table 7, and the stabilization energies are listed in Table 8.

Table 8. NBO Analysis (ΔE^a in kcal mol^{-1}) of $CH_3COEM(CH_3)_3$ (E = Se, Te; M = Ge, Sn, Pb) at the B3LYP/LANL2DZ+p Level



	$CH_3COSeM(CH_3)_3$		
	M = Ge (**9**)	M = Sn (**10**)	M = Pb (**11**)
$n_O \rightarrow \sigma^*_{MSe}$		1.33	1.23
$n_O \rightarrow \sigma^*_{MC(7)}$	1.55	1.88	1.98

	$CH_3COTeM(CH_3)_3$		
	M = Ge (**12**)	M = Sn (**13**)	M = Pb (**14**)
$n_O \rightarrow \sigma^*_{MTe}$			
$n_O \rightarrow \sigma^*_{MC(7)}$	1.08	1.54	1.71

[a] ΔE = stabilization energies associated with delocalization.

The orbital energy of σ^*_{GeE} (E = Se, Te) is higher than that of σ^*_{ME} (M = Sn, Pb; E = Se, Te). The σ^*_{GeC} and σ^*_{GeE} orbitals extend to the carbon and chalcogen atoms more deeply than those in the corresponding Sn and Pb derivatives. These tendencies were also observed for carbothioate derivatives. However, these orbital energies and atomic orbital contributions are not directly related to the unusual shortening of the C═O···Sn distances. In fact, NBO analysis suggested that two types of nonbonding orbital interactions ($n_O \rightarrow \sigma^*_{ME}$ and $n_O \rightarrow \sigma^*_{MC7}$) contribute to the shortening, as shown in Table 8. In carboselenoates, both interactions are equally important, whereas $n_O \rightarrow \sigma^*_{MC7}$ plays a dominant role in carbotelluroates. This is in sharp contrast to the case of carbothioates, in which $n_O \rightarrow \sigma^*_{MS}$ is more important.

Conclusion

We have described the synthesis and molecular and electronic structures of the first group 14 element derivatives of carbotelluroates. They were synthesized as stable compounds in low to good yields. X-ray molecular analysis and theoretical calculations revealed an unusual shortening of the C═O···Sn distances and nonbonding intramolecular interactions between the oxygen and Sn atoms. NBO analysis indicated that this is predominantly due to $n_O \rightarrow \sigma^*_{MC7}$.

Experimental Section

Reactions were carried out under argon using standard Schlenk techniques. Sodium carbotelluroates[11] were prepared as described in the literature. Ph_3GeCl, Ph_3SnCl, and Ph_3PbCl were used as purchased from Aldrich Chemical Co. All solvents were purified under argon and dried as indicated: Et_2O and hexane were refluxed with sodium benzophenone ketyl and distilled before use. CH_2Cl_2 and AcOEt were distilled over diphosphorus pentaoxide after refluxing for 5 h. All solvents were degassed before use. ^1H (399.7 MHz) and ^{13}C NMR (100.4

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Table 9. Crystallographic Data

	2b	**3b**	**4b**	**6**	**7**	**8**
formula	$C_{26}H_{22}OGeTe$	$C_{26}H_{22}OSnTe$	$C_{26}H_{22}OPbTe$	$C_{26}H_{22}OGeSe$	$C_{26}H_{22}OSnSe$	$C_{26}H_{22}OPbSe$
fw	550.65	596.75	685.26	502.01	548.11	636.62
color	yellow	pale yellow	pale yellow	colorless	colorless	yellow
cryst size (mm)	0.14 × 0.23 × 0.34	0.43 × 0.40 × 0.29	0.26 × 0.14 × 0.11	0.23 × 0.43 × 0.43	0.23 × 0.23 × 0.29	0.23 × 0.31 × 0.34
T (K)	193	193	193	193	296	193
cryst syst	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.376(1)	13.680(4)	13.703(2)	9.3795(9)	9.592(1)	9.618(1)
b (Å)	16.058(3)	9.625(2)	9.671(1)	16.058(1)	16.309(2)	16.052(3)
c (Å)	8.061(1)	18.774(2)	18.865(1)	7.9443(7)	7.8722(6)	7.811(1)
α (deg)	93.04(2)			91.582(7)	92.497(8)	92.83(2)
β (deg)	110.39(1)	110.72(1)	110.972(7)	111.759(7)	109.783(6)	109.32(1)
γ (deg)	92.10(1)			93.821(7)	91.956(10)	91.36(1)
V (Å^3)	1134.1(3)	2312.0(9)	2334.5(5)	1107.1(2)	1156.1(2)	1135.6(3)
Z	2	4	4	2	2	2
D_{calcd} (g cm^{-3})	1.612	1.714	1.950	1.506	1.574	1.862
μ (mm^{-1})	2.625	2.356	8.478	3.041	2.693	9.057
F(000)	540.00	1152.00	1280.00	504.00	540.00	604.00
no. of rflns: measd/unique	5527/5210	5874/5323	5929/5375	5406/5092	5619/5302	5406/5217
no. of observns ($I > 2\sigma(I)$)	4326	3565	2561	3867	3692	4449
R1, wR2	0.024, 0.077	0.032, 0.179	0.045, 0.136	0.027, 0.085	0.048, 0.120	0.025, 0.073
goodness of fit	1.00	1.88	0.98	1.00	1.17	0.96
final max, min $\Delta\rho$ (e Å^{-3})	0.59, 0.36	1.07, −0.97	2.80, −5.78	0.52, −0.54	1.18, −1.30	0.83, −1.16

MHz) were recorded using $CDCl_3$ as a solvent with Me_4Si as an internal standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR with a JEOL JNM-α400 spectrometer. In ^{119}Sn NMR spectra (126.0 MHz), Me_4Sn was used as an external standard. In ^{125}Te NMR spectra (149.0 MHz), Me_2Te was used as an external standard. IR spectra were measured on a Perkin-Elmer FT-IR 1640 spectrophotometer. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University.

X-ray Crystallography. Crystal samples were cut from grown crystals and mounted on a glass fiber. The crystals were coated with an epoxy resin because they were sensitive to air. Measurements were carried out on a Rigaku AFC7R four-circle diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\,69$ Å). The data were collected at 193 or 296 K. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. The intensities of 3 representative reflections were measured after every 150 reflections. The structure was solved by a direct method using SHELXS86[22] and expanded using DIRDIF94.[23] An empirical absorption correction (ψ-scan) was also applied. Neutral atom scattering factors for neutral atoms were from Cromer and Waber,[24] and anomalous dispersion effects[25] were used. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, and the weighting scheme was $w = 1/[\sigma^2(F_o^2)]$. Full-matrix least-squares refinement was executed, with non-hydrogen atoms being anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions for which each isotropic thermal parameter was set to 1.2 times that of the connecting atoms. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp. Crystallographic data of **2b**−**4b** and **6**−**8** are summarized in Table 9.

Synthesis of *Te*-Triphenyl Group 14 Element Derivatives of Carbotelluroates. The synthesis of *Te*-triphenylgermyl 1-adamantanecarbotelluroate **2a** is described in detail as a typical procedure for compounds **2**−**4**.

***Te*-Triphenylgermyl 1-Adamantanecarbotelluroate (2a).** Ph_3GeCl (0.385 g, 1.13 mmol) was added to a suspension of sodium 1-adamantanecarbotelluroate (0.356 g, 1.13 mmol) in Et_2O (10 mL) at 0 °C under an argon atmosphere. The mixture rapidly changed from yellow to pale yellow together with the precipitation of a small amount of black tellurium. After the mixture was stirred at the same temperature for 1.5 h, the insoluble parts (black tellurium and NaCl) were filtered off by a glass filter (G4) in vacuo. Hexane (7 mL) was added to the filtrate, and the solution was concentrated to ca. 15 mL under reduced pressure (0 °C, 26.7 Pa). Filtration of the resulting precipitates gave 0.104 g (15%) of **2a** as colorless microfine crystals. Mp: 99−104 °C dec. Anal. Calcd for $C_{29}H_{30}OGeTe$: C, 58.57; H, 5.08. Found: C, 58.28; H, 5.00. IR (KBr, cm^{-1}): 1701 ν(C═O). ^1H NMR ($CDCl_3$): δ 1.56 (m, 6 H, Ad), 1.68 (d, 6 H, $J = 2.7$ Hz, Ad), 1.94 (s, 3 H, Ad), 7.17−7.29 (m, 9 H, Ar), 7.51−7.54 (m, 6 H, Ar). ^{13}C NMR ($CDCl_3$): δ 28.2, 36.5, 39.2, 56.1, 128.3, 129.4, 135.0, 136.2, 207.4 (C═O). ^{125}Te NMR ($CDCl_3$): δ 276.7.

***Te*-Triphenylgermyl 4-Methylbenzenecarbotelluroate (2b).** The compound was obtained as pale yellow microfine crystals (62%). Mp: 117−118 °C dec. Anal. Calcd for $C_{26}H_{22}OGeTe$: C, 56.71; H, 4.03. Found: C, 56.69; H, 4.02. IR (KBr, cm^{-1}): 1676 ν(C═O). ^1H NMR ($CDCl_3$): δ 2.22 (s, 3 H, CH_3), 7.05 (d, 2 H, $J = 8.5$ Hz, Ar), 7.26−7.29 (m, 9 H, Ar), 7.54−7.59 (m, 8 H, Ar). ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3), 128.4, 129.3, 129.6, 134.1, 135.0, 135.8, 140.7, 144.8, 190.0 (C═O). ^{125}Te NMR ($CDCl_3$): δ 350.2.

***Te*-Triphenylgermyl 4-Chlorobenzenecarbotelluroate (2c).** The compound was obtained as pale yellow microfine crystals (39%). Mp: 105−107 °C dec. Anal. Calcd for $C_{25}H_{19}OClGeTe$: C, 52.58; H, 3.35. Found: C, 52.28; H, 3.54. IR (KBr, cm^{-1}): 1670 ν(C═O). ^1H NMR ($CDCl_3$): δ 7.18 (d, 2 H, $J = 8.8$ Hz, Ar), 7.25−7.27 (m, 9 H, Ar), 7.54−7.57 (m, 6 H, Ar), 7.57 (d, 2 H, $J = 8.8$ Hz, Ar). ^{13}C NMR ($CDCl_3$): δ 128.5, 128.8, 129.4, 129.7, 134.7, 135.5, 140.2, 141.5, 189.4 (C═O). ^{125}Te NMR ($CDCl_3$): δ 370.4.

***Te*-Triphenylstannyl 1-Adamantanecarbotelluroate (3a).** The compound was obtained as colorless microfine crystals (25%). Mp: 99−104 °C dec. Anal. Calcd for $C_{29}H_{30}OSnTe$: C, 54.35; H, 4.72. Found: C, 54.47; H, 4.84. IR (KBr, cm^{-1}): 1693 ν(C═O). ^1H NMR ($CDCl_3$): δ 1.55 (m, 6 H, Ad), 1.67 (d, 6 H, $J = 2.7$ Hz, Ad), 1.93 (s, 3 H, Ad), 7.24−7.29 (m,

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9 H, Ar), 7.48−7.61 (m, 6 H, Ar). ^{13}C NMR (CDCl$_3$): δ 28.2, 36.4, 39.5, 56.4, 128.6, 129.3, 136.8, 137.9 ($^1J_{^{13}\mathrm{C}-^{117}\mathrm{Sn}} = 494$ Hz, $^1J_{^{13}\mathrm{C}-^{119}\mathrm{Sn}} = 518$ Hz), 207.4 (C=O). ^{119}Sn NMR (CDCl$_3$): δ −136.3 ($^1J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 518$ Hz, $^1J_{^{119}\mathrm{Sn}-^{125}\mathrm{Te}} = 2792$ Hz). ^{125}Te NMR (CDCl$_3$): δ 204.5 ($^1J_{^{125}\mathrm{Te}-^{117}\mathrm{Sn}} = 2670$ Hz, $^1J_{^{125}\mathrm{Te}-^{119}\mathrm{Sn}} = 2792$ Hz).

***Te*-Triphenylstannyl 4-Methylbenzenecarbotelluroate (3b).** The compound was obtained as pale yellow microfine crystals (41%). Mp: 117−118 °C dec. Anal. Calcd for $C_{26}H_{22}OSnTe$: C, 52.33; H, 3.72. Found: C, 52.41; H, 3.79. IR (KBr, cm^{-1}): 1654 ν(C=O). ^{1}H NMR (CDCl$_3$): δ 2.14 (s, 3 H, CH$_3$), 6.96−7.26 (m, 12 H, Ar), 7.50−7.67 (m, 6 H, Ar). ^{13}C NMR (CDCl$_3$): δ 21.6 (CH$_3$), 128.5, 128.9, 129.4, 136.7, 137.7 ($^1J_{^{13}\mathrm{C}-^{117}\mathrm{Sn}} = 500$ Hz, $^1J_{^{13}\mathrm{C}-^{119}\mathrm{Sn}} = 523$ Hz), 138.0, 139.3, 140.8, 189.8 (C=O). ^{119}Sn NMR (CDCl$_3$): δ −131.8 ($^1J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 523$ Hz, $^1J_{^{119}\mathrm{Sn}-^{125}\mathrm{Te}} = 2681$ Hz). ^{125}Te NMR (CDCl$_3$): δ 288.2 ($^1J_{^{125}\mathrm{Te}-^{117}\mathrm{Sn}} = 2560$ Hz, $^1J_{^{125}\mathrm{Te}-^{119}\mathrm{Sn}} = 2681$ Hz).

***Te*-Triphenylstannyl 4-Chlorobenzenecarbotelluroate (3c).** The compound was obtained as pale yellow microfine crystals (55%). Mp: 105−107 °C dec. Anal. Calcd for $C_{25}H_{19}OClSnTe$: C, 48.65; H, 3.10. Found: C, 48.74; H, 3.24. IR (KBr, cm^{-1}): 1652 ν(C=O). ^{1}H NMR (CDCl$_3$): δ 7.23−7.33 (m, 11 H, Ar), 7.54−7.69 (m, 8 H, Ar). ^{13}C NMR (CDCl$_3$): δ 128.6, 128.8, 129.6, 129.8, 137.1, 137.5 ($^1J_{^{13}\mathrm{C}-^{117}\mathrm{Sn}} = 503$ Hz, $^1J_{^{13}\mathrm{C}-^{119}\mathrm{Sn}} = 527$ Hz), 140.4, 141.6, 189.2 (C=O). ^{119}Sn NMR (CDCl$_3$): δ −127.9 ($^1J_{^{119}\mathrm{Sn}-^{13}\mathrm{C}} = 526$ Hz, $^1J_{^{119}\mathrm{Sn}-^{125}\mathrm{Te}} = 2600$ Hz). ^{125}Te NMR (CDCl$_3$): δ 304.8 ($^1J_{^{125}\mathrm{Te}-^{117}\mathrm{Sn}} = 2475$ Hz, $^1J_{^{125}\mathrm{Te}-^{119}\mathrm{Sn}} = 2600$ Hz).

***Te*-Triphenylplumbyl 1-Adamantanecarbotelluroate (4a).** The compound was obtained as pale yellow microfine crystals (39%). Mp: 111−114 °C dec. Anal. Calcd for $C_{29}H_{30}OPbTe$: C, 47.76; H, 4.15. Found: C, 47.78; H, 4.18. IR (KBr, cm^{-1}): 1692 ν(C=O). ^{1}H NMR (CDCl$_3$): δ 1.55 (m, 6H, CH$_2$), 1.77 (d, 6 H, J = 2.7 Hz, CH$_2$), 1.92 (s, 3 H, CH), 7.11−7.35 (m, 9 H), 7.56−7.58 (m, 6 H). ^{13}C NMR (CDCl$_3$): δ 28.3, 36.4, 39.8, 56.5, 128.7, 129.5, 137.1, 150.4 ($J_{^{13}\mathrm{C}-^{207}\mathrm{Pb}} = 419$ Hz), 207.1 (C=O). ^{125}Te NMR (CDCl$_3$): δ 338.2 ($J_{^{125}\mathrm{Te}-^{207}\mathrm{Pb}} = 3561$ Hz).

***Te*-Triphenylplumbyl 4-Methylbenzenecarbotelluroate (4b).** The compound was obtained as pale yellow microfine crystals (61%). Mp: 111−112 °C dec. Anal. Calcd for $C_{26}H_{22}OPbTe$: C, 45.57; H, 3.24. Found: C, 45.27; H, 3.40. IR (KBr, cm^{-1}): 1655 ν(C=O). ^{1}H NMR (CDCl$_3$): δ 2.31 (s, 3H, CH$_3$), 7.14 (d, 2 H, J = 8.2 Hz), 7.29−7.47 (m, 9 H), 7.68 (d, 2 H, J = 8.2 Hz), 7.71−7.74 (m, 6 H). ^{13}C NMR (CDCl$_3$): δ 21.7 (CH$_3$), 128.9, 129.0, 129.3, 129.7, 137.2, 144.1, 144.7, 150.7 ($J_{^{13}\mathrm{C}-^{207}\mathrm{Pb}} = 431$ Hz), 189.8 (C=O). ^{125}Te NMR (CDCl$_3$): δ 409.4 ($J_{^{125}\mathrm{Te}-^{207}\mathrm{Pb}} = 3424$ Hz).

***Te*-Triphenylplumbyl 4-chlorobenzenecarbotelluroate (4c).** The compound was obtained as pale yellow microfine crystals (40%). Mp: 102−104 °C dec. Anal. Calcd for $C_{25}H_{19}ClOPbTe$: C, 42.55; H, 2.71. Found: C, 42.30; H, 2.66. IR (KBr, cm^{-1}): 1654 ν(C=O). ^{1}H NMR (CDCl$_3$): δ 7.23−7.27 (m, 5 H), 7.29−7.41 (m, 6 H), 7.62−7.65 (m, 8 H). ^{13}C NMR (CDCl$_3$): δ 128.8, 129.0, 129.9, 130.0, 137.2, 140.2, 142.1, 150.7 ($J_{^{13}\mathrm{C}-^{207}\mathrm{Pb}} = 438$ Hz), 189.3 (C=O). ^{125}Te NMR (CDCl$_3$): δ 420.6 ($J_{^{125}\mathrm{Te}-^{207}\mathrm{Pb}} = 3339$ Hz).

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Supporting Information Available: ORTEP drawings and X-ray crystal data for compounds **2b**−**4b** and **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 178958-178963, for the compounds **2b**−**4b** and **6**−**8**, respectively.

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