

# **Studies on Chalcogenocarboxylic Acid Derivatives**

研究報告 甲169

**Kazuyasu Tani**

**2002**

## Preface

The studies presented in this thesis have been carried out under the direction of Professor Satoshi Inagaki, Shinzi Kato and Toshiaki Murai at Department of Chemistry, Faculty of Engineering, Gifu University during 1996–2002.

The studies are concerned with the investigation of the studies on chalcogenocarboxylic acid derivatives.

Yanagido, Gifu

January 2002

Kazuyasu Tani



## List of Publications

The contents of this thesis are composed of the following papers.

- (1) Unusually Short Distances between the Carbonyl Oxygen and the Tin Atom in  $\text{RCOSMR}'_3$  ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ): The Importance of Intramolecular  $\text{nO} \rightarrow \sigma^*_{\text{MS}}$  Orbital Interactions  
Tani, K.; Kato, S.; Kanda, T.; Inagaki, S.  
*Org. Lett.* **2001**, Vol. 3, No. 5, 655–657.
- (2) Synthesis and Structure of Group 14 Element Derivatives of Carbotelluroates  
Tani, K.; Yamada, R.; Kanda, T.; Suzuki, M.; Kato, S.; Murai, T.  
*Organometallics* **2002**, in press.
- (3) Structural Analysis of Phenyl-Germanium, -Tin, and -Lead Dithiocarboxylates  $[(\text{RCSS})_x\text{MPh}_{4-x}]$ ,  $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ;  $x = 1-3$ : Affinity between Thiocarbonyl Sulfur and Group 14 Elements  
Kato, S.; Tani, K.; Kitaoka, N.; Yamada, K.; Mifune, H.  
*J. Organomet. Chem.* **2000**, Vol. 611, 190–199.
- (4) Acylthio- and Thioacylthiophosphines  $[(\text{RCES})_n\text{PPh}_{3-n}]$ ,  $\text{E} = \text{O}, \text{S}$ ;  $n = 1-3$ : Synthesis and Structural Analysis  
Tani, K.; Matsuyama, K.; Kato, S.; Yamada, K.; Mifune, H.  
*Bull. Chem. Soc. Jpn.* **2000**, Vol. 73, No. 5, 1243–1252.
- (5) Thioacylsulfanylarsines  $(\text{RCS}_2)_x\text{AsPh}_{3-x}$ ,  $x = 1-3$ : Synthesis, Structures, Natural Bond Order Analyses and Reactions with Piperidine  
Tani, K.; Hanabusa, S.-i.; Kato, S.; Mutoh, S.-y.; Suzuki, S.-i.; Ishida, M.  
*J. Chem. Soc., Dalton Trans.* **2001**, No. 5, 518–527.
- (6) Ammonium Diselenoates: Stable Heavy Congeners of Carboxylic Acid Salts  
Tani, K.; Murai, T. Kato, S.  
*J. Am. Chem. Soc.* to be publication.
- (7) Acyl Carbamoyl Selenides and Related Sulfur Isologues: Synthesis and X-Ray Structural Analyses  
Kageyama, H.; Tani, K.; Kato, S.; Kanda, T.  
*Heteroatom Chem.* **2001**, Vol. 12, No. 4, 250–258.

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## General Introduction

Chalcogenocarboxylic acids are the series of compounds in which one or two oxygen atoms of the carboxyl group are replaced by sulfur, selenium or tellurium atoms. These are 15 kinds of chalcogen isologues as shown in Chart 1. Among these, the chemistry of thio- and dithiocarboxylic acid and its derivatives, especially thio- and dithioesters, has been extensively investigated.<sup>1</sup> These have been found to be useful as pharmaceuticals,<sup>2</sup> bactericides and fungicides.<sup>3</sup> In contrast, selenium and tellurium derivatives have little been known to date except for their alkyl and aryl esters due to their unstability in air and/or to the lack of general synthetic method to construct such chalcogenocarboxyl group. Seleno- and tellurocarboxylate esters have been found to be effective as liquid crystals,<sup>4</sup> nerve impulses blocking agents<sup>5</sup> and high grade photosensitizers.<sup>6</sup>

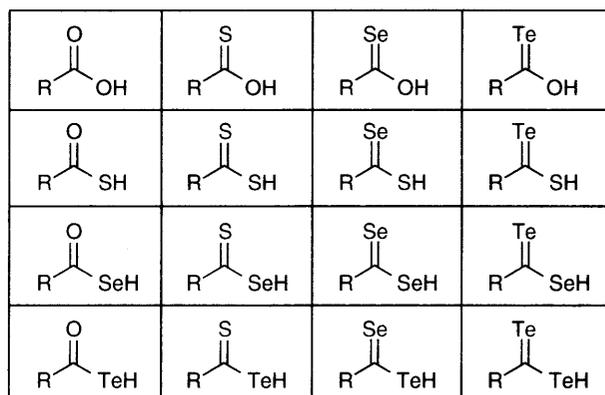
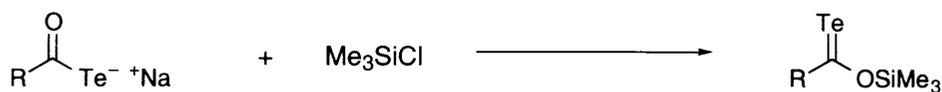


Chart 1. Chalcogenocarboxylic acids

### Monochalcogenocarboxylate derivatives

Recently, the synthetic methods of tellurocarboxylic acid salts have been developed in the author's laboratory.<sup>7</sup> Monochalcogenocarboxylate groups, RCOE (E = S, Se, Te), are an interesting class of compounds in the coordination chemistry because of the ligand with a soft chalcogen and a hard oxygen site. The reaction of tellurocarboxylic acid salts with  $\text{Me}_3\text{SiCl}$  gave tellurocarboxylic acid *O*-silyl esters owing of the strong affinity between the Si and O (Scheme 1).<sup>8</sup>

Scheme 1



The first synthesis for Group 14 element derivatives of thiocarboxylic acid was reported in 1949 by Heap and Saunders.<sup>9</sup> The general method for the synthesis of trimethyl-Group 14 element (Ge, Sn, Pb) derivatives of thiocarboxylic acid has also been reported (Scheme 2).<sup>10</sup>

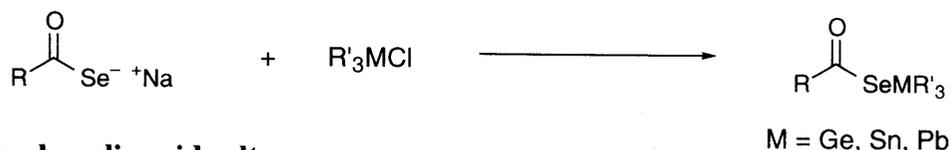
Scheme 2



In addition, three molecular structures of tin thiocarboxylates were reported.<sup>11</sup>

Furthermore, the synthesis of Group 14 element derivatives of selenocarboxylic acid has been disclosed (Scheme 3).<sup>12</sup>

**Scheme 3**



### **Diselenocarboxylic acid salts**

Chalcogenocarboxylic acid salts are one of the most important starting compounds for the synthesis of chalcogenocarboxylic acid derivatives. Facile syntheses of these salts are required for the developments of chalcogenocarboxylic acid and their derivatives. Further, the chalcogenocarboxylate anions are of great interest from the fundamental point of view since they are considered as heavy isologues of allylic anions.

Thiocarboxylic acid salts were synthesized from the reaction of benzoyl chloride with potassium hydrogen sulfide in 1868 by Engelhardt and Latschinoff.<sup>13</sup> After then, the first example of alkali metal dithiocarboxylates was reported in 1907 by Houben and Phol who synthesized sodium dithiocarboxylates by dithiocarboxylic acid with sodium hydride, although their isolation failed.<sup>14</sup> The first seleno- and tellurocarboxylic acid salts were reported in 1976 and 1987, respectively by Hirabayashi et al.<sup>15</sup> and Kato et al.<sup>16</sup> Moreover, several X-ray structural analyses of salts were reported.<sup>17</sup> Very recently, the synthesis of the ammonium salts<sup>18</sup> and alkali metal 18-crown-6 ether complexes<sup>19</sup> of selenothiocarboxylic acid and esters has been developed.

In this thesis, firstly, the author shows the results on the synthesis and structure of Group 14 (Ge, Sn, Pb) and 15 element derivatives (P, As) of chalcogenocarboxylic acid and the magnitude of the interaction between the carbonyl oxygen or thiocarbonyl sulfur and Group 14 and 15 elements. Secondly, the author describes the synthesis and structure of diselenocarboxylic acid salts.

Chapters 1 and 2 refer to the synthesis and structure of Group 14 (Ge, Sn, Pb) derivatives of thio-, seleno- and tellurocarboxylic acid and the magnitude of the interaction between the carbonyl oxygen and Group 14 elements.

Chapter 3 shows the synthesis and structure of Group 14 (Ge, Sn, Pb) derivatives of dithiocarboxylic acid.

Chapters 4 and 5 deal with the synthesis and structure of Group 15 (P, As) derivatives of thio- and dithio-carboxylic acid. Furthermore, the reaction of arsenic thio- and dithio-carboxylate derivatives with piperidine is outlined.

Chapter 6 describes the synthesis and structure of ammonium diselenoates. This is the first example of the isolation of the diselenoate salts.

Chapter 7 shows the synthesis and structure of carbamic selenocarboxylic mixed acid anhydrides.

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## Chapter 1

# Unusually Short Distances between the Carbonyl Oxygen and the Tin Atom in $\text{RCOSMR}'_3$ ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ): The Importance of Intramolecular $n_{\text{O}} \rightarrow \sigma^*_{\text{MS}}$ Orbital Interactions

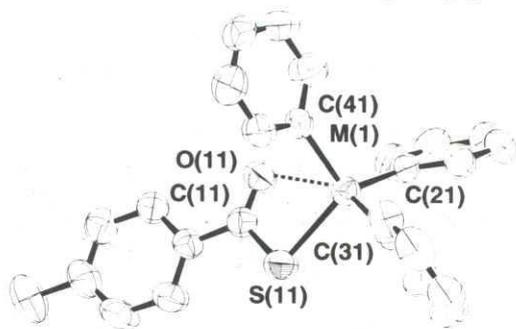
### 1.1. Introduction

The effects of nonbonded intramolecular as well as intermolecular interactions on the structures of molecules are a growing field of study.<sup>1</sup> Inter- and intramolecular interactions may reflect the affinity between elements. The strong affinity of silicon to an oxygen atom is well documented.<sup>2</sup> However, little is known about the magnitude of the interactions (affinity) between other Group 14 metals and oxygen or chalcogen atoms such as sulfur and selenium. The Author report here the unusually short distances between the carbonyl oxygen and tin atoms in Group 14 metal derivatives of thiocarboxylic acids ( $\text{RCOSMR}'_3$ ,  $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ) and the nature of this nonbonded interaction between the carbonyl oxygen and Group 14 metals: the interactions between the nonbonding orbitals on the carbonyl oxygen ( $n_{\text{O}}$ ) and the  $\sigma^*_{\text{MS}}$  orbitals are very important.

### 1.2. Results and Discussion

Triphenylgermanium (**1**), -tin (**2**), and -lead (**3**) 4-methylbenzenecarbothioates were synthesized by reacting the corresponding potassium carbothioate with  $\text{Ph}_3\text{GeCl}$ ,  $\text{Ph}_3\text{SnCl}$ , and  $\text{Ph}_3\text{PbCl}$ , respectively.<sup>2b</sup> The structures of **1–3** determined by X-ray analysis were isomorphous, a distorted tetrahedron in which the lengths of the  $\text{C}(11)\text{--O}(11)$ ,  $\text{C}(11)\text{--S}(11)$ , and  $\text{M}(1)\text{--S}(11)$  bonds in  $\text{RCOSMPh}_3$  ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ ) are comparable to  $\text{C}=\text{O}$  double and  $\text{C}\text{--S}$  and  $\text{M}\text{--S}$  single bonds, respectively (Table 1).<sup>3–4</sup>

The distances between the carbonyl oxygen and



**Figure 1.** Molecular structures of 4- $\text{CH}_3\text{C}_6\text{H}_4\text{COSMPh}_3$  (**1**,  $\text{M} = \text{Ge}$ ; **2**,  $\text{M} = \text{Sn}$ ; **3**,  $\text{M} = \text{Pb}$ ).

**Table 1.** X-ray Data for 4- $\text{CH}_3\text{C}_6\text{H}_4\text{COSMPh}_3$  and  $\text{CH}_3\text{SMPh}_3$  ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$ )

	Ge	Sn	Pb
4- $\text{CH}_3\text{C}_6\text{H}_4\text{COSMPh}_3$			
$\text{C}=\text{O}\cdots\text{M}$	3.003(2)	2.907(2)	2.990(4)
$\text{M}(1)\text{--S}(11)$	2.2547(8)	2.4453(9)	2.539(2)
$\text{C}(11)\text{--O}(11)$	1.209(3)	1.208(2)	1.222(7)
$\text{C}(11)\text{--S}(11)$	1.790(3)	1.775(3)	1.770(6)
$\text{M}(1)\text{--C}(21)$	1.944(3)	2.131(3)	2.205(5)
$\text{M}(1)\text{--C}(31)$	1.942(3)	2.141(3)	2.213(5)
$\text{M}(1)\text{--C}(41)$	1.934(3)	2.123(3)	2.202(5)
$\text{M}(1)\text{--S}(11)\text{--C}(11)$	98.25(10)	93.5(1)	94.1(2)
$\text{CH}_3\text{SMPh}_3^a$			
$\text{M}\text{--S}$	2.224(1)	2.391(2)	2.489(6)
$\text{M}\text{--C}_{\text{ipso}}$	1.931(1)	2.135(7)	2.201(13)
$\text{M}\text{--C}_{\text{ipso}}$	1.930(2)	2.139(7)	2.185(18)
$\text{M}\text{--C}_{\text{ipso}}$	1.932(1)	2.115(7)	2.186(16)
$\text{M}\text{--S}\text{--CH}_3$	101.4(3)	102.6(8)	100.5(12)

<sup>a</sup> Reference 6.

the central Group 14 metals are all within the sum of the van der Waals radii of both atoms,<sup>5</sup> respectively, indicating intramolecular attraction between the two atoms (Figure 1). Interestingly, despite the large atomic radius of tin compared with that of germanium, the C=O...Sn distance [2.907(2) Å] in **2** is about 0.1 Å shorter than C=O...Ge distance [3.003(2) Å] in **1**. The C=O...Pb distance [2.990(4) Å] in **3** is longer than that in **2**. The M(1)–S(11)–C(11) angles and the M(1)–S(11) distances in **1**, **2**, and **3** are 3–9° narrow and 0.03–0.05 Å longer, respectively, compared with those in CH<sub>3</sub>SMPPh<sub>3</sub> (M = Ge, Sn, Pb)<sup>6</sup> having no carbonyl group (Table 1).

To elucidate the nature of this unusual nonbonded attraction, ab initio geometry optimizations at the B3LYP/LANL2DZ+p level<sup>7</sup> with the Gaussian 98 program<sup>8</sup> were performed on the model compounds trimethylgermanium (**1'**), -tin (**2'**), and -lead (**3'**) ethanecarbothioates.

The calculations for **1'**, **2'**, and **3'** indicated that the C=O...Sn distance (3.058 Å) in **2'** is 0.1 Å shorter than that in **1'**, while the M–S distances increase in the order **1'** > **2'** > **3'** (Table 2). The bond angle Sn–S–C (95.2°) in **2'** also is narrow compared with that in **1'** (99.8°). These results are consistent with the results obtained by X-ray structural analyses of **1–3**.

To obtain further information regarding the electronic structures of **1–3**, NBO (natural bond orbital) analyses were carried out. The NBO analysis showed that the orbital interactions between the n orbital (n<sub>O</sub>) on the carbonyl oxygen and the σ\*<sub>MC</sub> orbitals (Figure 2a) are present, but their values are close to each other (Table 3). On the other hand, the interactions between the n<sub>O</sub> and σ\*<sub>MS</sub> orbitals (Figure 2b) are also appreciable, and interestingly the stabilization energies of the n<sub>O</sub> → σ\*<sub>MS</sub> in **2'** and **3'** are ca. 3.5 times that in **1'**. The contour maps of the n<sub>O</sub> and σ\*<sub>MS</sub> orbitals in the molecular plane M(1)–S(2)–C(4) for the model compounds were depicted by using the MOLDEN 3.6 program.<sup>9</sup> As shown in Figure 3, the overlaps (overlap integral, 0.0271) between the n<sub>O</sub> and the part on M in the σ\*<sub>MS</sub> orbitals in the tin **2'** are larger than that (overlap integral, 0.0253) in the germanium compound **1'**. Thus, the magnitude of such interactions agrees with the order of the shortness of the C=O...M distances. This may substantially contribute to the structure of such organo

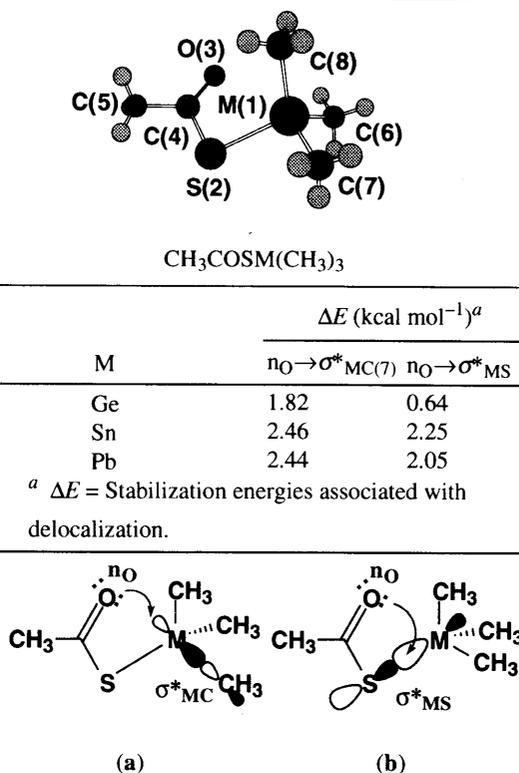
**Table 2.** Calculated Geometrical Parameter for CH<sub>3</sub>COSM(CH<sub>3</sub>)<sub>3</sub> (M = Ge, Sn, Pb) at B3LYP/LANL2DZ+p Level

	M		
	Ge ( <b>1'</b> )	Sn ( <b>2'</b> )	Pb ( <b>3'</b> )
M(1)···O(3)	3.147 Å	3.058 Å	3.113 Å
M(1)–S(2)	2.313 Å	2.496 Å	2.568 Å
C(4)–O(3)	1.217 Å	1.222 Å	1.223 Å
M(1)–S(2)–C(4)	99.8°	95.2°	95.3°

**Table 3.** NBO Analysis of CH<sub>3</sub>COSM(CH<sub>3</sub>)<sub>3</sub> at B3LYP/LANL2DZ+p Level

M	ΔE (kcal mol <sup>-1</sup> ) <sup>a</sup>	
	n <sub>O</sub> → σ* <sub>MC(7)</sub>	n <sub>O</sub> → σ* <sub>MS</sub>
Ge	1.82	0.64
Sn	2.46	2.25
Pb	2.44	2.05

<sup>a</sup> ΔE = Stabilization energies associated with delocalization.



**Figure 2.** Nonbonded attraction due to (a) the n<sub>O</sub> → σ\*<sub>MC</sub> and (b) n<sub>O</sub> → σ\*<sub>MS</sub>.

Group 14 metal derivatives of chalcogenocarboxylic acids and may also result in shortening the distance in  $C=O\cdots Sn$ , as has been observed by X-ray molecular structural analysis. The atomic charge (1.06) of the tin in **2'** is clearly larger than that in **1'** (0.76), while those of the carbonyl oxygens show similar values ( $-0.21$  to  $-0.23$ ), suggesting that the electrostatic interactions may also contribute to the short  $C=O\cdots Sn$  distances. The longer  $C=O\cdots Pb$  distance compared with the  $C=O\cdots Sn$  distance may arise from the corresponding  $M-S$  bond lengths, although the magnitude of the overlaps between the  $n_O$  and  $\sigma^*_{MS}$  orbitals in **3'** is close to that in **2'**.

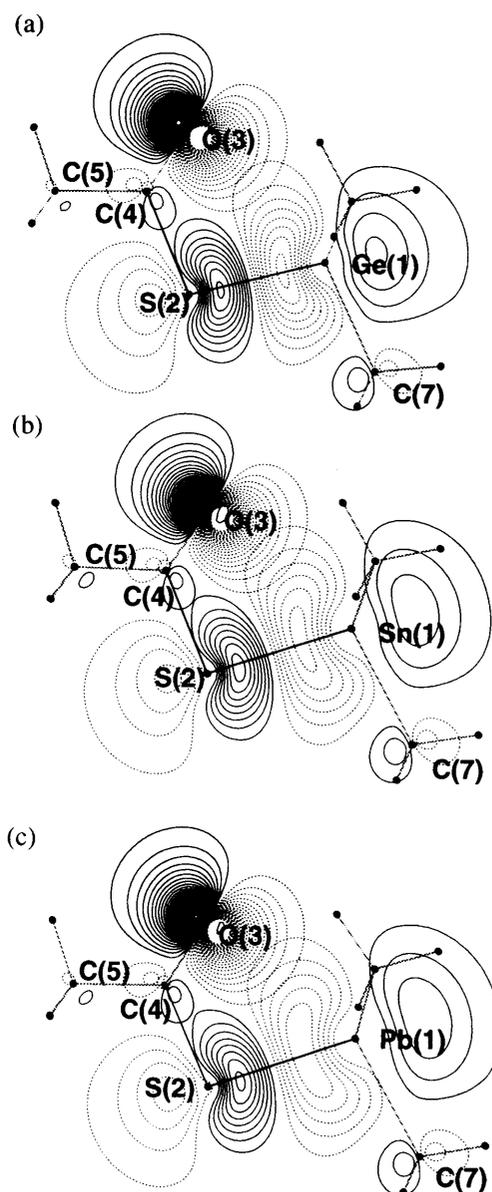
### 1.3. Conclusion

In summary, the crystal structure in **2** showed unusual intramolecular  $C=O\cdots Sn$  attractions compared with those in **1** and **3**. The short distance results from the interactions between the  $n_O$  and  $\sigma^*_{MS}$  orbitals rather than those between  $n_O$  and  $\sigma^*_{MC}$  orbitals. These findings may help us to understand not only organic synthesis using organotin compounds but also the biological activities of various organotin compounds.

### 1.4. Experimental Section

IR spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrophotometer.  $^1H$ ,  $^{13}C$ , and  $^{119}Sn$  NMR were recorded on a JEOL JNM- $\alpha$ 400 instrument at 400, 100, and 149 MHz, respectively.  $CDCl_3$  was employed as a solvent with tetramethylsilane as internal standard for  $^1H$  NMR.  $CDCl_3$  was used as an internal standard for  $^{13}C$  NMR.  $Me_4Sn$  was used as an external standard for  $^{119}Sn$  NMR. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University. All solvents were dried and distilled prior to use.  $Ph_3GeCl$ ,  $Ph_3SnCl$ , and  $Ph_3PbCl$  are of commercial grade were obtained from Aldrich.

**S-Triphenylgermanium 4-methylbenzenecarbothioate (1).** To a solution of  $Ph_3GeCl$  (0.340 g, 1.00 mmol) in ether (15 mL), potassium 4-methylthiobenzoate (0.191 g, 1.00 mmol) was added and the mixture was stirred at 20 °C for 1 h. After addition of  $CH_2Cl_2$  (100 mL), the mixture was washed with water (3 x 90 mL), followed by drying over  $MgSO_4$ . The solvents were removed under reduced pressure (30 °C/2.7 kPa). The resulting residue was dissolved into



**Figure 3.** The overlapping between  $n_O$  (p-type lone pair) and  $\sigma^*_{MS}$  orbitals in the molecular plane  $M(1)-S(2)-C(4)$  of (a) **1'**, (b) **2'**, and (c) **3'** calculated at the B3LYP/LANL2DZ+p level.

a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and hexane (3 mL) and allowed to stand in a refrigerator (-20 °C) for 24 h to give **1c** as colorless crystals (0.367 g, 85%); mp 110–112 °C; IR (KBr) 1651 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.24 (s, 3H, CH<sub>3</sub>), 7.06 (d, *J* = 8.1 Hz, 2H), 7.25–7.30 (m, 9H), 7.57–7.60 (m, 6H), 7.84 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.6 (CH<sub>3</sub>), 128.5, 128.6, 129.0, 129.8, 134.8, 134.9, 135.7, 144.2, 191.7 (C=O); Anal. Calcd for C<sub>26</sub>H<sub>22</sub>GeOS: C, 68.62; H, 4.87. Found: C, 68.59; H, 4.87.

**S-Triphenyltin 4-methylbenzenecarbothioate (2)**. Colorless crystals (83%): mp 234–235 °C; IR (KBr) 1621 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.37 (s, 3H, CH<sub>3</sub>), 7.11 (d, *J* = 7.9 Hz, 2H), 7.35–7.37 (m, 9H), 7.64–7.73 (m, 6H), 7.95 (d, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.6 (CH<sub>3</sub>), 128.8, 129.0, 129.1, 130.0, 135.1, 136.8, 138.1, 144.3, 196.0 (C=O); <sup>119</sup>Sn NMR (149 MHz, CDCl<sub>3</sub>) δ -97.7 (<sup>1</sup>*J*<sub>C-Sn</sub> = 594 Hz); Anal. Calcd for C<sub>26</sub>H<sub>22</sub>OSSn: C, 62.31; H, 4.42. Found: C, 62.21; H, 4.39.

**S-Triphenyllead 4-methylbenzenecarbothioate (3)**. Colorless crystals (91%): mp 106–107 °C; IR (KBr) 1618 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.30 (s, 3H, CH<sub>3</sub>), 7.12 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 6H), 7.76 (d, *J* = 7.5 Hz, 6H), 7.99 (d, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.5 (CH<sub>3</sub>), 128.8, 129.0, 129.3, 130.0, 136.0, 137.0, 143.6, 154.0 (<sup>1</sup>*J*<sub>C-Pb</sub> = 545 Hz), 196.4 (C=O); Anal. Calcd for C<sub>26</sub>H<sub>22</sub>OPbS: C, 52.96; H, 3.76. Found: C, 53.00; H, 3.80.

**X-Ray Structural Analysis.** The measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71069 Å). A Rigaku XR-TCS-2-050 temperature controller was used for low temperature measurement. All of the structures were solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. The crystals were cut from the grown crystals. The crystals were mounted on a glass fiber. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and showed no significant intensity variations during the data collection. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [DIFABS (2) and  $\Psi$ -scans (1 and 3)] were also applied. The structures were solved by direct methods using SHELXS86 and expanded using DIRDIF94. Scattering factors for neutral atoms were from Cromer and Waber, and anomalous dispersion was used. The function minimized was  $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ , and the weighting scheme employed was  $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$ . A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. Positional parameters, anisotropic displacement parameters and bond lengths and angles of **1**, **2**, and **3** are summarized in Tables S1 to S12.

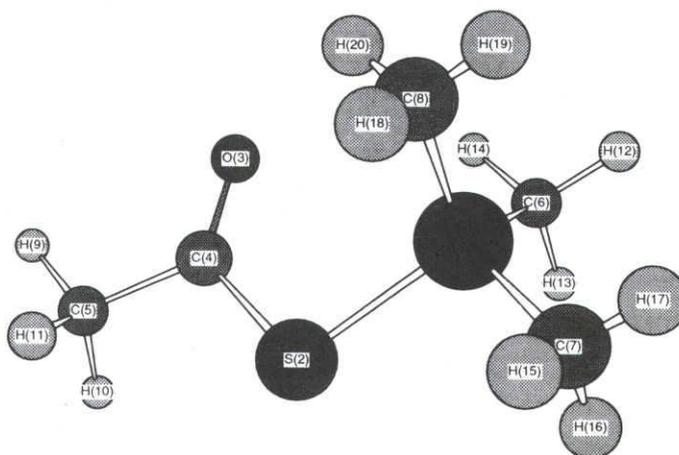
**Preparation of single crystals.** *S*-Triphenylgermanium 4-methylbenzenecarbothioate **1** (0.100 g) was single-crystallized from dichloromethane (0.6 mL), ether (0.2 mL) and hexane (0.8 mL) at 25 °C for 1 day. *S*-Triphenyltin 4-methylbenzenecarbothioate **2** (0.071 g) was single-crystallized from dichloromethane (0.5 mL), ether (0.2 mL) and hexane (0.5 mL) at 25 °C for 1 day. *S*-Triphenyllead 4-methylbenzenecarbothioate **3** (0.166 g) was single-crystallized from dichloromethane (1.2 mL) and hexane (2.0 mL) at 25 °C for 1 day.

Crystal data for **1** at 193 K: C<sub>26</sub>H<sub>22</sub>GeOS, M = 455.11, triclinic, space group *P*-1 (#2), *a* = 9.372(5) Å, *b* = 16.024(2) Å, *c* = 7.873(2) Å,  $\alpha$  = 91.27(2)°,  $\beta$  = 112.32(3)°,  $\gamma$  = 94.08(3)°, *V* = 1089.4(7) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.387 g cm<sup>-3</sup>,  $\mu$ (*Mo-K*α) = 15.15 cm<sup>-1</sup>, 5327 reflections measured, 5016 unique (*R<sub>int</sub>* = 0.029), 3746 reflections observed [*I* > 2σ(*I*)], *R* = 0.034, *R<sub>w</sub>* = 0.038.

Crystal data for **2** at 296 K: C<sub>26</sub>H<sub>22</sub>OSSn, M = 501.21, triclinic, space group *P*-1 (#2), *a* = 9.6152(4) Å, *b* = 16.3582(6) Å, *c* = 7.7772(4) Å,  $\alpha$  = 92.171(4)°,  $\beta$  = 110.186(3)°,  $\gamma$  = 92.483(3)°, *V* = 1145.22(9) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.453 g cm<sup>-3</sup>,  $\mu$ (*Mo-K*α) = 12.20 cm<sup>-1</sup>, 5562 reflections measured, 5247 unique (*R<sub>int</sub>* = 0.012), 4520 reflections observed [*I* > 2σ(*I*)], *R* = 0.031, *R<sub>w</sub>* = 0.037.

Crystal data for **3** at 193 K: C<sub>26</sub>H<sub>22</sub>OPbS, M = 589.72, triclinic, space group *P*-1 (#2), *a* = 9.6581(9) Å, *b* = 16.102(1) Å, *c* = 7.7097(5) Å,  $\alpha$  = 92.521(7)°,  $\beta$  = 109.511(6)°,  $\gamma$  = 91.951(8)°, *V* = 1127.5(2) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.737 g cm<sup>-3</sup>,  $\mu$ (*Mo-K*α) = 76.01 cm<sup>-1</sup>, 5469 reflections measured, 5157 unique (*R<sub>int</sub>* = 0.013), 4319 reflections observed [*I* > 2σ(*I*)], *R* = 0.034, *R<sub>w</sub>* = 0.035.

**Calculation Method.** Gaussian 98 was used as source program for ab initio MO calculations and NBO deletion analysis. Geometries of model compounds CH<sub>3</sub>COSM(CH<sub>3</sub>)<sub>3</sub> (**1'**; M = Ge, **2'**; M = Sn, **3'**; M = Pb) were optimized at the B3LYP/LANL2DZ+p. The d-polarization function for ECP basis set of all atoms except for H are taken from Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Raszio-Andzelm, Y.; Sakai, Y.; Tatewaki, H. *Gaussian basis sets for molecular calculations*; Elsevier: Amsterdam, 1984. NBO analyses were performed on the optimized conformations using the same basis sets. Calculated coordinates for all conformers are listed.



Z-matrix orientation for  $\text{CH}_3\text{COSGe}(\text{CH}_3)_3$  1'

Ge	1.032045	-0.046979	-0.000117
S	-0.931741	1.175027	-0.000264
O	-1.829069	-1.357552	0.000702
C	-2.140404	-0.180892	0.000347
C	-3.585058	0.300509	0.000322
C	1.120120	-1.130613	1.636112
C	2.397030	1.374814	-0.000826
C	1.119657	-1.131818	-1.635570
H	-4.255972	-0.565345	0.001162
H	-3.774490	0.922347	0.885299
H	-3.774873	0.920871	-0.885614
H	2.080105	-1.664577	1.682857
H	1.032771	-0.497123	2.527873
H	0.307275	-1.865419	1.641599
H	2.305340	2.010316	-0.891123
H	2.305662	2.010881	0.889100
H	3.402573	0.930776	-0.000867
H	1.032022	-0.498993	-2.527774
H	2.079643	-1.665788	-1.682206
H	0.306830	-1.866650	-1.640268

Z-matrix orientation for  $\text{CH}_3\text{COSSn}(\text{CH}_3)_3$  2'

Sn	0.885674	-0.047421	-0.000024
S	-1.229262	1.278355	0.000255
O	-1.900692	-1.306755	-0.000215
C	-2.323698	-0.160819	0.000007
C	-3.807665	0.175587	0.000117
C	0.983475	-1.207687	1.794144
C	2.363106	1.511970	0.000261
C	0.983431	-1.206967	-1.794661
H	-4.391985	-0.750873	-0.000219
H	-4.056256	0.775614	0.885457
H	-4.056265	0.776283	-0.884764
H	1.970060	-1.681743	1.889019
H	0.818795	-0.571342	2.672530
H	0.213325	-1.986359	1.770654
H	2.262274	2.146755	-0.889400
H	2.262315	2.146404	0.890178
H	3.373860	1.081090	0.000152
H	0.819045	-0.570217	-2.672810
H	1.969905	-1.681244	-1.889590
H	0.213076	-1.985448	-1.771599

Z-matrix orientation for  $\text{CH}_3\text{COSPb}(\text{CH}_3)_3$  3'

Pb	-0.718624	-0.042995	-0.000106
S	1.469393	1.300978	0.000421
O	2.134024	-1.290333	0.000662
C	2.553264	-0.141920	0.000564
C	4.039751	0.191264	0.000123
C	-0.760835	-1.220360	-1.852118
C	-2.214315	1.578701	-0.000295
C	-0.761646	-1.220655	1.851692
H	4.621490	-0.736980	0.003974
H	4.290772	0.786975	-0.887385
H	4.290260	0.794439	0.882672
H	0.068128	-1.934118	-1.822143
H	-1.715429	-1.756089	-1.929905
H	-0.646176	-0.553103	-2.713719
H	-2.090507	2.201841	0.893155
H	-2.090141	2.201986	-0.893593
H	-3.224715	1.149794	-0.000536
H	-0.646970	-0.553574	2.713428
H	-1.716430	-1.756091	1.929170
H	0.067109	-1.934655	1.821784

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## Chapter 2

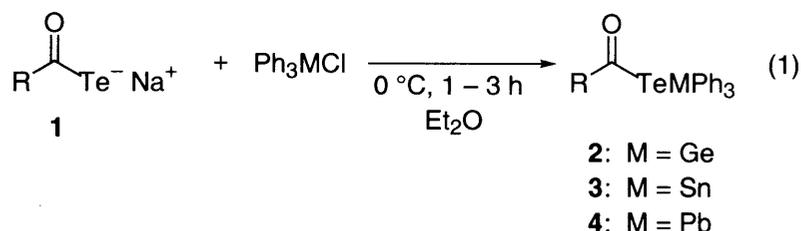
# Synthesis and Structure of Group 14 Element Derivatives of Carbotelluroates

### 2.1. 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 electronic-related applications.<sup>1,2</sup> Several organometallic compounds containing Ge–Te,<sup>3,4</sup> Sn–Te,<sup>2,4–9</sup> and Pb–Te bond(s)<sup>4,7–9</sup> 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 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.<sup>10</sup> Recently, we successfully synthesized and characterized solvent- and metal halide-free sodium carbotelluroates.<sup>11</sup> We also obtained Group 14 element derivatives of carboselenoate as stable compounds.<sup>12</sup> 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 carbothio- and carboselenoates.

### 2.2. Results and Discussion

**Synthesis.** Group 14 element derivatives of carbotelluroates RCOTeMPh<sub>3</sub> (M = Ge, Sn, Pb) were obtained by reacting sodium carbotelluroates **1** with Ph<sub>3</sub>MCl (eq 1, Table 1).



For example, to a degassed Et<sub>2</sub>O suspension of the sodium salts **1** was added Ph<sub>3</sub>GeCl (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 stirring 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 one-half, 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<sub>3</sub>SnCl and Ph<sub>3</sub>PbCl gave the corresponding *Te*-

stannyl **3** and *Te*-plumbyl carbotelluroates **4** as colorless or 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<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, black tellurium was liberated even at –20 °C, leading to a complex mixture containing (Ph<sub>3</sub>M)<sub>2</sub>Te (M = Ge,<sup>7</sup> Sn,<sup>8</sup> Pb<sup>8</sup>) within 6 h. This instability of **2–4** in solution is in marked contrast to the stability of Group 14 element derivatives of carboselenoates.<sup>12</sup>

Spectroscopic data for Group 14 element derivatives of carbotelluroates **2–4** are shown in Table 2. The  $\nu$  C=O bands in Ge derivatives **2** are nearly the same as those of the corresponding *Te*-methyl carbotelluroates (RCOTeMe) **5**,<sup>11</sup> whereas those in Sn and Pb derivatives **3, 4** show wavenumbers that are lower by 10–40 cm<sup>-1</sup>. In <sup>13</sup>C NMR spectra, the signals due to the carbonyl carbon atom were observed at higher fields (by 5 ppm) compared to those of *Te*-methyl carbotelluroates (RCOTeMe) **5**. The Te signals in the <sup>125</sup>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<sub>3</sub>MTePh and (Ph<sub>3</sub>M)<sub>2</sub>Te.<sup>13</sup> The coupling constants between the Sn or Pb and Te atoms are 500 Hz and 700 Hz, which are smaller than those for the M(IV)–Te single bonds in Ph<sub>3</sub>MTePh and (Ph<sub>3</sub>M)<sub>2</sub>Te (M = Sn: ca. 3200 Hz; M = Pb: ca. 4000 Hz).<sup>7,8</sup> These results imply that the Sn–Te and Pb–Te bonds in **3** and **4** are weaker than those in Ph<sub>3</sub>MTePh and (Ph<sub>3</sub>M)<sub>2</sub>Te.

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

R	M	No.	% yield <sup>a</sup>
1-Adamantyl	Ge	<b>2a</b>	15
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ge	<b>2b</b>	62
4-ClC <sub>6</sub> H <sub>4</sub>	Ge	<b>2c</b>	39
1-Adamantyl	Sn	<b>3a</b>	25
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Sn	<b>3b</b>	41
4-ClC <sub>6</sub> H <sub>4</sub>	Sn	<b>3c</b>	55
1-Adamantyl	Pb	<b>4a</b>	39
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Pb	<b>4b</b>	61
4-ClC <sub>6</sub> H <sub>4</sub>	Pb	<b>4c</b>	40

<sup>a</sup> Isolated yields.

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

No.	IR [cm <sup>-1</sup> ]	<sup>13</sup> C NMR <sup>b</sup>	<sup>125</sup> Te NMR <sup>b</sup>
	$\nu$ C=O <sup>a</sup>	$\delta$ C=O	$\delta$
<b>2a</b>	1701	207.4	276.7
<b>2b</b>	1676	190.0	350.2
<b>2c</b>	1670	189.4	370.4
<b>3a</b>	1693	207.4	204.5
<b>3b</b>	1654	189.8	288.2
<b>3c</b>	1652	189.2	304.8
<b>4a</b>	1692	207.1	338.2
<b>4b</b>	1655	189.8	409.4
<b>4c</b>	1654	189.3	420.6

<sup>a</sup> As KBr disc. <sup>b</sup> In CDCl<sub>3</sub>.

**Table 3. Spectroscopic Data for 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COEMPh<sub>3</sub>**

M	No.	E	IR [cm <sup>-1</sup> ]	<sup>13</sup> C NMR <sup>b</sup>
			$\nu$ C=O <sup>a</sup>	$\delta$ C=O
Ge	<b>6</b>	S <sup>c</sup>	1651	191.7
		Se <sup>d</sup>	1654	192.2
		Te	1676	190.0
Sn	<b>7</b>	S <sup>c</sup>	1621	196.0
		Se <sup>e</sup>	1644	194.9
		Te	1654	189.8
Pb	<b>8</b>	S <sup>c</sup>	1618	196.4
		Se <sup>f</sup>	1641	195.4
		Te	1655	189.8

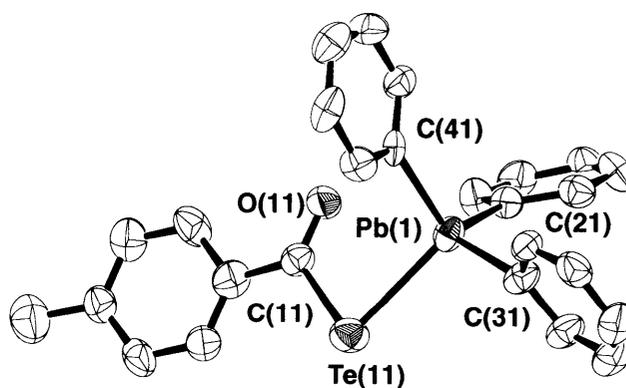
<sup>a</sup> As KBr disc. <sup>b</sup> In CDCl<sub>3</sub>. <sup>c</sup> ref. 14. <sup>d</sup> ref. 12c. <sup>e</sup> ref. 12a. <sup>f</sup> ref. 12b.

Some of the IR and  $^{13}\text{C}$  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  $^{13}\text{C}$  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  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$ ,  $\text{Et}_2\text{O}/\text{hexane}$ , and  $\text{Et}_2\text{O}/\text{AcOEt}/\text{hexane}$  at  $-20\text{ }^\circ\text{C}$ , respectively. Although the crystals of these compounds are not isomorphous, their forms are quite similar and resemble that of the corresponding sulfur homologue  $4\text{-CH}_3\text{C}_6\text{H}_4\text{COSPbPh}_3$ .<sup>14</sup> 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.<sup>15</sup> The lengths of the C(11)–O(11) and C(11)–Te(11) bonds in  $\text{RCOTeMPh}_3$  (M = Ge, Sn, Pb) are comparable to those in *Te*-methyl carbotelluroate,<sup>11</sup> diacyl telluride,<sup>16a</sup> carbotelluroato platinum complex<sup>16b</sup> and diacyl ditelluride,<sup>16c</sup> 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  $328^\circ$ , which is 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 non-cyclic compounds with Ge–Te<sup>3</sup> and Sn–Te single bonds.<sup>5</sup> 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)<sup>17</sup> and the Pb(IV) metallic radius (1.50 Å),<sup>18</sup> 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,<sup>17</sup> which suggests that nonbonding intramolecular interaction

is present between the nonbonding orbital on the carbonyl oxygen atom ( $n_{\text{O}}$ ) and the  $\sigma^*_{\text{MC}31}$  orbital [ $\angle \text{O}(11)\cdots\text{M}(1)\text{-C}(31) = 160^\circ$ ] and/or the  $\sigma^*_{\text{MTe}}$  orbital, similar to the corresponding carbothioate derivatives.<sup>14</sup>



**Figure 1.** The ORTEP drawing of **4b**. Hydrogen atoms have been omitted for purpose of clarity.

**Table 4. X-ray Data of Group 14 Element Derivatives 2b, 3b, and 4b**

	<b>2b</b>	<b>3b</b>	<b>4b</b>
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)

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<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COSeMPh<sub>3</sub> (**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. The molecular forms are comparable to those of the carbotelluroate derivatives and carbothioate derivatives.<sup>14</sup> 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.<sup>18,19</sup> 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,<sup>17</sup> 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**.

	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)–Se(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)

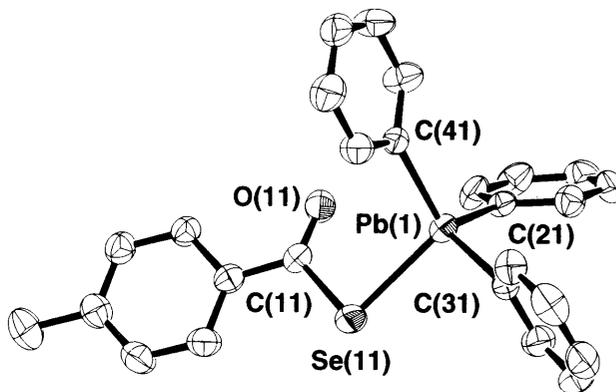


Figure 2. The ORTEP drawing of **8**. Hydrogen atoms have been omitted for purpose of clarity.

**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<sup>20</sup> were performed with the Gaussian 98 program<sup>21</sup> on the model compounds trimethylgermyl, stannyl, and plumbyl ethanechalcogenoate, CH<sub>3</sub>COEM(CH<sub>3</sub>)<sub>3</sub> (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 carboseleno- and telluroates 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.<sup>21</sup> The results regarding orbital energies and the magnitude of the contribution of atomic orbitals to  $\sigma^*_{ME}$  and  $\sigma^*_{MC7}$  are listed in Table 7 and the stabilization energies are listed in Table 8. The orbital energy of  $\sigma^*_{GeE}$  (E = Se, Te) is higher than that of  $\sigma^*_{ME}$  (M = Sn, Pb; E = Se, Te). The  $\sigma^*_{GeC}$  and  $\sigma^*_{GeE}$  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 ( $n_{\text{O}} \rightarrow \sigma^*_{\text{ME}}$  and  $n_{\text{O}} \rightarrow \sigma^*_{\text{MC7}}$ ) contribute to the shortening, as shown in Table 8. In carboselenoates, both interactions are equally important, whereas  $n_{\text{O}} \rightarrow \sigma^*_{\text{MC7}}$  plays a dominant role in carbotelluroates. This is in sharp contrast to the case of carbothioates, in which  $n_{\text{O}} \rightarrow \sigma^*_{\text{MS}}$  is more important.

### 2.3. 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  $n_{\text{O}} \rightarrow \sigma^*_{\text{MC7}}$ .

**Table 6. Calculated Geometrical Parameter for  $\text{CH}_3\text{COEM}(\text{CH}_3)_3$  (E = Se, Te; M = Ge, Sn, Pb) at B3LYP/LANL2DZ+p Level**

	Ge	Sn	Pb
$\text{CH}_3\text{COSeM}(\text{CH}_3)_3$	<b>9</b>	<b>10</b>	<b>11</b>
M(1)...O(3)	3.245	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
$\text{CH}_3\text{COTeM}(\text{CH}_3)_3$	<b>12</b>	<b>13</b>	<b>14</b>
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)	1.976	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 Contribution of Atomic Orbital for  $\text{CH}_3\text{COEM}(\text{CH}_3)_3$  (E = Se, Te; M = Ge, Sn, Pb) at B3LYP/LANL2DZ+p Level**

		Ge	Sn	Pb
$\text{CH}_3\text{COSeM}(\text{CH}_3)_3$		<b>9</b>	<b>10</b>	<b>11</b>
Orbital energy [a.u.]	$n_{\text{O}}(1)^a$	-0.67480	-0.67742	-0.67336
	$n_{\text{O}}(2)^b$	-0.27414	-0.27631	-0.27205
	$\sigma^*_{\text{MSe}}$	0.10997	0.07814	0.05593
	$\sigma^*_{\text{MC7}}$	0.26792	0.19951	0.14229
Percentage of $\sigma^*_{\text{MSe}}$ [%]	M	70.36	74.88	74.96
	Se	29.64	25.12	25.06
Percentage of $\sigma^*_{\text{MC7}}$ [%]	M	72.49	75.70	73.31
	C7	27.51	24.30	26.69
$\text{CH}_3\text{COTeM}(\text{CH}_3)_3$		<b>12</b>	<b>13</b>	<b>14</b>
Orbital energy [a.u.]	$n_{\text{O}}(1)^a$	-0.67637	-0.67909	-0.67650
	$n_{\text{O}}(2)^b$	-0.28023	-0.28221	-0.27957
	$\sigma^*_{\text{MTe}}$	0.08469	0.06247	0.04650
	$\sigma^*_{\text{MC7}}$	0.25843	0.19099	0.13618
Percentage of $\sigma^*_{\text{MTe}}$ [%]	M	64.52	69.88	70.05
	Te	35.48	30.12	29.95
Percentage of $\sigma^*_{\text{MC7}}$ [%]	M	72.23	75.52	73.19
	C7	27.77	24.48	26.81

<sup>a</sup>The p-type lone pair of the carbonyl oxygen. <sup>b</sup>The  $sp^{0.7}$  hybridized lone pair of the carbonyl oxygen.

**Table 8.** NBO Analysis of  $\text{CH}_3\text{COEM}(\text{CH}_3)_3$  (E = Se, Te; M = Ge, Sn, Pb) at B3LYP/LANL2DZ+p Level

	$\Delta E$ (kcal mol <sup>-1</sup> ) <sup>a</sup>		
	Ge	Sn	Pb
$\text{CH}_3\text{COSeM}(\text{CH}_3)_3$	<b>9</b>	<b>10</b>	<b>11</b>
$n_{\text{O}} \rightarrow \sigma^*_{\text{MSe}}$	—	1.33	1.23
$n_{\text{O}} \rightarrow \sigma^*_{\text{MC}(7)}$	1.55	1.88	1.98
$\text{CH}_3\text{COTeM}(\text{CH}_3)_3$	<b>12</b>	<b>13</b>	<b>14</b>
$n_{\text{O}} \rightarrow \sigma^*_{\text{MTe}}$	—	—	—
$n_{\text{O}} \rightarrow \sigma^*_{\text{MC}(7)}$	1.08	1.54	1.71

<sup>a</sup>  $\Delta E$  = Stabilization energies associated with delocalization.

## 2.4. Experimental section

Reactions were carried out under argon using standard Schlenk techniques. Sodium carbotelluroates<sup>11</sup> were prepared as described in the literature.  $\text{Ph}_3\text{GeCl}$ ,  $\text{Ph}_3\text{SnCl}$ , and  $\text{Ph}_3\text{PbCl}$  were used as purchased from Aldrich Chemical Co. All solvents were purified under argon and dried as indicated:  $\text{Et}_2\text{O}$  and hexane were refluxed with sodium benzophenone ketyl and distilled before use.  $\text{CH}_2\text{Cl}_2$  and  $\text{AcOEt}$  were distilled over diphosphorus pentoxide after refluxing for 5 h. All solvents were degassed before use.  $^1\text{H}$  (399.7 MHz) and  $^{13}\text{C}$  NMR (100.4 MHz) were recorded using  $\text{CDCl}_3$  as a solvent with  $\text{Me}_4\text{Si}$  as an internal standard for  $^1\text{H}$  NMR and  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR with a JEOL JNM-a400 spectrometer. In  $^{119}\text{Sn}$  NMR spectra (126.0 MHz),  $\text{Me}_4\text{Sn}$  was used as an external standard. In  $^{125}\text{Te}$  NMR spectra (149.0 MHz),  $\text{Me}_2\text{Te}$  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  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). 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 three representative reflections were measured after every 150 reflections. The structure was solved by a direct method using SHELXS86<sup>22</sup> and expanded using DIRDIF94.<sup>23</sup> An empirical absorption correction ( $\Psi$ -scan) was also applied. Neutral atom scattering factors for neutral atoms were from Cromer and Waber,<sup>24</sup> and anomalous dispersion effects<sup>25</sup> were used. The function minimized was  $\sum w(F_o^2 - F_c^2)^2$ , and the weighting scheme was  $w = 1/[\sigma^2(F_o^2)]$ . A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-square 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 Corporation. Crystallographic data of **2b**, **3b**, **4b**, **6**, **7**, and **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<sub>3</sub>GeCl (0.385 g, 1.13 mmol) was added to a suspension of sodium 1-adamantanecarbotelluroate (0.356 g, 1.13 mmol) in Et<sub>2</sub>O (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 stirring 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<sub>29</sub>H<sub>30</sub>OGeTe: C, 58.57; H, 5.08. Found: C, 58.28; H, 5.00. IR (KBr, cm<sup>-1</sup>): 1701 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.2, 36.5, 39.2, 56.1, 128.3, 129.4, 135.0, 136.2, 207.4 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 276.7.

***Te*-Triphenylgermyl 4-methylbenzenecarbotelluroate (2b).** Pale yellow microfine crystals (62%). 117–118 °C (dec). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>OGeTe: C, 56.71; H, 4.03. Found: C, 56.69; H, 4.02. IR (KBr, cm<sup>-1</sup>): 1676 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.22 (s, 3 H, CH<sub>3</sub>), 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.6 (CH<sub>3</sub>), 128.4, 129.3, 129.6, 134.1, 135.0, 135.8, 140.7, 144.8, 190.0 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 350.2.

***Te*-Triphenylgermyl 4-chlorobenzenecarbotelluroate (2c).** Pale yellow microfine crystals (39%). mp 105–107 °C (dec). Anal. Calcd for C<sub>25</sub>H<sub>19</sub>OClGeTe: C, 52.58; H, 3.35. Found: C, 52.28; H, 3.54. IR (KBr, cm<sup>-1</sup>): 1670 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 128.5, 128.8, 129.4, 129.7, 134.7, 135.5, 140.2, 141.5, 189.4 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 370.4.

***Te*-Triphenylstannyl 1-adamantanecarbotelluroate (3a).** Colorless microfine crystals (25%). mp 99–104 °C (dec). Anal. Calcd for C<sub>29</sub>H<sub>30</sub>OSnTe: C, 54.35; H, 4.72. Found: C, 54.47; H, 4.84. IR (KBr, cm<sup>-1</sup>): 1693 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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, 9 H, Ar), 7.48–7.61 (m, 6 H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.2, 36.4, 39.5, 56.4, 128.6, 129.3, 136.8, 137.9 (<sup>1</sup>*J*<sub>13C–117Sn</sub> = 494 Hz, <sup>1</sup>*J*<sub>13C–119Sn</sub> = 518 Hz), 207.4 (C=O). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ –136.3 (<sup>1</sup>*J*<sub>119Sn–13C</sub> = 518 Hz, <sup>1</sup>*J*<sub>119Sn–125Te</sub> = 2793 Hz). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 204.5 (<sup>1</sup>*J*<sub>125Te–117Sn</sub> = 2670 Hz, <sup>1</sup>*J*<sub>125Te–119Sn</sub> = 2792 Hz).

**Table 9. Crystallographic Data**

	<b>2b</b>	<b>3b</b>	<b>4b</b>
formula	C <sub>26</sub> H <sub>22</sub> OGeTe	C <sub>26</sub> H <sub>22</sub> OSnTe	C <sub>26</sub> H <sub>22</sub> OPbTe
fw	550.65	596.75	685.26
color	yellow	pale yellow	pale yellow
crystal size (mm)	0.14 × 0.23 × 0.34	0.43 × 0.40 × 0.29	0.26 × 0.14 × 0.11
<i>T</i> (K)	193	193	193
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.376(1)	13.680(4)	13.703(2)
<i>b</i> (Å)	16.058(3)	9.625(2)	9.671(1)
<i>c</i> (Å)	8.061(1)	18.774(2)	18.865(1)
$\alpha$ (deg)	93.04(2)		
$\beta$ (deg)	110.39(1)	110.72(1)	110.972(7)
$\gamma$ (deg)	92.10(1)		
<i>V</i> (Å <sup>3</sup> )	1134.1(3)	2312.0(9)	2334.5(5)
<i>Z</i>	2	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.612	1.714	1.950
$\mu$ (mm <sup>-1</sup> )	2.625	2.356	8.478
F(000)	540.00	1152.00	1280.00
no. of rflns measured/unique	5527/5210	5874/5323	5929/5375
no. of observations, ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	4326	3565	2561
R1; wR2	0.024; 0.077	0.032; 0.179	0.045; 0.136
goodness-of-fit	1.00	1.88	0.98
final max., min., ( $\Delta\rho$ , e Å <sup>-3</sup> )	0.59; -0.36	1.07, -0.97	2.80, -5.78

	<b>6</b>	<b>7</b>	<b>8</b>
formula	C <sub>26</sub> H <sub>22</sub> OGeSe	C <sub>26</sub> H <sub>22</sub> OSeSn	C <sub>26</sub> H <sub>22</sub> OPbSe
fw	502.21	550.65	550.65
color	colorless	colorless	yellow
crystal size (mm)	0.23 × 0.43 × 0.43	0.23 × 0.23 × 0.29	0.23 × 0.31 × 0.34
<i>T</i> (K)	193	296	193
crystal system	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.3795(9)	9.592(1)	9.618(1)
<i>b</i> (Å)	16.058(1)	16.309(2)	16.052(3)
<i>c</i> (Å)	7.9443(7)	7.8722(6)	7.811(1)
$\alpha$ (deg)	91.582(7)	92.497(8)	92.83(2)
$\beta$ (deg)	111.759(7)	109.783(6)	109.32(1)
$\gamma$ (deg)	93.821(7)	91.956(10)	91.36(1)
<i>V</i> (Å <sup>3</sup> )	1107.1(2)	1156.1(2)	1135.6(3)
<i>Z</i>	2	2	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.506	1.574	1.862
$\mu$ (mm <sup>-1</sup> )	3.041	2.693	9.057
F(000)	504.00	540.00	604.00
no. of rflns measured/unique	5406/5092	5619/5302	5406/5217
no. of observations, ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3867	3692	4449
R1; wR2	0.027; 0.085	0.048; 0.120	0.025; 0.073
goodness-of-fit	1.00	1.17	0.96
final max., min., ( $\Delta\rho$ , e Å <sup>-3</sup> )	0.52; -0.54	1.18; -1.30	0.83; -1.16

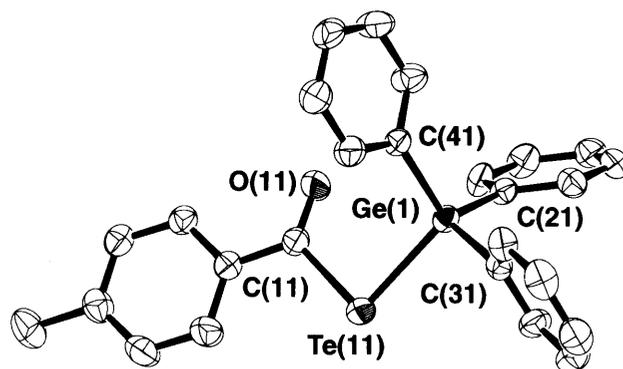
**Te-Triphenylstannyl 4-methylbenzenecarbotelluroate (3b).** Pale yellow microfine crystals (41%). mp 117–118 °C (dec). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>OSnTe: C, 52.33; H, 3.72. Found: C, 52.41; H, 3.79. IR (KBr, cm<sup>-1</sup>): 1654 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.14 (s, 3 H, CH<sub>3</sub>), 6.96–7.26 (m, 12 H, Ar), 7.50–7.67 (m, 6 H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.6 (CH<sub>3</sub>), 128.5, 128.9, 129.4, 136.7, 137.7 (<sup>1</sup>J<sub>13C-117Sn</sub> = 500 Hz, <sup>1</sup>J<sub>13C-119Sn</sub> = 523 Hz), 138.0, 139.3, 140.8, 189.8 (C=O). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ -131.8 (<sup>1</sup>J<sub>119Sn-13C</sub> = 523 Hz, <sup>1</sup>J<sub>119Sn-125Te</sub> = 2678 Hz). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 288.2 (<sup>1</sup>J<sub>125Te-117Sn</sub> = 2560 Hz, <sup>1</sup>J<sub>125Te-119Sn</sub> = 2683 Hz).

**Te-Triphenylstannyl 4-chlorobenzenecarbotelluroate (3c).** Pale yellow microfine crystals (55%). mp 105–107 °C (dec). Anal. Calcd for C<sub>25</sub>H<sub>19</sub>OClSnTe: C, 48.65; H, 3.10. Found: C, 48.74; H, 3.24. IR (KBr, cm<sup>-1</sup>): 1652 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.23–7.33 (m, 11 H, Ar), 7.54–7.69 (m, 8 H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 128.6, 128.8, 129.6, 129.8, 137.1, 137.5 (<sup>1</sup>J<sub>13C-117Sn</sub> = 503 Hz, <sup>1</sup>J<sub>13C-119Sn</sub> = 527 Hz), 140.4, 141.6, 189.2 (C=O). <sup>119</sup>Sn NMR (CDCl<sub>3</sub>): δ -127.9 (<sup>1</sup>J<sub>119Sn-13C</sub> = 526 Hz, <sup>1</sup>J<sub>119Sn-125Te</sub> = 2629 Hz). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 304.8 (<sup>1</sup>J<sub>125Te-117Sn</sub> = 2475 Hz, <sup>1</sup>J<sub>125Te-119Sn</sub> = 2570 Hz).

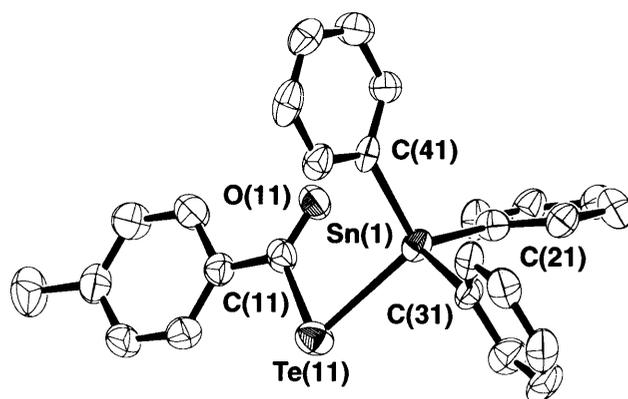
**Te-Triphenylplumbyl 1-adamantanecarbotelluroate (4a).** Pale yellow microfine crystals (39%). mp 111–114 °C (dec). Anal. Calcd for C<sub>29</sub>H<sub>30</sub>OPbTe: C, 47.76; H, 4.15. Found: C, 47.78; H, 4.18. IR (KBr, cm<sup>-1</sup>): 1692 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.55 (m, 6H, CH<sub>2</sub>), 1.77 (d, 6 H, J = 2.7 Hz, CH<sub>2</sub>), 1.92 (s, 3 H, CH), 7.11–7.35 (m, 9 H), 7.56–7.58 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.3, 36.4, 39.8, 56.5, 128.7, 129.5, 137.1, 150.4 (J<sub>13C-207Pb</sub> = 419 Hz), 207.1 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 338.2 (J<sub>125Te-207Pb</sub> = 3561 Hz).

**Te-Triphenylplumbyl 4-methylbenzenecarbotelluroate (4b).** Pale yellow microfine crystals (61%). mp 111–112 °C (dec). Anal. Calcd for C<sub>26</sub>H<sub>22</sub>OPbTe: C, 45.57; H, 3.24. Found: C, 45.27; H, 3.40. IR (KBr, cm<sup>-1</sup>): 1655 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.31 (s, 3H, CH<sub>3</sub>), 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). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.7 (CH<sub>3</sub>), 128.9, 129.0, 129.3, 129.7, 137.2, 144.1, 144.7, 150.7 (J<sub>13C-207Pb</sub> = 431 Hz), 189.8 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 409.4 (J<sub>125Te-207Pb</sub> = 3424 Hz).

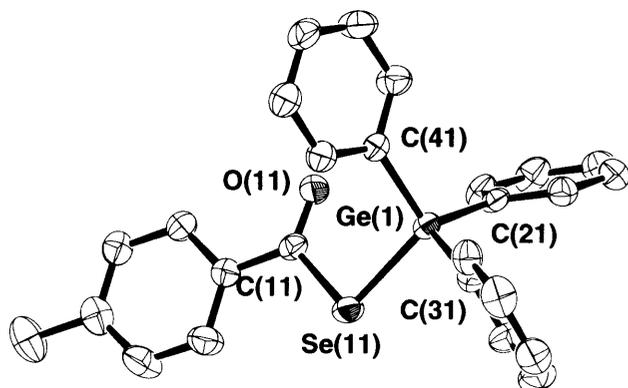
**Te-Triphenylplumbyl 4-chlorobenzenecarbotelluroate (4c).** Pale yellow microfine crystals (40%). mp 102–104 °C (dec). Anal. Calcd for C<sub>25</sub>H<sub>19</sub>ClOPbTe: C, 42.55; H, 2.71. Found: C, 42.30; H, 2.66. IR (KBr, cm<sup>-1</sup>): 1654 ν(C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.23–7.27 (m, 5 H), 7.29–7.41 (m, 6 H), 7.62–7.65 (m, 8 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 128.8, 129.0, 129.9, 130.0, 137.2, 140.2, 142.1, 150.7 (J<sub>13C-207Pb</sub> = 438 Hz), 189.3 (C=O). <sup>125</sup>Te NMR (CDCl<sub>3</sub>): δ 420.6 (J<sub>125Te-207Pb</sub> = 3339 Hz).



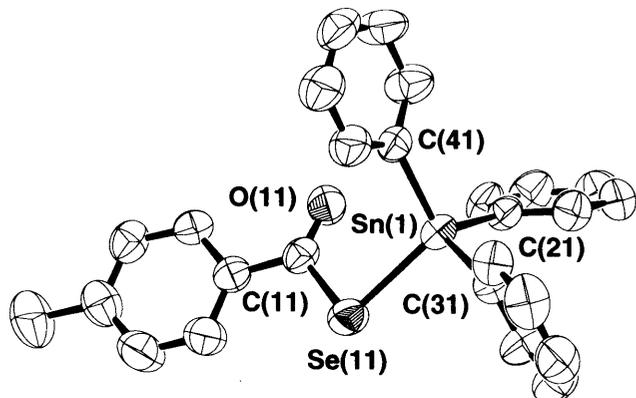
**Figure 3.** The ORTEP drawing of **2b**. Hydrogen atoms have been omitted for purpose of clarity.



**Figure 4.** The ORTEP drawing of **3b**. Hydrogen atoms have been omitted for purpose of clarity.



**Figure 5.** The ORTEP drawing of **6**. Hydrogen atoms have been omitted for purpose of clarity.



**Figure 6.** The ORTEP drawing of **7**. Hydrogen atoms have been omitted for purpose of clarity.

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## Chapter 3

# Structural analysis of phenyl-germanium, -tin, and lead dithiocarboxylates [(RCSS)<sub>x</sub>MPh<sub>4-x</sub>, M = Ge, Sn, Pb; x = 1–3]: affinity between thiocarbonyl sulfur and Group 14 elements

### 3.1. Introduction

In contrast to Group 14 element derivatives of dithiocarbamates, dithiocarbonates, and dithiophosphinates, little is known about the corresponding dithiocarboxylate derivatives.<sup>1</sup> Previously, we reported the synthesis of triphenyl-tin<sup>2b</sup> and lead arenecarbodithioates<sup>2d</sup> and diphenyltin bis(arenecarbodithioates).<sup>2b</sup> The corresponding germanium derivatives (RCSSGePh<sub>3</sub>, (RCSS)<sub>2</sub>GePh<sub>2</sub>) have not yet been synthesized. In addition, there has been no report of the X-ray structural analysis of organo-Group 14 element derivatives of dithiocarboxylates [(RCSS)<sub>x</sub>MR'<sub>4-x</sub>, (R, R' = alkyl, aryl; M = Si, Ge, Sn, Pb; x = 1–4)], perhaps due to the difficulty of purification and of obtaining single crystals. The Author report here the first X-ray structural analyses of a series of phenyl-Group 14 element derivatives of dithiocarboxylates together with the synthesis of phenyl-germanium dithiocarboxylates, phenyltin tris(dithiocarboxylates), and diphenyllead bis(dithiocarboxylates).

### 3.2. Results and discussion

**Synthesis.** The stoichiometric reactions of piperidinium dithiocarboxylates with Ph<sub>3</sub>GeCl, Ph<sub>2</sub>GeCl<sub>2</sub>, PhSnCl<sub>3</sub>, and Ph<sub>2</sub>PbCl<sub>2</sub> proceeded readily at room temperature and led to the quantitative formation of the expected triphenylgermanium dithiocarboxylates **1**, diphenylgermanium bis(dithiocarboxylates) **2**, phenyltin tris(dithiocarboxylates) **5**, and diphenyllead bis(dithiocarboxylates) **7** (Scheme 1). These dithiocarboxylate derivatives are less crystallizable than the corresponding thio-carboxylate derivatives. After several attempts, we successfully crystallized **1**, **2**, **5**, and **7** (Scheme 1).<sup>Scheme 1.</sup>

able than the corresponding thio-carboxylate derivatives. After several attempts, we successfully crystallized **1**, **2**, **5**, and **7**, except for triphenylgermanium 2-methylbenzenecarbodithioate (**1c**) and phenyltin tris(dithioacetate) (**5a**). We also attempted the synthesis and isolation of phenylgermanium tris(dithiocarboxylates) ((RCSS)<sub>3</sub>GePh) and Group 14 element derivatives of tetrakis(dithiocarboxylates) ((RCSS)<sub>4</sub>M, M = Ge, Sn), but failed. For example, the reaction of SnCl<sub>4</sub> with 4 M

No.	M	x	No.	M	x	No.	M	x
<b>1</b>	Ge	1	<b>3</b>	Sn	1	<b>6</b>	Pb	1
<b>2</b>	Ge	2	<b>4</b>	Sn	2	<b>7</b>	Pb	2
			<b>5</b>	Sn	3			

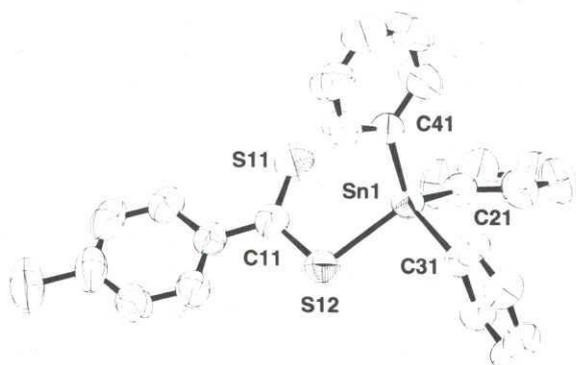
No.	R	No.	R
<b>a</b>	CH <sub>3</sub>	<b>d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>b</b>	C <sub>6</sub> H <sub>5</sub>	<b>e</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>
<b>c</b>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>f</b>	4-ClC <sub>6</sub> H <sub>4</sub>

amounts of sodium or piperidinium 4-methylbenzenecarbodithioate afforded not the desired product **8**, but rather dichlorotin bis(4-methylbenzenecarbodithioate) and bis(4-methylthiobenzoyl) disulfide.<sup>3</sup>

### Molecular structures.

**Mono dithiocarboxylates Group 14 elements derivatives 1, 3, and 6.** Selected bond lengths and angles in **1d**, **3d**, and **6d** are collected in Table 1. All molecular forms are similar to the ORTEP drawing of the Sn derivatives **3d** as is shown in Figure 1. The crystal data are listed in Table 2. The C11–S11 bond lengths (ca. 1.64 Å) are close to the sum of their double bond covalent bond radii,<sup>4</sup> and all C11–S12 bond lengths [1.71(1)–1.746(3) Å] are roughly intermediate between their single and double bond covalent bond radii.<sup>4</sup> All M1–S12 bond lengths are also shown in M–S single bonds, respectively.<sup>4</sup> In addition, they are comparable to the distances obtained in germanium-dithiocarbonates,<sup>5</sup> tin-dithiocarbamates and dithiocarbonates,<sup>6,7</sup> and lead-dithiocarbamates<sup>8</sup> and dithiophosphates.<sup>9,10</sup> The M1–S11 distances are longer than the sum of their covalent bond radii,<sup>4</sup> but significantly less than the sum of van der Waals radii of both atoms,<sup>11</sup> thus intramolecular interaction should be considered. On the basis of such interaction, the S12–M1–C31 angles significantly deviate from the ideal tetrahedral angle. However, other angles around the central Group 14 elements are relatively comparable to tetrahedral angle. Therefore, mono dithiocarboxylate derivatives show a distorted tetrahedron.

**Bis(dithiocarboxylates) group 14 element derivatives (4).** Diphenyltin bis(4-methylbenzenecarbodithioate) (**4d**) crystallized as four independent molecules. The ORTEP drawing and selected bond lengths and angles are shown in Figure 2 and Table 3. The two dithiocarboxyl groups and the tin atom exist in the same plane. The four C–S bond lengths of the two dithiocarboxylate groups are nearly same



**Figure 1.** The ORTEP drawing of 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CSSSnPh<sub>3</sub> (**3d**). Hydrogen atoms have been omitted for clarity.

**Table 1.** Selected bond lengths (Å) and angles (°) of 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CSSMPh<sub>3</sub>

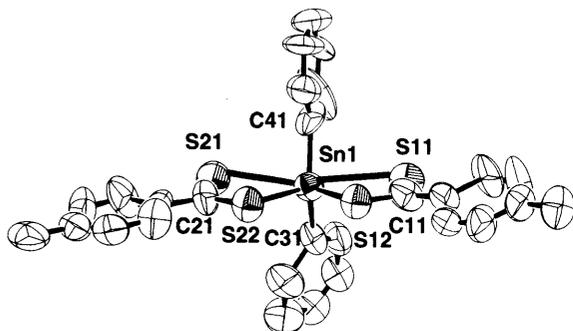
	Ge ( <b>1d</b> )	Sn ( <b>3d</b> )	Pb ( <b>6d</b> )
<i>Bond lengths</i>			
M1–S11	3.371(1)	3.207(2)	3.362(5)
M1–S12	2.2526(8)	2.446(1)	2.535(4)
C11–S11	1.637(3)	1.645(5)	1.64(2)
C11–S12	1.746(3)	1.737(5)	1.71(1)
M1–C21	1.942(3)	2.137(5)	2.19(2)
M1–C31	1.948(3)	2.146(4)	2.19(1)
M1–C41	1.934(3)	2.124(5)	2.16(2)
<i>Bond angles</i>			
S11–M1–S12	59.71(3)	60.92(4)	57.8(1)
S11–C11–S12	122.2(2)	120.8(3)	122(1)
M1–S11–C11	70.03(10)	76.5(2)	75.6(6)
M1–S12–C11	105.9(1)	100.4(2)	102.6(6)
S12–M1–C21	115.19(9)	119.9(1)	116.2(5)
S12–M1–C31	96.75(8)	94.4(1)	93.9(4)
S12–M1–C41	110.75(9)	109.2(1)	107.8(4)
C21–M1–C31	108.0(1)	114.5(1)	110.1(1)
C21–M1–C41	104.7(2)	117.3(2)	107.9(2)
C31–M1–C41	106.1(6)	119.3(6)	110.5(5)

**Table 2.** Crystal data for **1d**, **3d**, **4d**, **5c**, and **6d**

Empirical formula	C <sub>26</sub> H <sub>22</sub> GeS <sub>2</sub> ( <b>1d</b> )	C <sub>26</sub> H <sub>22</sub> S <sub>2</sub> Sn ( <b>3d</b> )	C <sub>28</sub> H <sub>24</sub> S <sub>4</sub> Sn ( <b>4d</b> )	C <sub>30</sub> H <sub>26</sub> S <sub>6</sub> Sn ( <b>5c</b> )	C <sub>26</sub> H <sub>22</sub> PbS <sub>2</sub> ( <b>6d</b> )
Formula weight	471.17	517.27	607.43	697.59	605.78
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Unit-cell dimensions					
<i>a</i> (Å)	11.224(3)	11.327(2)	9.126(6)	34.703(2)	11.405(3)
<i>b</i> (Å)	12.508(3)	12.306(2)	49.908(8)	10.112(2)	12.434(3)
<i>c</i> (Å)	9.767(3)	9.835(1)	23.955(7)	25.484(2)	9.807(2)
$\alpha$ (°)	90.23(3)	91.21(2)	95.60(5)	137.036(2)	91.44(3)
$\beta$ (°)	114.70(2)	112.56(1)			112.37(1)
$\gamma$ (°)	69.33(2)	109.14(1)			110.20(2)
<i>V</i> (Å <sup>3</sup> )	1148.7(6)	1178.9(4)	10858(6)	6095.0(9)	1187.2(6)
Space group	<i>P</i> 1(#2)	<i>P</i> 1(#2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> 1(#2)
<i>Z</i> value	2	2	16	8	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.362	1.457	1.486	1.520	1.694
Crystal size (mm)	0.40 x 0.25 x 0.20	0.10 x 0.10 x 0.45	0.51 x 0.46 x 0.14	0.29 x 0.23 x 0.17	0.23 x 0.14 x 0.09
$\mu$ (Mo-K $\alpha$ ) (cm <sup>-1</sup> )	15.24	12.70	104.74 <sup>c</sup>	12.68	73.03
Temp (°C)	23.0	23.0	23.0	23.0	23.0
2 $\theta$ <sub>max</sub> (deg.)	55.0	55.0	119.8	55.0	55.0
No. of measured reflections	4550	5690	17434	7102	5723
No. of unique reflections	4277	5414	16274	6988	5450
<i>R</i> <sub>int</sub>	0.013	0.024	0.106	0.019	0.080
No. of observations [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	3380	3576	5880	4503	1816
No. of variables	262	262	1179	335	262
Reflection / parameter ratio	12.90	13.65	4.99	13.44	6.93
Residuals: <i>R</i> , <sup>a</sup> <i>R</i> <sub>w</sub> <sup>b</sup>	0.032, 0.034	0.038, 0.039	0.067, 0.093	0.039, 0.040	0.040, 0.042
<i>p</i> value <sup>b</sup>	0.0150	0.0200	0.0700	0.0150	0.0350
Max. and min. of residual electron density (e Å <sup>-3</sup> )	0.33, -0.25	0.51, -0.73	0.59, -0.93	0.54, -0.62	0.63, -0.90
Goodness of fit indicator	1.55	1.42	1.90	1.65	1.07

$$^a R = \sum (|F_o| - |F_c|) / \sum |F_o|, \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}, \quad w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}, \quad ^c \mu \text{ (Cu-K}\alpha\text{)} \text{ (cm}^{-1}\text{)}.$$

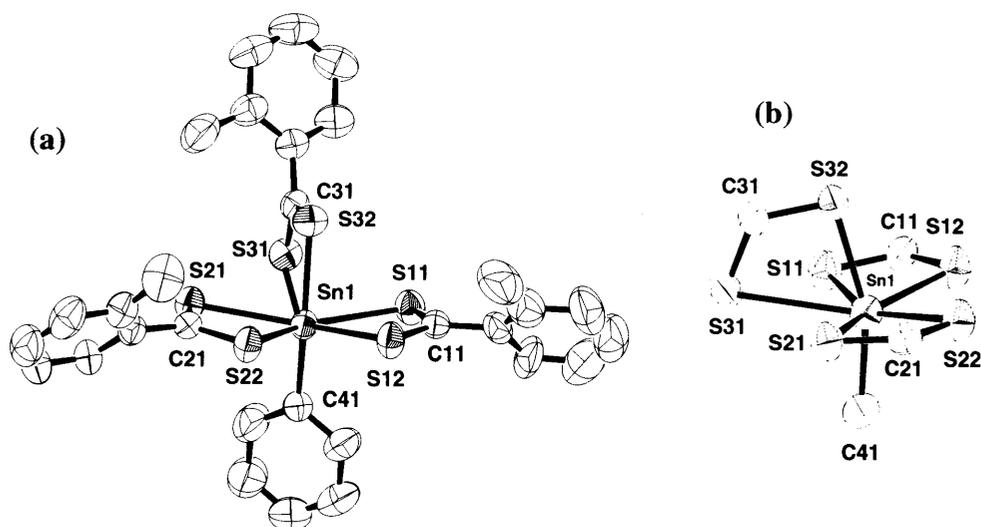
values, and are roughly midway between their single and double bond covalent bond radii.<sup>4</sup> The Sn–S bond lengths [av. 2.483(7) Å] are slightly longer than the sum of their covalent bond radii,<sup>4</sup> which they are comparable to the distances observed in dimethyltin bis(dithiocarbamates).<sup>12</sup> On the other hand, the other Sn–S distances [av. 3.056(7) Å] are longer than the sum of their covalent bond radii, which are ca. 0.7 Å shorter than the sum of their van der Waals radii<sup>11</sup> and ca. 0.15 Å shorter than those of mono derivative **3d** [3.207(2) Å]. The longer Sn–S distances are far apart [S11–Sn–S21 = 152.1(3)°], while the shorter Sn–S distances are close together [S12–Sn–S22 = 84.2(3)°]. The S–Sn–*C*<sub>ipso</sub> bond angles [106.6(7)–110.4(7)°] are close to the tetrahedral angle, while the *C*<sub>ipso</sub>–Sn–*C*<sub>ipso</sub> bond angles

**Figure 2.** The ORTEP drawing of one molecule of (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CSS)<sub>2</sub>SnPh<sub>2</sub> (**4d**). Hydrogen atoms have been omitted for clarity.**Table 3.** Selected bond lengths (Å) and angles (°) of diphenyltin bis(4-methylbenzenecarbothioate) (**4d**)

Bond lengths			
Sn1–S11	3.006(7)	Sn1–S21	3.111(7)
Sn1–S12	2.482(7)	Sn1–S22	2.484(7)
C11–S11	1.69(3)	C21–S21	1.69(3)
C11–S12	1.69(3)	C21–S22	1.66(3)
Sn1–C31	2.07(2)	Sn1–C41	2.07(3)
Bond angles			
S11–Sn1–S21	152.1(3)	C31–Sn1–C41	129(1)
S12–Sn1–S22	84.2(3)	S21–Sn1–S22	61.8(2)
S11–Sn1–S12	61.9(2)	S21–C21–S22	121(1)
S11–C11–S12	115(1)	Sn1–S21–C21	77.4(7)
Sn1–S11–C11	82.1(9)	Sn1–S22–C21	99(1)
Sn1–S12–C11	100.1(10)	S22–Sn1–C31	107.6(7)
S12–Sn1–C31	110.4(7)	S22–Sn1–C41	108.6(7)
S12–Sn1–C41	106.6(7)		

[129(1)°] are quite different. Since there are two additional Sn–S(*x*1) interactions, the steric effects of S(*x*1) would increase the  $C_{ipso}$ –Sn– $C_{ipso}$  angles from an ideal tetrahedral angle to 129(1)° and would decrease the S12–Sn–S22 angle to 84.2(3)°. Thus, the two dithiocarboxylate groups are coordinated as anisobidentate ligands toward the tin atom. These results are typical for a highly distorted octahedral or skew trapezoidal bipyramidal structure.

**Tris(dithiocarboxylates) group 14 element derivatives 5.** Although the crystallization of phenyltin tris(4-methylbenzenecarbodithioate) (**5d**) was examined under many different conditions, no suitable single crystals for X-ray structural analysis was obtained. However, we have succeeded in the preparation of single crystals of phenyltin tris(2-methylbenzenecarbodithioate) (**5c**). The molecular form of **5c** differs from the corresponding thiocarboxylate derivative,<sup>13</sup> where the two dithiocarboxyl groups and the tin atom exist in the same plane [Figure 3(a)]. In Table 4, the six C–S bond lengths of the three dithiocarboxyl groups are comparable to those in **4d**, and can be separated into shorter C–S bond lengths (av. 1.661(5) Å) and longer C–S bond lengths [av. 1.701(4) Å]. The former are significantly longer than the sum of the double bond covalent bond radii, while the latter are roughly intermediate between their single and double bond covalent bond radii.<sup>4</sup> The Sn–S bond lengths of the two dithiocarboxylate groups in the same plane are av. 2.597(1) Å and av. 2.794(1) Å, respectively, which are close to the distances observed in divalent tin compounds with bidentate ligands.<sup>14,15</sup> Therefore, these seem to be coordinated in a bidentate form toward the tin atom. The Sn–S bond lengths of the remaining dithiocarboxylate group are 2.492(1) Å and 2.987(1) Å, respectively, where the former is close to the smallest Sn–S bond lengths observed in tris(dithiocarbamate) tin derivatives.<sup>16</sup> On the other hand, the latter is the longest of the six Sn–S bond lengths, and is longer than the sum of their covalent bond radii.<sup>4</sup> However, these are shorter than the sum of their van der Waals radii [11], and are also shorter than those of **3d** (3.207(2) Å) and **4d** (av. 3.056(7) Å). The S11–Sn1–S21 angle (72.22(4)°) is comparable to the ideal pentagonal angle,



**Figure 3.** The ORTEP drawing of (2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CSS)<sub>3</sub>SnPh (**5c**) (a). The coordination surrounding the Sn1 atom (b). Hydrogen atoms have been omitted for clarity.

and the S32–Sn1–C41 angle [160.7(1)°] is approximately linear. These results are consistent with a seven-coordinated pentagonal bipyramidal structure, where the S11, S12, S21, S22, and S31 atoms are equatorial and S32 and C41 are axial [Figure 3(b)].

**Comparison of germanium, tin, and lead dithiocarboxylates.** The results from X-ray structural analyses have been explained as follows. In the mono derivatives **1d**, **3d**, and **6d**, the shorter C–S bond lengths are nearly the same [1.637(3)–1.645(5) Å], while the longer C–S bond lengths slightly shorten in the order Ge > Sn > Pb. Presumably, delocalization of the dithiocarboxylate group may occur in the lead derivative **6d**. The shorter M–S bond lengths indicate single bonds. It is noteworthy that the distance between the sulfur of the shorter C–S

**Table 4** Selected bond lengths (Å) and angles(°) of phenyltin tris(2-methylbenzenecarbodithioate) (**5c**)

<i>Bond lengths</i>			
Sn1–S11	2.813(1)	Sn1–S12	2.594(1)
Sn1–S21	2.751(1)	Sn1–S22	2.600(1)
Sn1–S31	2.987(1)	Sn1–S32	2.492(1)
Sn1–C41	2.138(1)		
C11–S11	1.663(5)	C12–S11	1.701(4)
C21–S21	1.673(5)	C22–S21	1.691(4)
C31–S31	1.648(4)	C32–S31	1.712(4)
<i>Bond angles</i>			
S11–Sn1–S12	65.00(4)	Sn1–S11–C11	84.3(2)
S11–Sn1–S21	144.43(4)	Sn1–S12–C11	90.8(2)
S11–Sn1–S31	72.22(4)	S11–C11–S12	119.9(3)
S12–Sn1–S22	82.79(4)	Sn1–S21–C21	79.4(2)
S12–Sn1–S32	90.87(4)	Sn1–S22–C21	94.6(2)
S12–Sn1–C41	101.5(1)	S21–C21–S22	121.9(3)
S21–Sn1–S22	66.00(4)	S31–Sn1–S32	64.10(4)
S21–Sn1–S31	72.22(4)	S32–Sn1–C41	160.7(1)
S22–Sn1–S32	95.33(5)	Sn1–S31–C31	84.5(2)
S22–Sn1–C41	100.8(1)	Sn1–S32–C31	89.1(2)
		S31–C31–S32	120.3(3)

bond (thiocarbonyl sulfur) and the central tin atom is shorter than S...Ge and S...Pb distances. The ratio of these distances and the sum of the corresponding van der Waals radii<sup>11</sup> become smaller in the order Sn **3d** (19%) > Pb **6d** (12%) ≥ Ge **1d** (11%). This suggests that the electron affinity of the tin atom for the sulfur atom is much stronger than those of the germanium and lead atoms. Sulfur does not generally show a stronger affinity with silicon than oxygen.<sup>17</sup> In CH<sub>3</sub>C(S)OSiH<sub>3</sub>, the distance between the thiocarbonyl sulfur and the silicon atom is 3.185(9) Å, indicating very weak interaction, although less than the van der Waals distance.<sup>11</sup> Thus, the affinity between sulfur atom and Group 14 elements may decrease in the order Sn > Pb ≥ Ge > Si > C. These non-bonding interactions are considered to reflect interaction between the sulfur lone-pair and the non-bonding orbital (σ\* orbital) of C–M or S–M (M = Ge, Sn, Pb). In comparing mono **3d**, bis **4d**, and tris derivatives **5c**, the two C–S bond lengths of **4d** and **5c** are nearly same value, which suggests that the dithiocarboxylate groups in **4d** and **5c** seem more strongly delocalized than those of **3d**. The Sn–S bond lengths increase in the order **4d** < **3d** < **5c**, but the distances between the thiocarbonyl sulfur and the tin atoms shorten in the order **3d** > **4d** > **5c**. The bidentate characters of dithiocarboxylate groups are considered to increase with their number.

**Spectra.** Thiocarbonyl stretching frequencies in the germanium, tin, and lead derivatives are observed at 1160–1200 cm<sup>-1</sup> for aliphatic derivatives and 1210–1270 cm<sup>-1</sup> for aromatic ones. The <sup>13</sup>C=S chemical shifts appear at  $\delta$  230–250, and those of aliphatic are at lower frequencies than those of aromatic. The <sup>119</sup>Sn-NMR chemical shifts are observed at  $\delta$  -125 to -130 for mono derivatives **3**,  $\delta$  -250 to -400 for bis derivatives **4**, and  $\delta$  -650 to -740 for tris derivatives **5**, and those of aliphatic derivatives are at a lower field than those of aromatic derivatives. The coupling constants of tin–carbon appear at 600 Hz and 800 Hz, respectively, with a difference of 200 Hz. The thiocarbonyl stretching frequencies and the thiocarbonyl carbon and <sup>119</sup>Sn chemical shifts of 4-methylbenzene derivatives are shown in Table 5. The thiocarbonyl stretching frequencies are nearly the same, but the <sup>13</sup>C=S chemical shifts show 3 ppm downfield shift with an increase in dithiocarboxylate groups. On the other hand, the <sup>119</sup>Sn chemical shifts show upfield shifts in the order **3d** < **4d** < **5d**, with a difference of 250 ppm between **3d** and **4d** and of 350 ppm between **4d** and **5d**. In these spectroscopic data of mono-, bis-, and tris(4-methylbenzene-carboxylates) germanium, tin, and lead derivatives, the  $\nu$  (C=S) stretching frequencies are nearly the same, but the <sup>13</sup>C=S chemical shifts are in the order Ge < Sn < Pb and mono- < bis- < tris(dithio-carboxylate) derivatives.

**Table 5.** Selected features in the spectroscopic data of (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CSS)<sub>x</sub>MPh<sub>4-x</sub><sup>a</sup>

No.	M	x	$\nu$ (C=S) <sup>b</sup> (cm <sup>-1</sup> )	$\delta_{C=S}$ <sup>c</sup>	$\delta_{119Sn}$ <sup>d</sup>
<b>1d</b>	Ge	1	1220, 1212	227.7	
<b>3d</b>	Sn	1	1242, 1224	232.1	-138.8
<b>6d</b>	Pb	1	1219, 1210	234.5	
<b>2d</b>	Ge	2	1238, 1221	228.0	
<b>4d</b>	Sn	2	1239, 1221	235.9	-392.0
<b>7d</b>	Pb	2	1222	239.4	
<b>5d</b>	Sn	3	1242, 1224	238.2	-739.5

<sup>a</sup> Standard: Me<sub>4</sub>Sn. <sup>b</sup> In KBr. <sup>c</sup> In CDCl<sub>3</sub>. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub>.

### 3.3. Conclusion

A series of germanium, tin, and lead derivatives of dithiocarboxylates were synthesized, and their structures were analyzed by X-ray. These molecules show the existence of intramolecular non-bonding interactions between the thiocarbonyl sulfur atoms and the central Group 14 element metals.

Comparative studies of the compounds RCSSMPh<sub>3</sub> (M = Ge, Sn, Pb) revealed that the distance between the thiocarbonyl sulfur and the tin atom is shorter than those of the germanium and lead derivatives. These non-bonding interactions reflect the affinity between the sulfur atoms and the Group 14 elements, i.e. this affinity decreases in the order Sn > Pb ≥ Ge > Si > C. Such order of the affinity would contribute not only to the synthesis of the relevant compounds but also elucidation of biological mechanism in which the Group 14 elements and sulfur participate.

### 3.4. Experimental

Melting points were determined by a Yanagimoto micromelting point apparatus, but not corrected. The IR spectra were measured on Perkin-Elmer FT-IR 1640 spectrophotometer. <sup>1</sup>H- (400 MHz) and <sup>13</sup>C-NMR spectra (100 MHz) were measured on a JEOL JNM- $\alpha$ 400 in CDCl<sub>3</sub> containing Me<sub>4</sub>Si as an internal standard. <sup>119</sup>Sn-NMR spectra (149 MHz) were also measured on a JEOL JNM- $\alpha$ 400 with Me<sub>4</sub>Sn as an external standard. UV-vis spectra were obtained from a JASCO U-Best 55. Elemental analyses were performed by the Elemental Analysis Center of

Kyoto University. All solvents were dried and distilled prior to use.  $\text{Ph}_3\text{GeCl}$ ,  $\text{Ph}_2\text{GeCl}_2$ ,  $\text{Ph}_3\text{SnCl}$ ,  $\text{Ph}_2\text{SnCl}_2$ ,  $\text{PhSnCl}_3$ ,  $\text{SnCl}_4\text{-CH}_2\text{Cl}_2$  1.0 M solution, and  $\text{Ph}_3\text{PbCl}$  are of commercial grade were obtained from Aldrich.  $\text{Ph}_2\text{PbCl}_2$  was obtained from Alfa Chemical Co. Piperidinium<sup>18</sup> and sodium dithiocarboxylates<sup>2f</sup> were prepared by the previously described method. A series of  $\text{RCSSMPH}_3$  (M = Sn: **3**<sup>2b,f</sup>, Pb: **6**<sup>2d</sup>) and  $(\text{RCSS})_2\text{SnPh}_2$  **4**<sup>2b</sup> were synthesized according to the procedures reported previously.

**General procedures.** The synthesis of triphenylgermanium 4-methylbenzenecarbodithioate (**1d**) is described in detail as a typical procedure for compounds **1**, **2**, **5**, and **7**. For **3**<sup>2b</sup>, **4**<sup>2b</sup>, and **6**<sup>2b</sup>, the additional spectral data and elemental analysis are described.

**1a.** Recrystallizing solvents: hexane; orange crystals (28%); m.p. 89–90°C. IR (KBr): 1193 (C=S), 1158 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  2.91 (s, 3H, CH<sub>3</sub>), 7.39–7.44 (m, 9H, Ar), 7.62–7.65 (m, 6H, Ar). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ ):  $\delta$  43.8 (CH<sub>3</sub>), 128.0, 129.3, 134.7, 136.8, 236.6 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.05), 289 (3.95), 309 (3.48), 518 (2.13) nm.

**1b.** Recrystallizing solvents: 1:1 Et<sub>2</sub>O–hexane; purple crystals (60%); m.p. 108–110°C. IR (KBr): 1218 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  7.39–7.44 (m, 11H, Ar), 7.68–7.71 (m, 7H, Ar), 8.19–8.22 (m, 2H, Ar). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ ):  $\delta$  127.1, 128.0, 128.5, 129.9, 132.5, 134.7, 134.8, 145.7, 228.7 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.36), 270 (4.46), 306 (4.13), 519 (2.58) nm. Anal. Found: C, 65.62; H, 4.47. C<sub>25</sub>H<sub>20</sub>GeS<sub>2</sub> Calcd.: C, 65.68; H, 4.41%.

**1c.** Reddish-purple oil (88%). IR (neat): 1240 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  2.38 (s, 3H, CH<sub>3</sub>), 7.12–7.20 (m, 3H, Ar), 7.32–7.43 (m, 10H, Ar), 7.69–7.71 (m, 6H, Ar). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ ):  $\delta$  19.7 (CH<sub>3</sub>), 125.5, 125.9, 128.6, 128.8, 130.0, 130.7, 132.2, 134.1, 134.8, 150.1, 235.7 (C=S).

**1d.** To a solution of  $\text{Ph}_3\text{GeCl}$  (0.339 g, 1.00 mmol) in Et<sub>2</sub>O (15 ml), piperidinium 4-methylbenzenecarbodithioate (0.254 g, 1.00 mmol) was added and the mixture was stirred at 20°C for 1 h. After addition of  $\text{CH}_2\text{Cl}_2$  (100 ml), the mixture was washed with water (3 x 90 ml), followed by drying over  $\text{MgSO}_4$ . The solvents were removed under reduced pressure (30°C/2.7 kPa), and the resulting residue was dissolved into a mixed solvent of  $\text{CH}_2\text{Cl}_2$  (4.0 ml) and hexane (3.0 ml) and allowed to stand in a refrigerator (–20°C) for 24 h to give **1d** as purple crystals (0.306 g, 65%); m.p. 129–130°C. IR (KBr): 1220 (C=S), 1212 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H, CH<sub>3</sub>), 7.15 (d,  $J$  = 8.4 Hz, 2H, Ar), 7.39–7.47 (m, 9H, PhGe), 7.73–7.75 (m, 6H, PhGe), 8.19 (d,  $J$  = 8.4 Hz, 2H, Ar). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ ):  $\delta$  21.5 (CH<sub>3</sub>), 127.2, 128.5, 128.7, 129.8, 134.6, 134.8, 143.2, 143.5, 227.7 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.46), 273 (4.71), 320 (4.27), 527 (2.65) nm. Anal. Found: C, 66.30; H, 4.75. C<sub>26</sub>H<sub>22</sub>GeS<sub>2</sub> Calcd.: C, 66.27; H, 4.71%.

**1e.** Recrystallizing solvents: 1:1  $\text{CH}_2\text{Cl}_2$ –hexane; purple crystals (60%); m.p. 117–118°C. IR (KBr): 1261 (C=S), 1243 (C=S), 1228 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  3.79 (s, 3H, CH<sub>3</sub>O), 6.78 (d,  $J$  = 8.9 Hz, 2H, Ar), 7.36–7.43 (m, 9H, PhGe), 7.69–7.71 (m, 6H, PhGe), 8.28 (d,  $J$  = 8.9 Hz, 2H, Ar). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ )  $\delta$  55.5 (CH<sub>3</sub>O), 113.0, 128.0, 128.4, 129.5, 129.8, 134.8, 138.9, 163.8, 225.5 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.50), 270 (5.42), 341 (4.40), 520 (2.81) nm. Anal. Found: C, 64.36; H, 4.75. C<sub>26</sub>H<sub>22</sub>GeOS<sub>2</sub> Calcd.: C, 64.10; H, 4.55%.

**1f.** Recrystallizing solvents: 4:3  $\text{CH}_2\text{Cl}_2$ –hexane; purple crystals (57%); m.p. 120–121°C. IR (KBr): 1211 (C=S)  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  7.23 (d,  $J$  = 8.3 Hz, 2H, Ar), 7.31–

7.36 (m, 9H, PhGe), 7.60–7.62 (m, 6H, PhGe), 8.08 (d,  $J = 8.3$  Hz, 2H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  128.0, 128.1, 128.4, 128.6, 130.0, 134.2, 134.4, 134.9, 226.6 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.35), 273 (4.13), 316 (4.24), 531 (2.59) nm. Anal. Found: C, 61.17; H, 3.95.  $\text{C}_{25}\text{H}_{19}\text{ClGeS}_2$  Calc.: C, 61.08; H, 3.90%.

**2a.** Recrystallizing solvents: hexane; orange crystals (54%); m.p. 78–79°C. IR (KBr): 1197 (C=S), 1183 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.61 (s, 6H,  $\text{CH}_3$ ), 7.15 (t,  $J = 6.6$  Hz, 4H, PhGe), 7.38 (t,  $J = 6.6$  Hz, 4H, PhGe), 7.48 (d,  $J = 6.6$  Hz, 2H, PhGe).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  45.7 ( $\text{CH}_3$ ), 128.1, 130.2, 133.5, 135.9, 229.4 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.14), 270 (3.42), 309 (3.39), 409 (3.00), 520 (3.58) nm.

**2b.** Recrystallizing solvents: 4:3  $\text{CH}_2\text{Cl}_2$ –hexane; red crystals (62%); m.p. 196–198°C. IR (KBr): 1237 (C=S), 1222 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.31–7.53 (m, 8H, Ar), 7.67–7.74 (m, 2H, PhGe), 7.90–7.96 (m, 6H, Ar), 8.07–8.22 (m, 4H, Ar);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  128.3, 128.5, 128.6, 128.7, 128.8, 131.0, 133.2, 133.7, 228.7 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.39), 270 (4.52), 305 (3.17), 515 (2.63) nm. Anal. Found: C, 58.62; H, 3.81.  $\text{C}_{26}\text{H}_{20}\text{GeS}_4$  Calc.: C, 58.55; H, 3.78%.

**2c.** Red oil (82%); IR (neat): 1241 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.31 (s, 6H,  $\text{CH}_3$ ), 7.09–7.96 (m, 18H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  19.8 ( $\text{CH}_3$ ), 125.5, 126.0, 128.6, 128.8, 129.2, 130.8, 132.5, 133.6, 134.3, 148.8, 235.7 (C=S).

**2d.** Recrystallizing solvents: 7:5  $\text{CH}_2\text{Cl}_2$ –hexane; red crystals (69%); m.p. 114–116°C. IR (KBr): 1238 (C=S), 1221 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.34 (s, 6H,  $\text{CH}_3$ ), 7.17 (d,  $J = 8.1$  Hz, 4H, Ar), 7.21 (t,  $J = 6.9$  Hz, 6H, PhGe), 7.31 (d,  $J = 8.1$  Hz, 4H, Ar), 7.48 (d,  $J = 6.9$  Hz, 4H, PhGe).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  21.6 ( $\text{CH}_3$ ), 127.1, 128.5, 128.7, 129.1, 130.2, 134.2, 142.2, 144.1, 228.0 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.41), 271 (4.22), 324 (4.73), 515 (2.52) nm. Anal. Found: C, 60.01; H, 4.33.  $\text{C}_{28}\text{H}_{24}\text{GeS}_4$  Calc.: C, 59.91; H, 4.31%.

**2e.** Recrystallizing solvents: 5:4  $\text{CH}_2\text{Cl}_2$ –hexane; red crystals (60%); m.p. 119–121°C. IR (KBr): 1240 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.77 (s, 6H,  $\text{CH}_3\text{O}$ ), 6.76 (d,  $J = 9.0$  Hz, 4H, Ar), 7.23–7.58 (m, 6H, Ar), 7.81–7.99 (m, 4H, PhGe), 8.02 (d,  $J = 9.0$  Hz, 4 H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  55.5 ( $\text{CH}_3\text{O}$ ), 113.5, 128.4, 128.6, 129.3, 133.1, 134.1, 137.8, 164.1, 225.7 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.42), 272 (4.31), 349 (4.55), 516 (2.83) nm. Anal. Found: C, 56.69; H, 4.10.  $\text{C}_{28}\text{H}_{24}\text{GeO}_2\text{S}_4$  Calc.: C, 56.68; H, 4.08%.

**2f.** Recrystallizing solvents: 4:3  $\text{CH}_2\text{Cl}_2$ –hexane; red crystals (62%); m.p. 146–148°C. IR (KBr): 1236 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.20 (d,  $J = 8.7$  Hz, 4H, Ar), 7.30–7.50 (m, 6H, PhGe), 7.76–7.81 (m, 4H, PhGe), 8.02 (d,  $J = 8.7$  Hz, 4H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  128.1, 128.5, 128.6, 130.2, 133.1, 134.1, 139.6, 142.5, 226.4 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.45), 273 (4.24), 312 (4.28), 516 (2.69) nm. Anal. Found: C, 51.89; H, 3.11.  $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{GeS}_4$  Calcd.: C, 51.86; H, 3.01%.

**3a.** Orange oil (92%). IR (neat): 1187 (C=S), 1174 (C=S), 1152 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.94 (s, 3H,  $\text{CH}_3$ ), 7.36–7.40 (m, 9H, PhSn), 7.64–7.67 (m, 6H, PhSn).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  42.0 ( $\text{CH}_3$ ), 128.8, 129.7, 136.5, 136.8, 242.0 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  –127.4 ( $^1J_{\text{C-Sn}} = 595$  Hz). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 319 (3.94), 461 (1.74) nm.

**3b<sup>2b</sup>.** Recrystallizing solvents: 5:3  $\text{CH}_2\text{Cl}_2$ –hexane; red crystals (78%).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  127.9, 128.5, 128.9, 129.7, 136.5, 136.7, 136.8, 143.9, 233.1 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  –135.4 ( $^1J_{\text{C-Sn}} = 597$  Hz). Anal. Found: C, 59.72; H, 4.15.  $\text{C}_{25}\text{H}_{20}\text{S}_2\text{Sn}$  Calcd.: C,

59.66; H, 4.01%.

**3c<sup>2b</sup>**. Recrystallizing solvents: 1:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (74%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 20.1 (CH<sub>3</sub>), 125.5, 126.1, 128.9, 129.1, 129.8, 130.8, 132.4, 136.8, 138.7, 148.8, 240.1 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –126.5 (<sup>1</sup>J<sub>C–Sn</sub> = 591 Hz). Anal. Found: C, 60.52; H, 4.39. C<sub>26</sub>H<sub>22</sub>S<sub>2</sub>Sn Calc.: C, 60.37; H, 4.29%.

**3d<sup>2b,f</sup>**. Recrystallizing solvents: 7:5 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (70%).

**3e<sup>2b</sup>**. Recrystallizing solvents: 5:4 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (75%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 55.5 (CH<sub>3</sub>O), 113.0, 128.8, 129.5, 130.1, 134.6, 136.8, 139.8, 164.0, 229.8 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –143.1 (<sup>1</sup>J<sub>C–Sn</sub> = 597 Hz). Anal. Found: C, 58.61; H, 4.22. C<sub>26</sub>H<sub>22</sub>OS<sub>2</sub>Sn Calc.: C, 58.56; H, 4.16%.

**3f<sup>2b</sup>**. Recrystallizing solvents: 6:5 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (69%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 128.0, 128.7, 129.3, 130.3, 134.7, 141.3, 141.4, 143.6, 230.2 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –130.4 (<sup>1</sup>J<sub>C–Sn</sub> = 612 Hz). Anal. Found: C, 55.92; H, 3.66. C<sub>25</sub>H<sub>19</sub>ClS<sub>2</sub>Sn Calc.: C, 55.84; H, 3.56%.

**4a**. Recrystallizing solvents: hexane; orange crystals (87%); m.p. 98–99°C. IR (KBr): 1172 (C=S), 1151 (C=S) cm<sup>–1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.64 (s, 6H, CH<sub>3</sub>), 7.24–7.35 (m, 6H, PhSn), 7.48–7.50 (m, 4H, PhSn). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 51.1 (CH<sub>3</sub>), 128.7, 129.8, 135.4, 140.5, 252.4 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –251.5 (<sup>1</sup>J<sub>C–Sn</sub> = 741 Hz). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (log ε): 320 (3.88), 417 (2.11) nm.

**4b<sup>2b</sup>**. Recrystallizing solvents: 8:5 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (82%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 127.3, 128.0, 129.0, 130.0, 133.8, 134.7, 142.7, 144.8, 236.9 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –385.0 (<sup>1</sup>J<sub>C–Sn</sub> = 817 Hz). Anal. Found: C, 53.96; H, 3.52. C<sub>26</sub>H<sub>20</sub>S<sub>4</sub>Sn Calc.: C, 53.90; H, 3.48%.

**4c**. Recrystallizing solvents: 1:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (70%); m.p. 79–80°C. IR (KBr): 1233 (C=S) cm<sup>–1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.43 (s, 6H, CH<sub>3</sub>), 7.11–7.24 (m, 6H, Ar), 7.41–7.49 (m, 8H, Ar), 7.95–8.01 (m, 4H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 20.5 (CH<sub>3</sub>), 125.6, 126.7, 129.1, 129.8, 131.0, 133.1, 134.7, 135.8, 144.2, 146.9, 244.2 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –367.4 (<sup>1</sup>J<sub>C–Sn</sub> = 805 Hz). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (log ε): 338 (4.32), 457 (2.93) nm. Anal. Found: C, 55.39; H, 4.00. C<sub>28</sub>H<sub>24</sub>S<sub>4</sub>Sn Calc.: C, 55.36; H, 3.98%.

**4d<sup>2b</sup>**. Recrystallizing solvents: 7:5 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (88%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 21.7 (CH<sub>3</sub>), 127.4, 128.6, 128.8, 129.4, 134.6, 140.3, 145.1, 145.4, 235.9 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –392.0 (<sup>1</sup>J<sub>C–Sn</sub> = 807 Hz). Anal. Found: C, 55.44; H, 4.07. C<sub>28</sub>H<sub>24</sub>S<sub>4</sub>Sn Calc.: C, 55.36; H, 3.98%.

**4e**. Recrystallizing solvents: 3:2 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (81%); m.p. 169–170°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 3.81 (s, 6H, CH<sub>3</sub>O), 6.78 (d, *J* = 8.9 Hz, 4H, Ar), 7.32–7.40 (m, 6H, PhSn), 7.90–7.93 (m, 4H, PhSn), 8.32 (d, *J* = 8.9 Hz, 4H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 55.6 (CH<sub>3</sub>O), 113.0, 128.8, 129.3, 130.0, 134.6, 136.0, 146.2, 164.9, 233.5 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>) δ –402.7 (<sup>1</sup>J<sub>C–Sn</sub> = 812 Hz). Anal. Found: C, 52.61; H, 3.82. C<sub>28</sub>H<sub>24</sub>O<sub>2</sub>S<sub>4</sub>Sn Calcd.: C, 52.59; H, 3.78%.

**4f<sup>2b</sup>**. Recrystallizing solvents: 6:5 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (79%). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 128.1, 128.6, 129.1, 129.8, 134.7, 140.6, 141.0, 144.0, 234.6 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –378.9 (<sup>1</sup>J<sub>C–Sn</sub> = 826 Hz). Anal. Found: C, 48.22; H, 2.83. C<sub>26</sub>H<sub>18</sub>Cl<sub>2</sub>S<sub>4</sub>Sn Calcd.: C, 48.17; H, 2.80%.

**5a.** Orange oil (41%). IR (neat): 1196 (C=S), 1148 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.78 (s, 9H,  $\text{CH}_3$ ), 7.37–7.48 (m, 3H, PhSn), 7.77–7.79 (m, 2H, PhSn).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  48.5 ( $\text{CH}_3$ ), 128.8, 131.6, 134.5, 139.0, 250.5 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -652.2. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (5.12), 270 (4.52), 310 (3.85), 401 (2.75) nm.

**5b.** Recrystallizing solvents: 5:1:7  $\text{CH}_2\text{Cl}_2$ -AcOEt-hexane; orange crystals (82%); m.p. 144–147°C. IR (KBr): 1236 (C=S), 1221 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.32–7.40 (m, 9H, Ar), 7.54–7.58 (m, 3H, Ar), 8.06–8.08 (m, 2H, Ar), 8.29–8.31 (m, 6H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  127.3, 128.1, 129.1, 130.0, 131.1, 134.1, 144.4, 151.8, 239.4 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -737.2. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.52), 262 (4.33), 313 (4.96), 445 (3.70) nm. Anal. Found: C, 49.52; H, 3.14.  $\text{C}_{27}\text{H}_{20}\text{S}_6\text{Sn}$  Calc.: C, 49.47; H, 3.08%.

**5c.** Recrystallizing solvents: 7:3:8 AcOEt-Et<sub>2</sub>O-hexane; orange crystals (85%); m.p. 110–113°C. IR (KBr): 1226 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 9H,  $\text{CH}_3$ ), 7.13–7.16 (m, 6H, Ar), 7.23–7.26 (m, 3H, Ar), 7.44–7.46 (m, 3H, Ar), 7.56–7.58 (m, 3H, Ar), 8.08–8.10 (m, 2H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  20.9 ( $\text{CH}_3$ ), 125.6, 127.1, 129.1, 130.1, 130.2, 131.1, 131.2, 133.5, 145.0, 151.1, 246.5 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -710.7. Anal. Found: C, 51.66; H, 3.73.  $\text{C}_{30}\text{H}_{26}\text{S}_6\text{Sn}$  Calc.: C, 51.65; H, 3.76%.

**5d.** Recrystallizing solvents: 2:6:5  $\text{CH}_2\text{Cl}_2$ -AcOEt-hexane; orange crystals (77%); m.p. 130–132°C. IR (KBr): 1242 (C=S), 1224 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.24 (s, 9H,  $\text{CH}_3$ ), 7.04 (d,  $J$  = 8.4 Hz, 6H, Ar), 7.32–7.37 (m, 3H, PhSn), 7.70–7.80 (m, 2H, PhSn), 8.21 (d,  $J$  = 8.4 Hz, 6H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  22.0 ( $\text{CH}_3$ ), 127.5, 128.7, 128.9, 129.8, 131.1, 139.1, 145.4, 152.3, 238.2 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -739.5. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 221 (5.21), 258 (4.73), 340 (5.01), 445 (2.45) nm. Anal. Found: C, 51.72; H, 3.82.  $\text{C}_{30}\text{H}_{26}\text{S}_6\text{Sn}$  Calc.: C, 51.65; H, 3.76%.

**5e.** Recrystallizing solvents: 1:1  $\text{CH}_2\text{Cl}_2$ -hexane; orange crystals (78%); m.p. 157–159°C. IR (KBr): 1269 (C=S), 1244 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.88 (s, 9H,  $\text{CH}_3\text{O}$ ), 6.79 (d,  $J$  = 9.0 Hz, 6H, Ar), 7.34–7.41 (m, 3H, PhSn), 8.05–8.09 (m, 2H, PhSn), 8.32 (d,  $J$  = 9.0 Hz, 6H, Ar).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  55.7 ( $\text{CH}_3\text{O}$ ), 113.1, 128.8, 129.7, 130.1, 131.1, 134.9, 152.8, 165.1, 235.5 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -748.2. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 223 (5.13), 264 (4.69), 369 (4.95), 463 (2.47) nm. Anal. Found: C, 48.39; H, 3.56.  $\text{C}_{30}\text{H}_{26}\text{O}_3\text{S}_6\text{Sn}$  Calc.: C, 48.32; H, 3.51%.

**5f.** Recrystallizing solvents: 2:4:7  $\text{CH}_2\text{Cl}_2$ -AcOEt-hexane; red crystals (53%); m.p. 137–140°C. IR (KBr): 1235 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.25–7.43 (m, 12H, Ar), 8.00–8.03 (m, 2H, PhSn), 8.21–8.23 (m, 3H, PhSn).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  128.2, 128.7, 129.2, 130.2, 131.0, 139.8, 141.2, 151.5, 237.5 (C=S).  $^{119}\text{Sn-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -739.8. UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 223 (5.14), 263 (4.72), 331 (4.65), 429 (2.45) nm. Anal. Found: C, 42.80; H, 2.31.  $\text{C}_{27}\text{H}_{17}\text{Cl}_3\text{S}_6\text{Sn}$  Calc.: C, 42.73; H, 2.26%.

**6a.** Orange oil (86%). IR (neat): 1161 (C=S), 1132 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.92 (s, 3H,  $\text{CH}_3$ ), 7.29–7.44 (m, 9H, PhPb), 7.57–7.68 (m, 6H, PhPb).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  45.2 ( $\text{CH}_3$ ), 128.3, 128.8, 135.9, 153.2 ( $^1J_{\text{C-Pb}}$  = 541 Hz), 259.9 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.41), 270 (4.55), 334 (3.74), 470 (1.66) nm.

**6b<sup>2d</sup>.** Recrystallizing solvents: 5:4  $\text{CH}_2\text{Cl}_2$ -hexane; purple crystals (60%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.26 (t,  $J$  = 8.5 Hz, 1H, Ar), 7.33 (t,  $J$  = 7.6 Hz, 3H, PhPb), 7.45 (t,  $J$  = 7.6 Hz, 6H, PhPb), 7.50 (t,  $J$  = 8.5 Hz, 2H, Ar), 7.77 (d,  $J$  = 7.6 Hz, 6H, PhPb), 8.26 (d,  $J$  = 8.5 Hz, 2H, Ar).

$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  127.5, 127.7, 128.5, 129.3, 130.1, 132.3, 137.0, 156.0 ( $^1J_{\text{C-Pb}} = 544$  Hz), 235.4 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.47), 271 (4.62), 303 (4.30), 519 (2.15) nm. Anal. Found: C, 50.89; H, 3.61.  $\text{C}_{25}\text{H}_{20}\text{PbS}_2$  Calc.: C, 50.74; H, 3.41%.

**6c<sup>2d</sup>**. Recrystallizing solvents: 5:7 Et<sub>2</sub>O–hexane; orange crystals (83%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  2.39 (s, 3H, CH<sub>3</sub>), 7.08–7.15 (m, 4H, Ar), 7.34–7.53 (m, 9H, Ar), 7.64–7.92 (m, 6H, Ar).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  19.8 (CH<sub>3</sub>), 125.4, 125.7, 128.4, 129.4, 130.1, 130.6, 131.9, 137.0, 150.0, 155.6 ( $^1J_{\text{C-Pb}} = 533$  Hz), 242.2 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 307 (3.83), 504 (2.23) nm. Anal. Found: C, 51.75; H, 3.90.  $\text{C}_{26}\text{H}_{22}\text{PbS}_2$  Calc.: C, 51.55; H, 3.66%.

**6d<sup>2d</sup>**. Recrystallizing solvents: 3:2 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (88%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  2.34 (s, 3H, CH<sub>3</sub>), 7.10 (d,  $J = 8.2$  Hz, 2H, Ar), 7.36 (t,  $J = 7.6$  Hz, 3H, PhPb), 7.48 (t,  $J = 7.6$  Hz, 6H, PhPb), 7.78 (d,  $J = 7.6$  Hz, 6H, PhPb), 8.20 (d,  $J = 8.2$  Hz, 2H, Ar).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  21.6 (CH<sub>3</sub>), 127.8, 128.5, 129.3, 130.1, 137.0, 137.6, 143.4, 156.2 ( $^1J_{\text{C-Pb}} = 543$  Hz), 234.5 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.43), 272 (4.57), 318 (4.38), 520 (2.23) nm.

**6e<sup>2d</sup>**. Recrystallizing solvents: 5:3 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (78%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  3.68 (s, 3H, CH<sub>3</sub>O), 6.86 (d,  $J = 9.0$  Hz, 2H, Ar), 7.29 (t,  $J = 7.3$  Hz, 3H, PhPb), 7.42 (t,  $J = 7.3$  Hz, 6H, PhPb), 7.78 (d,  $J = 7.3$  Hz, 6H, PhPb), 8.34 (d,  $J = 9.0$  Hz, 2H, Ar).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  55.3 (CH<sub>3</sub>O), 112.7, 127.4, 129.3, 129.9, 136.8, 138.4, 156.2 ( $^1J_{\text{C-Pb}} = 545$  Hz), 163.6, 232.0 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.44), 272 (4.62), 344 (4.45), 515 (2.32) nm. Anal. Found: C, 50.39; H, 3.62.  $\text{C}_{26}\text{H}_{22}\text{OPbS}_2$  Calc.: C, 50.22; H, 3.57%.

**6f<sup>2d</sup>**. Recrystallizing solvents: 2:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane; red crystals (73%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  7.18 (d,  $J = 8.5$  Hz, 2H, Ar), 7.31 (t,  $J = 7.6$  Hz, 3H, PhPb), 7.44 (t,  $J = 7.6$  Hz, 6H, PhPb), 7.76 (d,  $J = 7.6$  Hz, 6H, PhPb), 8.17 (d,  $J = 8.5$  Hz, 2H, Ar).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  127.8, 128.8, 129.4, 130.1, 136.9, 138.0, 143.7, 155.9 ( $^1J_{\text{C-Pb}} = 544$  Hz), 233.2 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 221 (4.43), 272 (4.71), 313 (4.34), 524 (2.18) nm. Anal. Found: C, 47.99; H, 3.11.  $\text{C}_{25}\text{H}_{19}\text{ClPbS}_2$  Calc.: C, 47.95; H, 3.06%.

**7a**. Recrystallizing solvents: hexane; orange crystals (35%); m.p. 87–88°C. IR (KBr): 1162 (C=S), 1152 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  2.67 (s, 6H, CH<sub>3</sub>), 7.31 (t,  $J = 7.5$  Hz, 2H, PhPb), 7.44 (t,  $J = 7.5$  Hz, 4H, PhPb), 7.92 (d,  $J = 7.5$  Hz, 4H, PhPb);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  44.9 (CH<sub>3</sub>), 129.5, 130.2, 136.7, 137.0, 250.7 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.61), 270 (4.54), 335 (4.41), 467 (2.11) nm.

**7b**. Recrystallizing solvents: 2:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (74%); m.p. 196–198°C. IR (KBr): 1217 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  7.38 (t,  $J = 7.7$  Hz, 4H, PhPb), 7.42 (t,  $J = 7.8$  Hz, 4H, Ar), 7.51 (t,  $J = 7.7$  Hz, 2H, PhPb), 7.56 (t,  $J = 7.8$  Hz, 2H, Ar), 7.95 (d,  $J = 7.7$  Hz, 4H, PhPb), 8.09 (d,  $J = 7.8$  Hz, 4H, Ar).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  128.3, 129.0, 130.2, 130.5, 133.5, 135.1, 138.4, 157.8, 243.3 (C=S). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 222 (4.49), 272 (4.09), 316 (4.49), 472 (2.67) nm. Anal. Found: C, 46.82; H, 3.11.  $\text{C}_{26}\text{H}_{20}\text{PbS}_4$  Calc.: C, 46.76; H, 3.02%.

**7c**. Recrystallizing solvents: 4:5 Et<sub>2</sub>O–hexane; orange crystals (83%); m.p. 211–214°C. IR (KBr): 1230 (C=S)  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.35 (s, 6H, CH<sub>3</sub>), 7.10 (t,  $J = 7.3$  Hz, 4H, Ar), 7.20 (t,  $J = 7.3$  Hz, 2H, Ar), 7.33 (d,  $J = 7.3$  Hz, 2H, Ar), 7.44 (t,  $J = 7.5$  Hz, 2H, PhPb), 7.57 (t,  $J = 7.5$  Hz, 4H, PhPb), 8.16 (d,  $J = 7.5$  Hz, 4H, PhPb).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  20.0 (CH<sub>3</sub>), 125.5, 125.8, 129.0, 130.0, 130.3, 130.8, 132.1, 134.4, 151.1, 161.1, 244.0 (C=S). Anal. Found: C,

48.42; H, 3.57. C<sub>28</sub>H<sub>24</sub>PbS<sub>4</sub> Calc.: C, 48.32; H, 3.48%.

**7d.** Recrystallizing solvents: 2:1 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (83%); m.p. 214–217°C. IR (KBr): 1222 (C=S) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.35 (s, 6H, CH<sub>3</sub>), 7.13 (d, *J* = 8.2 Hz, 4H, Ar), 7.35 (t, *J* = 7.3 Hz, 2H, PhPb), 7.49 (t, *J* = 7.3 Hz, 4H, PhPb), 8.11 (d, *J* = 7.3 Hz, 4H, PhPb), 8.20 (d, *J* = 8.2 Hz, 4H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 21.7 (CH<sub>3</sub>), 127.2, 128.4, 129.2, 129.4, 130.0, 130.7, 134.9, 144.4, 239.4 (C=S). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (log ε): 222 (4.44), 273 (4.06), 333 (4.70), 474 (2.70) nm. Anal. Found: C, 48.37; H, 3.52. C<sub>28</sub>H<sub>24</sub>PbS<sub>4</sub> Calc.: C, 48.32; H, 3.48%.

**7e.** Recrystallizing solvents: 3:2 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (82%); m.p. 209–211°C. IR (KBr): 1261 (C=S), 1235 (C=S) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 3.89 (s, 6H, CH<sub>3</sub>O), 6.91 (d, *J* = 9.0 Hz, 2H, Ar), 7.44 (t, *J* = 7.8 Hz, 4H, PhPb), 7.50 (t, *J* = 7.8 Hz, 2H, PhPb), 8.01 (d, *J* = 7.8 Hz, 4H, PhPb), 8.19 (d, *J* = 9.0 Hz, 2H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 55.6 (CH<sub>3</sub>O), 113.6, 129.2, 129.5, 129.6, 129.8, 135.7, 137.6, 164.0, 243.1 (C=S). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (log ε): 222 (4.43), 271 (4.11), 348 (4.71), 470 (2.73) nm. Anal. Found: C, 46.27; H, 3.37. C<sub>28</sub>H<sub>24</sub>O<sub>2</sub>PbS<sub>4</sub> Calc.: C, 46.20; H, 3.32%.

**7f.** Recrystallizing solvents: 4:3 CH<sub>2</sub>Cl<sub>2</sub>–hexane; orange crystals (85%); m.p. 194–197°C. IR (KBr): 1226 (C=S) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.38 (d, *J* = 7.7 Hz, 4H, Ar), 7.42–7.52 (m, 6H, PhPb), 7.91–7.98 (m, 4H, PhPb), 8.01 (d, *J* = 7.7 Hz, 4H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 128.5, 128.8, 128.9, 129.0, 129.3, 130.2, 135.0, 140.1, 247.9 (C=S). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (log ε): 222 (4.47), 272 (4.21), 322 (4.72), 478 (2.76) nm. Anal. Found: C, 42.40; H, 2.51. C<sub>26</sub>H<sub>18</sub>Cl<sub>2</sub>PbS<sub>4</sub> Calc.: C, 42.38; H, 2.46%.

**General procedure for reaction of SnCl<sub>4</sub> with piperidinium or sodium 4-methylbenzenecarbodithioate.** To a solution of piperidinium 4-methylbenzenecarbodithioate (1.016 g, 4.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml), SnCl<sub>4</sub>–CH<sub>2</sub>Cl<sub>2</sub> 1.0 M solution (1.0 ml, 1.0 mmol) was added and the mixture was stirred at 20°C for 1 h. The solvent was removed under reduced pressure (20°C/2.7 kPa). The mixtures were dissolved into a solvent of CH<sub>2</sub>Cl<sub>2</sub> (15 ml). Filtration of the resulting precipitate gave a mixture of dichlorotin bis(4-methylbenzenecarbodithioate) and bis(4-methylthiobenzoyl) disulfide<sup>3</sup> as orange solid. Fractional crystallization of the solid gave chemically pure dichlorotin bis(4-methylbenzenecarbodithioate) in 8% yield: Yellow crystals; m.p. 191–193°C. IR (KBr): 1249 (C=S), 1228 (C=S) cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 2.46 (s, 6 H, CH<sub>3</sub>), 7.25 (d, *J* = 8.3 Hz, 4 H, Ar), 8.14 (d, *J* = 8.3 Hz, 4 H, Ar). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 22.2 (CH<sub>3</sub>), 128.1, 129.4, 135.9, 149.1, 237.0 (C=S). <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ –715.3. Anal. Found: C, 36.40; H, 2.61. C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>S<sub>4</sub>Sn Calc.: C, 36.66; H, 2.69%.

**Preparation of single crystals.** **1d** (0.124 g) was single-crystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.4 ml), Et<sub>2</sub>O (0.1 ml), and hexane (0.5 ml) at 25°C for 6 day. **3d** (0.151 g) was single-crystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.6 ml), Et<sub>2</sub>O (0.1 ml), and hexane (0.5 ml) at 25°C for 5 days. **4d** (0.120 g) was single-crystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.5 ml), Et<sub>2</sub>O (0.3 ml), and hexane (0.5 ml) at 25°C for 10 days. **5c** (0.107 g) was single-crystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.6 ml) and hexane (0.5 ml) at 25°C for 9 days. **6d** (0.131 g) was single-crystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.8 ml), Et<sub>2</sub>O (0.3 ml), and hexane (0.5 ml) at 25°C for 2 weeks.

**X-ray structural analysis.** The measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-K<sub>α</sub> (λ = 0.71069 Å) and Cu-K<sub>α</sub> radiation (λ = 1.54178 Å). All of the structures were solved and refined using the TEXSAN

crystallographic software package on an IRIS Indigo computer. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [DIFABS<sup>19</sup> (**3d**, **4d**, **5c**, and **6d**) and  $\Psi$ -scans<sup>20</sup> (**1d**)] were also applied. The structures were solved by direct method using SHELXS-86<sup>21</sup> for **1d**, **3d**, **4d**, **5c**, and **6d** and expanded using DIRDIF-94<sup>22</sup>. Scattering factors for neutral atoms were from Cromer and Waber<sup>23</sup> and anomalous dispersion<sup>24</sup> was used. Crystal data and measurement description are summarized in Table 2.

### 3.5. References

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## Chapter 4

### Acylthio- and Thioacylthiophosphines [(RCES)<sub>n</sub>PPh<sub>3-n</sub>, E = O, S; n = 1–3]: Synthesis and Structural Analysis

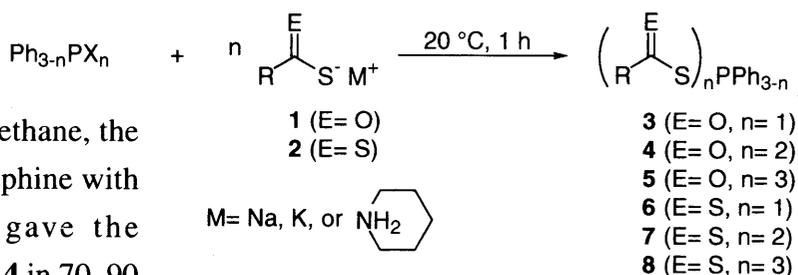
#### 4.1. Introduction

In contrast to the dithiocarbamato-,<sup>1a,1b</sup> dithiophosphinato-,<sup>1b,1c</sup> and dithiocarbonato-phosphorus derivatives,<sup>1b</sup> little is known about the chemistry of the thio- and dithiocarboxylic acid derivatives, most likely due to the difficulty of purification. Surprisingly, no structural analyses of thio- and dithiocarboxylatophosphorus compounds except for (PhCOS)<sub>3</sub>P,<sup>1b</sup> have been reported so far. Previously, Author's laboratory reported the preparation of diphenyl(thioacylthio)-phosphines RCS<sub>2</sub>PPh<sub>2</sub> and diphenyl(thioacylthio)phosphine sulfides RCS<sub>2</sub>P(S)Ph<sub>2</sub> by reacting piperidinium dithiocarboxylates with Ph<sub>2</sub>PCl and Ph<sub>2</sub>P(S)Cl, respectively.<sup>2</sup> As a part of the Author's study concerning main group element derivatives of new chalcogenocarboxylic acids, the Author has focused on the systematic synthesis of group 15 element derivatives of chalcogenocarboxylates. In this paper, the Author report the full details of the synthesis and structure of the acylthio- and thioacylthiophosphines [(RCES)<sub>n</sub>PPh<sub>3-n</sub>, E = O, S; n = 1–3] 3–8.

#### 4.2. Results and Discussion

**Synthesis:** The thiocarboxylatophosphorus derivatives were synthesized first (Eq. 1). Sodium and potassium thiocarboxylates **1** readily reacted with chlorodiphenylphosphine in ether to give the corresponding acylthiodiphenyl-phosphines RCOSPPH<sub>2</sub> **3a–g** in good yields (Table 1). In dichloromethane, the reaction of dichlorophenylphosphine with two molar amounts of **1** gave the bis(acylthio)-phenylphosphines **4** in 70–90 % yields. Similarly, the stoichiometric reaction of tribromophosphine with **1** in dichloromethane gave tris(acylthio)-phosphines **5** in 70–90% yields.

Next, dithiocarboxylatophosphorus derivatives were synthesized. Under the conditions used for the synthesis of the thiocarboxylic acid derivatives **3–5**, the reactions of piperidinium or sodium dithio-



3–5	R	6–8	R
<b>a</b>	CH <sub>3</sub>	<b>a</b>	C <sub>6</sub> H <sub>5</sub>
<b>b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<b>b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>c</b>	C <sub>6</sub> H <sub>5</sub>	<b>c</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>
<b>d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>
<b>e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>e</b>	4-ClC <sub>6</sub> H <sub>4</sub>
<b>f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>
<b>g</b>	4-ClC <sub>6</sub> H <sub>4</sub>		

(1)

carboxylates with the corresponding halophosphines were examined. As expected, diphenyl(thioacylthio)-phosphines **6**, phenylbis(thioacylthio)phosphines **7**, and tris(thioacylthio)-phosphines **8** were isolated in yields of 20–90%, 10–70%, and 30–70%, respectively (Table 2). Such low yields are due to the difficulty of purification (loss during purification).

Thiocarboxylic acid derivatives **3–5** are fairly stable thermally and toward oxygen and moisture, and show no appreciable change for 1 week upon exposure to air. In contrast, the dithiocarboxylic acid derivatives **6–8** are unstable thermally and are moisture-sensitive. For example, upon exposure to air, the 4-methyl-substituted derivatives were gradually hydrolyzed to the dithiocarboxylic acid. In particular, bis (**4** and **7**) and tris derivatives (**5** and **8**) are readily hydrolyzed even in ether.

Table 1. Yields and Melting Points of Mono-, Bis-, and Tris(acylthio)phosphines **3–5**

No.	(RCOS) <sub>n</sub> PPh <sub>3-n</sub>		Yield %	Mp °C
	R	n		
<b>3a</b>	CH <sub>3</sub>	1	74	Oil
<b>3b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	1	75	Oil
<b>3c</b>	C <sub>6</sub> H <sub>5</sub>	1	95	Oil
<b>3d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	93	96–97
<b>3e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	80	111–114
<b>3f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	93	Oil
<b>3g</b>	4-ClC <sub>6</sub> H <sub>4</sub>	1	90	91–92
<b>4a</b>	CH <sub>3</sub>	2	74	Oil
<b>4b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	2	75	Oil
<b>4c</b>	C <sub>6</sub> H <sub>5</sub>	2	99	103–105
<b>4d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	88	133–134
<b>4e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	97	108–110
<b>4f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	99	104–106
<b>4g</b>	4-ClC <sub>6</sub> H <sub>4</sub>	2	87	146–147
<b>5a</b>	CH <sub>3</sub>	3	82	Oil
<b>5b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	3	82	Oil
<b>5c</b>	C <sub>6</sub> H <sub>5</sub>	3	91	98–101
<b>5d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	77	95–98
<b>5e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3	90	100–103
<b>5f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3	66	97–100
<b>5g</b>	4-ClC <sub>6</sub> H <sub>4</sub>	3	75	154–156

Table 2. Yields and Melting Points of Mono-, Bis-, and Tris(thioacylthio)phosphines **6–8**

No.	(RCS <sub>2</sub> ) <sub>n</sub> PPh <sub>3-n</sub>		Yield %	Mp °C
	R	n		
<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	1	35	74–76
<b>6b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	94	98–99
<b>6c</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	93	Oil
<b>6d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	61	95–97
<b>6e</b>	4-ClC <sub>6</sub> H <sub>4</sub>	1	25	75–77
<b>6f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	1	54	112–117
<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	2	71	Oil
<b>7b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	36	127–131
<b>7c</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	19	56–60
<b>7d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	11	109–114
<b>7f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	2	44	126–129
<b>8b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	38	150–153
<b>8e</b>	4-ClC <sub>6</sub> H <sub>4</sub>	3	53	87–90
<b>8f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	3	71	169–173

**Molecular Structures:** The ORTEP drawing of (4-methylbenzoylthio)diphenylphosphine **3d** is shown in Fig. 1. The crystal data are collected in Table 3. Selected bond distances and angles are shown in Table 4. The compound **3d** crystallizes in a monoclinic system with space

Table 3. Crystal Data, Data Collection, and Refinement Parameters for **3d**, **4d**, **5d**, and **7b**

	<b>3d</b>	<b>4d</b>	<b>5d</b>	<b>7b</b>
Empirical formula	C <sub>20</sub> H <sub>17</sub> OPS	C <sub>22</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub>	C <sub>24</sub> H <sub>21</sub> O <sub>3</sub> PS <sub>3</sub>	C <sub>22</sub> H <sub>19</sub> PS <sub>4</sub>
Formula weight	336.39	410.48	484.58	442.61
Color	Colorless	Colorless	Colorless	Red
Crystal system	Monoclinic	Monoclinic	Trigonal	Orthorhombic
<i>a</i> /Å	34.855(2)	5.906(2)	13.479(3)	16.296(2)
<i>b</i> /Å	8.318(1)	16.073(2)	27.597(3)	21.708(2)
<i>c</i> /Å	5.941(1)	21.489(2)		6.029(1)
$\beta$ /deg.	89.59(1)	96.07(2)		
Volume of unit cell/Å <sup>3</sup>	1722.4(4)	2028.4(6)	4341(1)	2132.6(5)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>R</i> 3 <i>c</i> (#161)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)
<i>Z</i> value	4	4	8	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.297	1.344	1.482	1.344
Crystal size/mm	0.23 x 0.23 x 0.43	0.23 x 0.17 x 0.23	0.06 x 0.23 x 0.31	0.09 x 0.14 x 0.29
$\mu$ (MoK $\alpha$ )/cm <sup>-1</sup>	2.82	3.56	4.41	5.26
Transmission factor				
for absorption correction		0.6834–1.0000		0.6548–1.0000
Temp/°C	23.0	23.0	23.0	23.0
2 $\theta$ <sub>max</sub> /deg.	55.0	55.0	55.0	55.0
No. of measured reflections	4018	5101	2390	3221
No. of unique reflections	3955	4659	1119	2819
<i>R</i> <sub>int</sub>	0.033	0.063	0.132	0.043
No. of observations	2116/ <i>I</i> >2.3 $\sigma$ ( <i>I</i> )	2310/ <i>I</i> >1.5 $\sigma$ ( <i>I</i> )	393/ <i>I</i> >2.0 $\sigma$ ( <i>I</i> )	1865/ <i>I</i> >2.0 $\sigma$ ( <i>I</i> )
No. of variables	209	245	94	246
Reflection / parameter ratio	10.12	9.43	4.18	7.58
Residuals: <i>R</i> , <sup>a)</sup> <i>R</i> <sub>w</sub> <sup>b)</sup>	0.049, 0.050	0.055, 0.056	0.087, 0.287 <sup>c)</sup>	0.043, 0.046
<i>p</i> value <sup>b)</sup>	0.0230	0.0350		0.0350
max. and min. of residual				
Electron density/e Å <sup>-3</sup>	0.41, -0.25	0.28, -0.31	0.92, -0.62	0.24, -0.24
Goodness of fit indicator	1.67	1.35	1.26	1.21

a)  $R = \sum(|F_o| - |F_c|) / \sum |F_o|$ . b)  $R_w = [\sum(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ ,  $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$ .

c)  $R = \sum(|F_o| - |F_c|) / \sum |F_o|$ .  $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]^{-1}$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

group *P*2<sub>1</sub>/*c* (#14). The dihedral angles suggest that the thiocarboxylato ligand is in approximately same plane as the benzene ring containing C21 atom and is roughly perpendicular to that containing C31 atom. The C–O and C–S bond lengths of **3d** are 1.207(4) and 1.802(4) Å, which reflect C=O double and C–S single bonds, respectively. The P–S bond length [2.136(1) Å] is close to the sum of the single covalent bond radii of both atoms (2.14 Å),<sup>3</sup> and is comparable to the distance observed for Et<sub>2</sub>NCS<sub>2</sub>PPh<sub>2</sub> (2.123 Å).<sup>1b</sup> The distance between the carbonyl oxygen and the phosphorus atom [2.917(3) Å] is considerably longer than the sum of the covalent bond radii of both atoms (1.74 Å),<sup>3</sup> but less than the sum of the van der Waals radii of both atoms (3.28 Å),<sup>4</sup> indicating a weak interaction. The bond angles around the phosphorus atom [S11–P1–C21 = 98.4(1)°, S11–P1–C31 = 102.3(1)°, C21–P1–C31 = 100.7(2)°] are close to right angles, and the phosphorus atom can be considered to exhibit a *p*-type bond, thus forming a distorted tetrahedral structure with the unshared electron pair orbital at the apex.

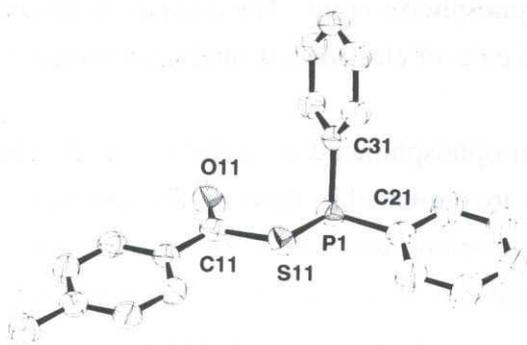


Figure 1. An ORTEP drawing of 4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COSPPH<sub>2</sub> **3d**.

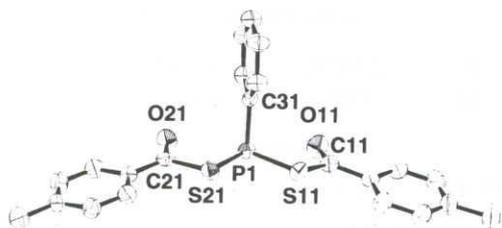


Figure 2. An ORTEP drawing of (4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COS)<sub>2</sub>PPh **4d**.

In bis(4-methylbenzoylthio)phenylphosphine **4d**, the two thiocarboxylato ligands exist in the same plane with the same orientation, where each oxygen atom is located in the same direction (Fig. 2). The phenyl ring is nearly perpendicular to the plane. The C–O and C–S bond lengths of the two thiocarboxylato ligands are av 1.213(5) Å and av 1.787(4) Å, respectively, indicating C=O double and C–S single bonds (Table 5). The two P–S bond lengths [P1–S11 = 2.146(2) Å, P1–S21 = 2.144(2) Å] are close to the sum of the single covalent bond radii of both atoms (2.14 Å),<sup>3</sup> indicating a single bond. The

distances between the two carbonyl oxygen and the phosphorus atoms [P1–O11 = 2.784(3) Å, P1–O21 = 2.747(3) Å] are different, and shorter than that in the monothiocarboxylate **3d** [2.917(3) Å], indicating a strong intramolecular interaction (nonbonding interaction). The bond angles around the phosphorus atom [S11–P1–S21 = 91.42(6)°, S11–P1–C31 = 101.4(1)°, S21–P1–C31 = 102.3(2)°] are nearly right angles, where the two sulfur and the *ipso*-carbon atoms of the

Table 4. Selected Bond Lengths (Å), Angles (deg.), Torsion Angles (deg.), and Dihedral Angles (deg.) of (4-Methylbenzoylthio)diphenylphosphine **3d**

Bond lengths			
P1–S11	2.136(1)	P1–C21	1.838(4)
P1–O11	2.917(3)	P1–C31	1.828(4)
C11–S11	1.802(4)		
C11–O11	1.207(4)		
Angles			
S11–P1–O11	60.48(6)	S11–P1–C21	98.4(1)
S11–C11–O11	120.8(3)	S11–P1–C31	102.3(1)
P1–S11–C11	97.1(1)	C21–P1–C31	100.7(2)
P1–O11–C11	80.1(2)		
Torsion angles			
S11–C11–C12–C17	6.0(5)	C11–S11–P1–C21	171.8(2)
		C11–S11–P1–C31	85.2(2)
Dihedral angles			
Plane (S11–C11–O11) – Plane (C21 benzene ring)			164.21
Plane (S11–C11–O11) – Plane (C31 benzene ring)			108.59
Plane (C31 benzene ring) – Plane (C31 benzene ring)			75.39

Table 5. Selected Bond Lengths (Å), Angles (deg.), and Torsion Angles (deg.) of Bis(4-methylbenzoylthio)phenylphosphine **4d**

Bond lengths			
P1–S11	2.146(2)	P1–S21	2.144(2)
P1–O11	2.784(3)	P1–O21	2.747(3)
C11–S11	1.785(5)	C21–S21	1.788(4)
C11–O11	1.211(5)	C21–O21	1.214(5)
P1–C31	1.825(4)		
Angles			
S11–P1–S21	91.42(6)	O11–P1–O21	142.1(1)
S11–P1–O11	62.65(8)	S21–P1–O21	63.25(8)
S11–C11–O11	120.8(4)	S21–C21–O21	120.0(4)
P1–S11–C11	93.7(2)	P1–S21–C21	92.9(2)
P1–O11–C11	82.1(3)	P1–O21–C21	82.8(3)
S11–P1–C31	101.4(1)	S21–P1–C31	102.3(2)
Torsion angles			
S11–P1–S21–C21	172.8(1)		
S11–C11–C12–C17	8.8(6)	S21–C21–C22–C27	4.4(6)
C11–S11–P1–C31	87.3(2)	C21–S21–P1–C31	85.2(2)

phenyl ring are bound to the 3p orbitals of the central phosphorus atom. The compound **4d** also exists in a distorted tetrahedral structure with unshared pairs of electrons, in analogy with that of **3d**.

The ORTEP drawing of tris(4-methylbenzoylthio)phosphine **5d** is shown in Fig. 3. The principal bond distances and angles and torsion angles are presented in Table 6. The structure of **5d** is essentially comparable to that of tris(benzoylthio)phosphine reported by Russian chemists,<sup>1b</sup> in that the three thiocarboxylato ligands display  $C_3$  symmetry [Fig. 3a]. The C–O, C–S, and P–S bond lengths are 1.22(2), 1.79(2), and 2.142(5) Å, respectively, which indicate C=O double and C–S and P–S single bonds. The distance between the carbonyl oxygen and the phosphorus atom [2.82(1) Å] is between those of mono- **3d** [2.917(3) Å] and bis derivatives **4d** [av 2.766(3) Å], indicating a weak interaction. The three covalent phosphorus–sulfur bonds are nearly at right angles [95.4(2)°] to one another, again indicative of a distorted tetrahedron similar to those of **3d** and **4d** [Fig. 3b].

Table 6. Selected Bond Lengths (Å), Angles (deg.), and Torsion Angles (deg.) of Tris(4-methylbenzoylthio)phosphine **5d**

Bond lengths			
P1–S1	2.142(5)	C1–S1	1.79(2)
P1–O1	2.82(1)	C1–O1	1.22(2)
Angles			
S1–P1–O1	61.6(3)	P1–S1–C1	96.0(5)
S1–C1–O1	119.3(10)	P1–O1–C1	82.8(8)
S1–P1–S1*	95.4(2)		
Torsion angles			
S1–C1–C2–C7	2(2)	S1–P1–S1*–C1*	89.2(7)

\*) -Y, X-Y, Z.

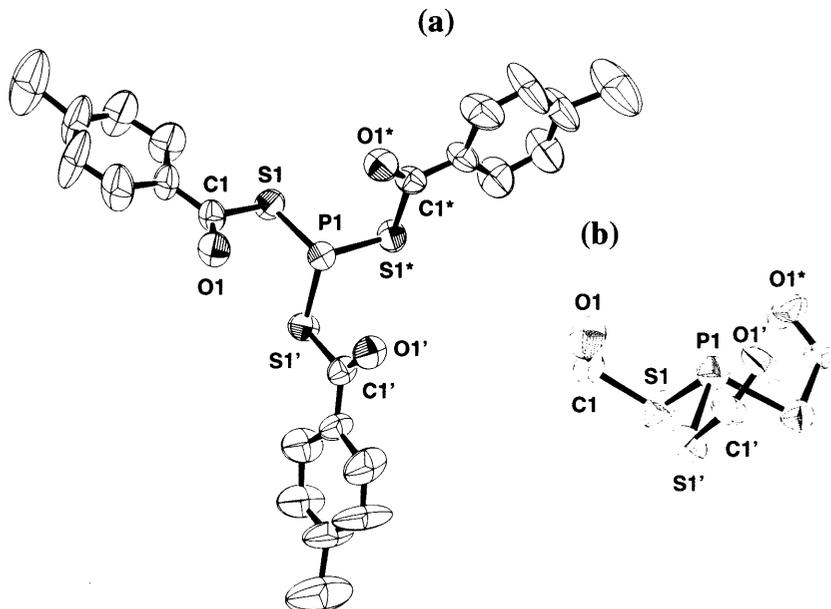


Figure. 3. An ORTEP drawing of (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COS)<sub>3</sub>P **5d**.  
(\*') -Y, X-Y, Z. (') -X+Y, -X, Z.

On the other hand, the crystallization of dithiocarboxylatophosphorus derivatives is very difficult. After several attempts, single crystals of bis(4-methylthiobenzoylthio)phenylphosphine **7b** were obtained. The ORTEP drawing and selected bond lengths and angles are shown in Fig. 4 and Table 7, respectively. As in **4d**, the two dithiocarboxylato ligands exist in the same plane,

where each thiocarbonyl sulfur atom is located in the same direction. The C–S bond lengths of the dithiocarboxylato ligands are different, and can be divided into shorter C–S bond lengths [av 1.632(6) Å] and longer C–S bond lengths [av 1.751(6) Å]. The former is close to the general C=S double bond value (1.61 Å),<sup>3</sup> while the latter is roughly intermediate between C=S double and C–S single bonds.<sup>3</sup> A similar difference in the C–S bonds is found in (Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>PPh (av 1.678 Å and av 1.777 Å).<sup>1b</sup> The P–S bond lengths [P1–S12 = 2.170(3) Å, P1–S22 = 2.158(2) Å] are close to the sum of the single covalent bond radii of both atoms (2.14 Å),<sup>3</sup> indicating a single bond. The distances between the two thiocarbonyl sulfur and the phosphorus atoms [P1–S11 = 2.965(3) Å, P1–S21 = 2.975(3) Å] are longer than the sum of their covalent bond radii,<sup>3</sup> but shorter than the sum of their van der Waals radii (3.66 Å),<sup>4</sup> indicating a weak interaction. The S–P1–

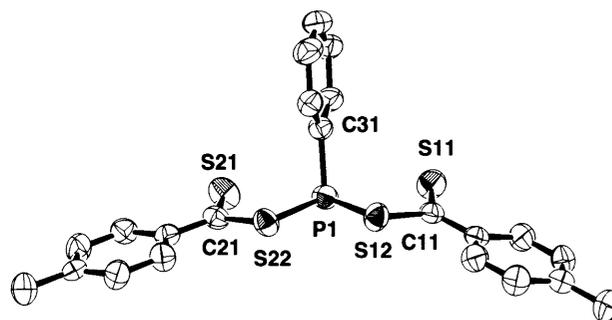


Figure 4. An ORTEP drawing of (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CS<sub>2</sub>)<sub>2</sub>PPh **7b**.

Table 7. Selected Bond Lengths (Å), Angles (deg.), and Torsion Angles (deg.) of Bis(4-methylthiobenzoylthio)phenylphosphine **7b**

Bond lengths			
P1–S11	2.965(3)	P1–S21	2.975(3)
P1–S12	2.170(3)	P1–S22	2.158(2)
C11–S11	1.630(6)	C21–S21	1.634(6)
C11–S12	1.761(6)	C21–S22	1.740(6)
P1–C31	1.836(7)		
Angles			
S11–P1–S21	138.11(8)	S12–P1–S22	86.20(9)
S11–P1–S12	67.73(7)	S21–P1–S22	67.45(7)
S11–C11–S12	120.0(4)	S21–C21–S22	120.5(3)
P1–S11–C11	73.6(2)	P1–S21–C21	73.5(2)
P1–S12–C11	96.8(2)	P1–S22–C21	98.3(2)
S12–P1–C31	101.6(2)	S22–P1–C31	101.0(2)
Torsion angles			
S12–P1–S22–C21	173.7(2)		
S12–C11–C12–C17	2.5(8)	S22–C21–C22–C27	3.5(8)
C11–S12–P1–C31	100.6(3)	C21–S22–P1–C31	85.2(3)

C31 angles [av 101.3(2)°] are similar to those in thiocarboxylate derivative **4d**, while the S12–P1–S22 angle [86.20(9)°] is slightly smaller than that of the corresponding thiocarboxylate derivative **4d** [91.42(6)°]. The two phosphorus–sulfur and one phosphorus–benzene *ipso*-carbon bonds are nearly at right angles to one another, and the structure of **7b** is similar to those of **3d**, **4d**, and **5d**.

**Structural Comparison of Mono-, Bis-, and Tris(arene-carbonylthio)phosphine:** Selected bond lengths and torsion angles of **3d**, **4d**, and **5d** are shown in Tables 8 and 9, respectively. The C–O, C–S, and P–S bond lengths are nearly the same. On the other hand, the distance between the carbonyl oxygen and the phosphorus atoms decrease in the order mono **3d**, tris **5d**, and bis **4d**. Presumably, the greater distance in **3d** may be due to weak interaction, i.e. the interaction of the P–C σ\* orbital with the lone-pair electron on the carbonyl oxygen is longer

than that of the P-S  $\sigma^*$  orbital. The interaction between the carbonyl oxygen and the phosphorus atoms would take an important role in the planarity of the thiocarboxylate moieties with the phosphorus atoms.

**Spectra:** The spectroscopic data of  $(\text{RCOS})_n\text{PPh}_{3-n}$  (**3**:  $n = 1$ , **4**:  $n = 2$ , **5**:  $n = 3$ ) are shown in Table 10. The  $\nu_{\text{C=O}}$  bands of **3–5** appear at about  $1690\text{ cm}^{-1}$  for aliphatic derivatives ( $\text{R} = \text{CH}_3, t\text{-C}_4\text{H}_9$ ) and at  $1630\text{--}1670\text{ cm}^{-1}$  for aromatic derivatives, which is comparable to the corresponding *S*-alkyl esters. The  $^{13}\text{C=O}$  chemical shifts of **3–5** appear at  $\delta = 188.6 \pm 1.3$  for aromatic derivatives and  $\delta = 198.3 \pm 5.8$  for aliphatic derivatives, and the coupling constants [ $^2J(\text{CP})$ ] are about 14 Hz. The  $^{31}\text{P}$  NMR spectra are observed at  $\delta = 10\text{--}14$  for **3**,  $\delta = 25\text{--}35$  for **4**, and about  $\delta = 50$  for **5**, which indicates a downfield shift with an increase in the number of thiocarboxylate ligands bonded to the phosphorus atom.

The spectroscopic data of  $(\text{RCS}_2)_n\text{PPh}_{3-n}$  (**6**:  $n = 1$ , **7**:  $n = 2$ , **8**:  $n = 3$ ) are tabulated in Table 11. The thiocarbonyl stretching frequencies of **6** appear at  $1200\text{--}1250\text{ cm}^{-1}$ , and that for 2,4,6-trimethylphenyl derivative **6f** is about  $30\text{ cm}^{-1}$  lower than those of other aromatic derivatives **6a–e**. Those of bis **7** and tris derivatives **8** appear

Table 8. Selected Bond Distances of Mono-, Bis-, and Tris(acylthio)phosphines **3–5**

No.	R	$n$	Bond/Å			
			C–O	C–S	P...O	P–S
<b>3d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	1.207(4)	1.802(4)	2.917(3)	2.136(1)
<b>4d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	1.211(5) 1.214(5)	1.785(5) 1.788(4)	2.784(3) 2.747(3)	2.146(2) 2.144(2)
<b>5d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	1.22(2)	1.79(2)	2.82(1)	2.142(5)

Table 9. Selected Torsion Angles of Mono-, Bis-, and Tris(acylthio)phosphines **3–5**

No.	R	$n$	Torsion angles/deg.	
			O11–C11–S11–P1	O21–C21–S21–P1
<b>3d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	14.6(3)	
<b>4d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	9.2(4) 11.2(4)	
<b>5d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	6(1)	

Table 10. Spectroscopic Data of Mono-, Bis-, and Tris(acylthio)phosphines **3–5**

No.	$(\text{RCOS})_n\text{PPh}_{3-n}$	R	$n$	IR/cm <sup>-1</sup>	NMR/ $\delta$ <sup>c)</sup>		
					$\nu_{\text{C=O}}$	$^{13}\text{C=O}$	$^{31}\text{P}$ <sup>d)</sup>
<b>3a</b>	CH <sub>3</sub>		1	1694 <sup>a)</sup>	193.9	14.2	15
<b>3b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>		1	1682 <sup>a)</sup>	198.7	10.3	15
<b>3c</b>	C <sub>6</sub> H <sub>5</sub>		1	1652 <sup>a)</sup>	189.8	13.0	13
<b>3d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		1	1652 <sup>b)</sup>	189.8	12.3	12
<b>3e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		1	1630 <sup>b)</sup>	189.2	11.1	12
<b>3f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		1	1652 <sup>a)</sup>	188.3	12.3	13
<b>3g</b>	4-ClC <sub>6</sub> H <sub>4</sub>		1	1657 <sup>b)</sup>	189.3	14.0	12
<b>4a</b>	CH <sub>3</sub>		2	1703 <sup>a)</sup>	193.1	34.8	14
<b>4b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>		2	1694 <sup>a)</sup>	204.1	28.0	12
<b>4c</b>	C <sub>6</sub> H <sub>5</sub>		2	1655 <sup>b)</sup>	189.8	24.5	14
<b>4d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		2	1643 <sup>b)</sup>	189.3	29.3	14
<b>4e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		2	1629 <sup>b)</sup>	188.8	24.6	13
<b>4f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		2	1654 <sup>b)</sup>	188.1	29.2	14
<b>4g</b>	4-ClC <sub>6</sub> H <sub>4</sub>		2	1658 <sup>b)</sup>	188.6	32.0	14
<b>5a</b>	CH <sub>3</sub>		3	1694 <sup>a)</sup>	192.5	55.1	17
<b>5b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>		3	1680 <sup>a)</sup>	203.6	52.3	14
<b>5c</b>	C <sub>6</sub> H <sub>5</sub>		3	1648 <sup>b)</sup>	189.2	51.6	16
<b>5d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>		3	1647 <sup>b)</sup>	188.8	51.4	16
<b>5e</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		3	1620 <sup>b)</sup>	188.6	44.7	14
<b>5f</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>		3	1659 <sup>b)</sup>	187.3	51.8	16
<b>5g</b>	4-ClC <sub>6</sub> H <sub>4</sub>		3	1677 <sup>b)</sup>	188.0	52.2	17

a) Neat. b) KBr. c) NMR spectra recorded in CDCl<sub>3</sub>. d) Standard in H<sub>3</sub>PO<sub>4</sub>.

at 1230–1260 cm<sup>-1</sup>. The <sup>13</sup>C=S chemical shifts appear in the narrow region  $d = 223$ – $227$ , excluding the 2,4,6-trimethylphenyl derivatives **6f**, **7f**, and **8f** (about  $d = 237$ ). Steric hindrance of the mesityl group would reduce p conjugation between the aromatic ring and C=S moiety, resulting in downfield shift of <sup>13</sup>C=S chemical shifts. On the other hand, the <sup>31</sup>P NMR spectra are observed at about  $\delta = 20$  for **6**,  $\delta = 9$ – $15$  for **7**, and about  $\delta = -4$  for **8**, which indicate upfield shifts

with an increase in the number of dithiocarboxylato ligands bonded to the phosphorus atom. The spectroscopic data of the (4-methylbenzoylthio)phosphines **3d**, **4d**, and **5d** are shown in Table 12. The  $\nu_{C=O}$  bands show high wavenumber shifts in the order **4d**, **5d**, and **3d**. In X-ray structural analyses, the C=O double

bond lengths are nearly the same, while the distances between the carbonyl oxygen and the phosphorus atoms follow this same order. Therefore, a high wavenumber shift of the  $\nu_{C=O}$  may be related to interaction between the carbonyl oxygen and the phosphorus atoms. The <sup>13</sup>C=O chemical shifts show upfield shifts in the order **3d**, **4d**, and **5d**. On the other hand, the <sup>31</sup>P NMR chemical shifts show downfield shifts in the order **3d**, **4d**, and **5d**, which may be due to the electron-withdrawing effect of the thiocarboxylato ligands. In the dithiocarboxylate derivatives, the  $\nu_{C=S}$  bands show high wavenumber shifts in the order **6b**, **7b**, and **8b**. However, the <sup>13</sup>C=S chemical shifts show downfield shifts and the <sup>31</sup>P NMR chemical shifts show upfield shifts in the order **6b**, **7b**, and **8b**, which are opposite to the trends seen with the corresponding thiocarboxylic acid derivatives. Presumably, the electron on the dithiocarboxylate groups may

Table 11. Spectroscopic Data of Mono-, Bis-, and Tris(thioacylthio)phosphines **6–8**

No.	(RCS <sub>2</sub> ) <sub>n</sub> PPh <sub>3-n</sub>		IR/cm <sup>-1</sup> a)		NMR/ $\delta$ c)		
	R	n	$\nu_{C=S}$	<sup>13</sup> C=S	<sup>31</sup> P d)	<sup>2</sup> J <sub>13C-31P</sub> / Hz	
<b>6a</b>	C <sub>6</sub> H <sub>5</sub>	1	1222	225.7	21.3	21	
<b>6b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1	1231	225.5	20.2	20	
<b>6c</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	1252 <sup>b)</sup>	222.7	22.1	17	
<b>6d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	1241	223.5	19.4	19	
<b>6e</b>	4-ClC <sub>6</sub> H <sub>4</sub>	1	1242	224.2	22.8	21	
<b>6f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	1	1195	236.3	22.0	19	
<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	2	1239 <sup>b)</sup>	226.9	12.5	23	
<b>7b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2	1244	226.3	11.0	22	
<b>7c</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	1250	227.9	14.9	24	
<b>7d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	2	1249	224.2	8.73	24	
<b>7f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	2	1261	236.5	12.7	22	
<b>8b</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	1251	227.6	-3.99	25	
<b>8e</b>	4-ClC <sub>6</sub> H <sub>4</sub>	3	1231	227.0	-3.46	26	
<b>8f</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	3	1243	238.9	-3.96	25	

a) KBr. b) Neat. c) NMR spectra recorded in CDCl<sub>3</sub>. d) Standard in H<sub>3</sub>PO<sub>4</sub>.

Table 12. Selected Feature in Spectra of 4-Methylbenzoylthio- and 4-Methyl(thiobenzoylthio)phosphine Derivatives

No.	(RCES) <sub>n</sub> PPh <sub>3-n</sub>			IR/cm <sup>-1</sup> a)		NMR/ $\delta$ b)		
	R	E	n	$\nu_{C=E}$	<sup>13</sup> C=E	<sup>31</sup> P c)	<sup>2</sup> J <sub>13C-31P</sub> / Hz	
<b>3d</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	O	1	1652	189.8	12.3	12	
<b>4d</b>		O	2	1643	189.3	29.3	14	
<b>5d</b>		O	3	1647	188.8	51.4	16	
<b>6b</b>		S	1	1231	225.5	20.2	20	
<b>7b</b>		S	2	1244	226.3	11.0	22	
<b>8b</b>		S	3	1251	227.6	-3.99	25	

a) KBr. b) NMR spectra recorded in CDCl<sub>3</sub>. c) Standard in H<sub>3</sub>PO<sub>4</sub>.

be backdonated through the thiocarbonyl sulfur atoms.

### 4.3. Conclusion

A series of thio- and dithiocarboxylatophosphorus derivatives were synthesized and their X-ray structural analyses were obtained. The crystal structures of these compounds show intramolecular-nonbonding interactions between the carbonyl oxygen or thiocarbonyl sulfur and the central phosphorus atoms. However, these intramolecular interactions are weak, and the covalent phosphorus–sulfur and/or phosphorus–benzene *ipso*-carbon bonds are nearly at right angles to one another, forming essentially distorted tetrahedral structures with the unshared electron pair orbital at the apex. In the bis-derivatives [(RCES)<sub>2</sub>PPh, E = O, S], the two thio- and dithiocarboxylato ligands exist in the same plane with the same orientation, where each carbonyl oxygen or thiocarbonyl sulfur atom is located in the same direction.

### 4.4. Experimental

Melting points were determined by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a Perkin-Elmer FT-IR 1640 spectrophotometer. The <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-α400 (400 MHz); the following abbreviations were used; s: singlet, d: doublet, t: triplet, m: multiplet. The <sup>13</sup>C NMR were recorded on a JEOL JNM-α400 (100 MHz). The <sup>31</sup>P NMR were recorded on a JEOL JNM-α400 (162 MHz) with phosphoric acid as an external standard. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

**Materials.** The following solvents were purified under argon and dried as indicated: Diethyl ether and hexane were refluxed with sodium metal using benzophenone as an indicator and distilled before use: Dichloromethane was distilled over diphosphorus pentoxide, after refluxing for 4 h. Chlorodiphenylphosphine, dichlorophenylphosphine, and tribromophosphine / dichloromethane (1.0 M solution, 1 M = 1 mol dm<sup>-3</sup>) were obtained from Aldrich.

**X-Ray Structure Analysis.** Measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated MoKα radiation ( $\lambda = 0.71069 \text{ \AA}$ ). All the structures were solved and refined using the teXsan<sup>®</sup> crystallographic software package on an IRIS Indigo computer. Crystal samples were cut from grown crystals and mounted on a glass fiber. Since (4-methylbenzoylthio)diphenylphosphine (**3d**), bis(4-methylbenzoylthio)phenylphosphine (**4d**), tris(4-methylbenzoylthio)phosphine (**5d**), and bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) were unstable in air, the crystals of **3d**, **4d**, **5d**, and **7b** were coated with an epoxy resin. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and showed no significant intensity variations during data collection. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [DIFABS<sup>5</sup> (**4d** and **7b**) and  $\Psi$ -scans<sup>6</sup> (**3d** and **5d**)] were also applied. The structures were solved by a direct method using SHELXS86<sup>7</sup> for **3d**, **4d**, **7b**, and **5d** and expanded using DIRDIF94.<sup>8</sup> Scattering factors for neutral atoms were obtained from Cromer and Waber<sup>9</sup> and anomalous dispersion<sup>10</sup> was used. The function minimized was  $\sum w(IF_{\text{obs}} - IF_{\text{calc}})^2$ , and the weighting scheme used was  $w = [\sigma^2(F_o) + p^2(F_o)^2/4]^{-1}$  for **3d**, **4d**, and **7b**,

while  $[\sum w(IF_{\text{obs}}I - IF_{\text{calc}}I)^2 / (N_o - N_v)]^{1/2}$  and  $[\sigma^2(F_o) + (0.1000P)^2 + 0.0000P]^{-1}$ ,  $P = (F_o^2 + 2F_c^2) / 3$  were used for **5d**. A full-matrix least-squares refinement was executed, with non-hydrogen atoms being anisotropic for **3d**, **4d**, and **7b**, and using SHELXL93 for **5d**.<sup>11</sup> The final least-square cycle included fixed hydrogen atoms at calculated positions, for which each isotropic thermal parameter was set to 1.2 times that of the connecting atom. Crystal data and a description of the measurement are summarized in Table 3.

**Preparation of Single Crystals.** (4-Methylbenzoylthio)diphenylphosphine (**3d**) (0.090 g) was single-crystallized from dichloromethane (1.0 mL) and hexane (1.0 mL) at 25 °C for 5 d. Bis(4-methylbenzoylthio)phenylphosphine (**4d**) (0.150 g) was single-crystallized from dichloromethane (1.2 mL) and hexane (1.0 mL) at 25 °C for 1 week. Tris(4-methylbenzoylthio)phosphine (**5d**) (0.109 g) was single-crystallized from dichloromethane (3.0 mL) and hexane (4.0 mL) at 25 °C for 1 week. Bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) (0.065 g) was single-crystallized from dichloromethane (0.5 mL) and hexane (0.6 mL) at 25 °C for 4 d.

**Acetylthiodiphenylphosphine (3a).** To a solution of chlorodiphenylphosphine (0.225 g, 1.02 mmol) in ether (10 mL), sodium thioacetate (0.114 g, 1.16 mmol) was added. The mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa) to give acetylthiodiphenylphosphine (**3a**) as colorless oil (0.199 g, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 2.42 (s, 3H, CH<sub>3</sub>), 7.30–7.32 (m, 6H), 7.47–7.50 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 32.1 (CH<sub>3</sub>), 128.4 (<sup>3</sup>J<sub>13C-31P</sub> = 6.8 Hz), 129.4, 132.8 (<sup>2</sup>J<sub>13C-31P</sub> = 21 Hz), 135.5 (<sup>1</sup>J<sub>13C-31P</sub> = 24 Hz), 193.9 (<sup>2</sup>J<sub>13C-31P</sub> = 14 Hz, C=O).

**(2,2-Dimethylpropionylthio)diphenylphosphine (3b).** As with **3a**, the reaction of chlorodiphenylphosphine (0.220 g, 1.00 mmol) with sodium 2,2-dimethylthiopropionate (0.150 g, 1.07 mmol) gave (2,2-dimethylpropionylthio)diphenylphosphine (**3b**) as colorless oil (0.226 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 1.16 (s, 9H, CH<sub>3</sub>), 7.19–7.21 (m, 6H), 7.37–7.41 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 26.4 (CH<sub>3</sub>), 47.4 [C(CH<sub>3</sub>)<sub>2</sub>], 128.3 (<sup>3</sup>J<sub>13C-31P</sub> = 6.8 Hz), 129.3, 132.7 (<sup>2</sup>J<sub>13C-31P</sub> = 21 Hz), 135.8 (<sup>1</sup>J<sub>13C-31P</sub> = 24 Hz), 198.7 (<sup>2</sup>J<sub>13C-31P</sub> = 15 Hz, C=O).

**Benzoylthiodiphenylphosphine (3c).** As with **3d**, the reaction of chlorodiphenylphosphine (0.226 g, 1.02 mmol) with potassium thiobenzoate (0.185 g, 1.06 mmol) gave benzoylthiodiphenylphosphine (**3c**) as yellow oil (0.312 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.28–7.39 (m, 9H), 7.55–7.59 (m, 4H), 7.97–7.99 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 127.9, 128.1, 128.4 (<sup>3</sup>J<sub>13C-31P</sub> = 5.9 Hz), 129.4, 132.8 (<sup>2</sup>J<sub>13C-31P</sub> = 22 Hz), 135.4 (<sup>1</sup>J<sub>13C-31P</sub> = 24 Hz), 134.2, 136.7, 189.8 (<sup>2</sup>J<sub>13C-31P</sub> = 13 Hz, C=O).

**(4-Methylbenzoylthio)diphenylphosphine (3d).** To a solution of chlorodiphenylphosphine (0.221 g, 1.00 mmol) in ether (10 mL) was added potassium 4-methylthiobenzoate (0.198 g, 1.04 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (KCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (0.5 mL), ether (1.0 mL), and then hexane (1.3 mL) were added and this mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave (4-methylbenzoylthio)diphenylphosphine (**3d**) as colorless crystals (0.312 g, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 2.31 (s, 3H, CH<sub>3</sub>), 7.15 (d, *J* = 8.2 Hz, 2H), 7.27–7.29 (m, 6H), 7.48–7.52 (m, 4H), 7.86 (d, *J* = 8.2 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  = 21.7 (CH<sub>3</sub>),

128.3, 128.6 ( $^3J_{13C-31P} = 6.8$  Hz), 129.3, 129.6, 130.8, 133.1 ( $^2J_{13C-31P} = 21$  Hz), 135.8 ( $^1J_{13C-31P} = 24$  Hz), 144.7, 189.8 ( $^2J_{13C-31P} = 12$  Hz, C=O). Found: C, 71.46; H, 5.11%. Calcd for C<sub>20</sub>H<sub>17</sub>OPS: C, 71.41; H, 5.09%.

**(2-Methoxybenzoylthio)diphenylphosphine (3e).** As with **3d**, the reaction of chlorodiphenylphosphine (0.223 g, 1.01 mmol) with potassium 2-methoxythiobenzoate (0.210 g, 1.02 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL), ether (0.5 mL), and then hexane (2.0 mL) gave (2-methoxybenzoylthio)diphenylphosphine (**3e**) as colorless crystals (0.282 g, 80%).  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta = 3.88$  (s, 3H, CH<sub>3</sub>O), 6.87–6.91 (m, 2H), 7.26–7.28 (m, 6H), 7.48–7.52 (m, 4H), 7.62–7.67 (m, 1H), 7.73–7.75 (m, 1H).  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta = 55.8$  (CH<sub>3</sub>O), 112.1, 120.4, 126.9, 128.5 ( $^3J_{13C-31P} = 6.8$  Hz), 129.4, 130.4, 133.2 ( $^2J_{13C-31P} = 21$  Hz), 134.1, 136.0 ( $^1J_{13C-31P} = 24$  Hz), 158.2, 189.2 ( $^2J_{13C-31P} = 12$  Hz, C=O). Found: C, 68.20; H, 4.92%. Calcd for C<sub>20</sub>H<sub>17</sub>O<sub>2</sub>PS: C, 68.17; H, 4.86%.

**(4-Methoxybenzoylthio)diphenylphosphine (3f).** As with **3d**, the reaction of chlorodiphenylphosphine (0.228 g, 1.03 mmol) with potassium 4-methoxythiobenzoate (0.218 g, 1.06 mmol) gave (4-methoxybenzoylthio)diphenylphosphine (**3f**) as yellow oil (0.337 g, 93%).  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta = 3.80$  (s, 3H, CH<sub>3</sub>O), 6.90 (d,  $J = 8.8$  Hz, 2H), 7.35–7.37 (m, 6H), 7.60–7.64 (m, 4H), 8.04 (d,  $J = 8.8$  Hz, 2H).  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta = 55.4$  (CH<sub>3</sub>O), 113.6, 128.4 ( $^3J_{13C-31P} = 6.8$  Hz), 129.4, 130.3, 131.5, 132.9 ( $^2J_{13C-31P} = 22$  Hz), 135.7 ( $^1J_{13C-31P} = 24$  Hz), 163.9, 188.3 ( $^2J_{13C-31P} = 13$  Hz, C=O).

**(4-Chlorobenzoylthio)diphenylphosphine (3g).** As with **3d**, the reaction of chlorodiphenylphosphine (0.224 g, 1.02 mmol) with potassium 4-chlorothiobenzoate (0.244 g, 1.06 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL), ether (1.0 mL), and then hexane (2.0 mL) gave (4-chlorobenzoylthio)diphenylphosphine (**3g**) as colorless crystals (0.329 g, 90%).  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta = 7.29$ –7.36 (m, 8H), 7.48–7.52 (m, 4H), 7.97–7.99 (m, 2H);  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta = 128.7$  ( $^3J_{13C-31P} = 6.8$  Hz), 129.0, 129.6, 129.8, 132.7, 133.1 ( $^2J_{13C-31P} = 21$  Hz), 135.4 ( $^1J_{13C-31P} = 24$  Hz), 140.2, 189.3 ( $^2J_{13C-31P} = 12$  Hz, C=O). Found: C, 64.01; H, 4.02%. Calcd for C<sub>19</sub>H<sub>14</sub>ClOPS: C, 63.96; H, 3.95%.

**Bis(acetylthio)phenylphosphine (4a).** To a solution of dichlorophenylphosphine (0.180 g, 1.01 mmol) in dichloromethane (10 mL) was added sodium thioacetate (0.201 g, 2.05 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa) to give bis(acetylthio)phenylphosphine (**4a**) as pale yellow oil (0.203 g, 74%).  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta = 2.29$  (s, 6H, CH<sub>3</sub>), 7.20–7.77 (m, 5H).  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta = 31.9$  (CH<sub>3</sub>), 128.2, 128.6, 130.5, 132.1 ( $^1J_{13C-31P} = 24$  Hz), 193.1 ( $^2J_{13C-31P} = 14$  Hz, C=O).

**Bis(2,2-dimethylpropionylthio)phenylphosphine (4b).** As with **4a**, the reaction of dichlorophenylphosphine (0.185 g, 1.03 mmol) with sodium 2,2-dimethylthiopropionate (0.295 g, 2.10 mmol) gave bis(2,2-dimethylpropionylthio)phenylphosphine (**4b**) as colorless oil (0.251 g, 75%).  $^1H$  NMR (CDCl<sub>3</sub>)  $\delta = 1.13$  (s, 18H, CH<sub>3</sub>), 7.24–7.90 (m, 5H).  $^{13}C$  NMR (CDCl<sub>3</sub>)  $\delta = 27.2$  (CH<sub>3</sub>), 47.6 [C(CH<sub>3</sub>)], 128.1, 128.4, 130.3, 132.2 ( $^1J_{13C-31P} = 25$  Hz), 204.1 ( $^2J_{13C-31P} = 12$  Hz, C=O).

**Bis(benzoylthio)phenylphosphine (4c).** As with **4d**, the reaction of dichlorophenylphosphine (0.200 g, 1.12 mmol) with potassium thiobenzoate (0.403 g, 2.30 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL) and then hex-

ane (2.0 mL), gave bis(benzoylthio)phenylphosphine (**4c**) as colorless crystals (0.423 g, 99%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 7.41\text{--}7.48$  (m, 6H),  $7.56\text{--}7.62$  (m, 3H),  $7.89\text{--}7.93$  (m, 2H),  $7.98\text{--}8.01$  (m, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta = 127.9, 128.3, 128.7, 128.8, 130.8, 132.7$  ( $^1J_{13\text{C}\text{--}31\text{P}} = 25$  Hz),  $134.0, 136.6, 189.8$  ( $^2J_{13\text{C}\text{--}31\text{P}} = 14$  Hz, C=O). Found: C, 62.93; H, 4.06%. Calcd for  $\text{C}_{20}\text{H}_{15}\text{O}_2\text{PS}_2$ : C, 62.81; H, 3.95%.

**Bis(4-methylbenzoylthio)phenylphosphine (4d).** To a solution of dichlorophenylphosphine (0.187 g, 1.04 mmol) in dichloromethane (10 mL) was added potassium 4-methylthiobenzoate (0.409 g, 2.15 mmol), and the mixture was stirred at  $20^\circ\text{C}$  for 1 h. The insoluble parts (KCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure ( $23^\circ\text{C}/53$  Pa). Dichloromethane (1.0 mL) and then hexane (2.0 mL) were added and this mixture was allowed to stand at  $-20^\circ\text{C}$  for 24 h. Filtration of the resulting crystals gave bis(4-methylbenzoylthio)phenylphosphine (**4d**) as colorless crystals (0.376 g, 88%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 2.39$  (s, 6H,  $\text{CH}_3$ ),  $7.23$  (d,  $J = 8.2$  Hz, 4H),  $7.40\text{--}7.42$  (m, 3H),  $7.87\text{--}7.89$  (m, 2H),  $7.89$  (d,  $J = 8.2$  Hz, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta = 21.7$  ( $\text{CH}_3$ ),  $128.4, 128.6, 128.7, 129.4, 130.6, 132.7$  ( $^1J_{13\text{C}\text{--}31\text{P}} = 24$  Hz),  $134.1, 145.1, 189.3$  ( $^2J_{13\text{C}\text{--}31\text{P}} = 14$  Hz, C=O). Found: C, 64.09; H, 5.14%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{PS}_2$ : C, 64.37; H, 4.67%.

**Bis(2-methoxybenzoylthio)phenylphosphine (4e).** As with **4d**, the reaction of dichlorophenylphosphine (0.180 g, 1.01 mmol) with potassium 2-methoxythiobenzoate (0.426 g, 2.06 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.5 mL) and then hexane (3.0 mL), gave bis(2-methoxybenzoylthio)phenylphosphine (**4e**) as colorless crystals (0.434 g, 97%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 3.90$  (s, 6H,  $\text{CH}_3\text{O}$ ),  $6.95\text{--}7.03$  (m, 8H),  $7.36\text{--}7.38$  (m, 3H),  $7.85\text{--}7.90$  (m, 2H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta = 55.8$  ( $\text{CH}_3\text{O}$ ),  $112.1, 120.4, 128.5, 128.6, 130.0, 130.2, 130.5, 132.7$  ( $^1J_{13\text{C}\text{--}31\text{P}} = 24$  Hz),  $134.5, 158.6, 188.8$  ( $^2J_{13\text{C}\text{--}31\text{P}} = 13$  Hz, C=O). Found: C, 59.58; H, 4.82%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_4\text{PS}_2$ : C, 59.72; H, 4.33%.

**Bis(4-methoxybenzoylthio)phenylphosphine (4f).** As with **4d**, the reaction of dichlorophenylphosphine (0.356 g, 1.99 mmol) with potassium 4-methoxythiobenzoate (0.826 g, 4.00 mmol), followed by recrystallization from a mixed solvent of dichloromethane (1.0 mL) and then hexane (1.0 mL), gave bis(4-methoxybenzoylthio)phenylphosphine (**4f**) as pale yellow crystals (0.871 g, 99%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 3.84$  (s, 6H,  $\text{CH}_3\text{O}$ ),  $6.90$  (d,  $J = 8.7$  Hz, 4H),  $7.39\text{--}7.41$  (m, 3H),  $7.85\text{--}7.90$  (m, 2H),  $7.97$  (d,  $J = 8.7$  Hz, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta = 55.6$  ( $\text{CH}_3\text{O}$ ),  $113.9, 128.6, 128.7, 130.2, 130.5, 130.6, 132.6$  ( $^1J_{13\text{C}\text{--}31\text{P}} = 25$  Hz),  $164.3, 188.1$  ( $^2J_{13\text{C}\text{--}31\text{P}} = 14$  Hz, C=O). Found: C, 59.62; H, 4.83%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_4\text{PS}_2$ : C, 59.72; H, 4.33%.

**Bis(4-chlorobenzoylthio)phenylphosphine (4g).** As with **4d**, the reaction of dichlorophenylphosphine (0.173 g, 0.97 mmol) with potassium 4-chlorothiobenzoate (0.410 g, 1.95 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave bis(4-chlorobenzoylthio)phenylphosphine (**4g**) as colorless crystals (0.381 g, 87%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta = 7.42$  (d,  $J = 8.8$  Hz, 4H),  $7.42\text{--}7.44$  (m, 3H),  $7.88\text{--}7.92$  (m, 2H),  $7.94$  (d,  $J = 8.8$  Hz, 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta = 128.8, 128.9, 129.1, 129.6, 131.0, 128.7$  ( $^1J_{13\text{C}\text{--}31\text{P}} = 25$  Hz),  $134.9, 140.7, 188.6$  ( $^2J_{13\text{C}\text{--}31\text{P}} = 14$  Hz, C=O). Found: C, 53.02; H, 3.36%. Calcd for  $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{O}_2\text{PS}_2$ : C, 53.22; H, 2.90%.

**Tris(acetylthio)phosphine (5a).** To a suspension of sodium thioacetate (0.272 g, 2.77 mmol) in dichloromethane (10 mL) was added tribromophosphine/dichloromethane 1.0 M solu-

tion (0.8 mL, 0.80 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C / 0.4 Torr) to give tris(acetylthio)phosphine (**5a**) as yellow oil (0.168 g, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 2.29 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 32.0 (CH<sub>3</sub>), 192.5 (<sup>2</sup>J<sub>13C-31P</sub> = 17 Hz, C=O).

**Tris(2,2-dimethylpropionylthio)phosphine (5b).** As with **5a**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with sodium 2,2-dimethylthiopropionate (0.420 g, 3.00 mmol) gave tris(2,2-dimethylpropionylthio)phosphine (**5b**) as yellow oil (0.250 g, 82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 1.19 (s, 27H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 27.2 (CH<sub>3</sub>), 47.9 [C(CH<sub>3</sub>)], 203.6 (<sup>2</sup>J<sub>13C-31P</sub> = 14 Hz, C=O).

**Tris(benzoylthio)phosphine (5c).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium thiobenzoate (0.530 g, 3.02 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave tris(benzoylthio)phosphine (**5c**) as colorless crystals (0.320 g, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.46 (t, *J* = 7.4 Hz, 6H), 7.60 (t, *J* = 7.4 Hz, 3H), 8.00 (d, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 128.4, 128.8, 134.3, 136.2, 189.2 (<sup>2</sup>J<sub>13C-31P</sub> = 16 Hz, C=O). Found: C, 57.08; H, 3.57%. Calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>PS<sub>3</sub>: C, 57.00; H, 3.42%.

**Tris(4-methylbenzoylthio)phosphine (5d).** To a suspension of potassium 4-methylthiobenzoate (0.574 g, 3.02 mmol) in dichloromethane (10 mL) was added tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (KBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (6.0 mL) and then hexane (4.0 mL) were added and this mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave tris(4-methylbenzoylthio)phosphine (**5d**) as colorless crystals (0.299 g, 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 2.39 (s, 9H, CH<sub>3</sub>), 7.22 (d, *J* = 8.2 Hz, 6H), 7.87 (d, *J* = 8.2 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 21.8 (CH<sub>3</sub>), 128.4, 129.4, 133.7, 145.4, 188.8 (<sup>2</sup>J<sub>13C-31P</sub> = 16 Hz, C=O). Found: C, 59.52; H, 4.40%. Calcd for C<sub>24</sub>H<sub>21</sub>O<sub>3</sub>PS<sub>3</sub>: C, 59.49; H, 4.37%.

**Tris(2-methoxybenzoylthio)phosphine (5e).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 2-methoxythiobenzoate (0.609 g, 2.95 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (4.0 mL), gave tris(2-methoxybenzoylthio)-phosphine (**5e**) as colorless crystals (0.382 g, 90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 3.90 (s, 9H, CH<sub>3</sub>O), 6.95 (d, *J* = 7.9 Hz, 3H), 6.97 (t, *J* = 7.9 Hz, 3H), 7.47 (t, *J* = 7.9 Hz, 3H), 7.86 (d, *J* = 7.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 55.8 (CH<sub>3</sub>O), 112.0, 120.5, 125.6, 130.6, 134.8, 158.9, 188.6 (<sup>2</sup>J<sub>13C-31P</sub> = 14 Hz, C=O). Found: C, 54.29; H, 4.09%. Calcd for C<sub>24</sub>H<sub>21</sub>O<sub>6</sub>PS<sub>3</sub>: C, 54.13; H, 3.97%.

**Tris(4-methoxybenzoylthio)phosphine (5f).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 4-methoxythiobenzoate (0.630 g, 3.05 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (4.0 mL), gave tris(4-methoxybenzoylthio)-phosphine (**5f**) as colorless crystals (0.280 g, 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 3.78 (s, 9H, CH<sub>3</sub>O), 6.84 (d, *J* = 8.9 Hz, 6H), 7.89 (d, *J* = 8.9 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 55.5 (CH<sub>3</sub>O), 113.8, 128.7, 130.5, 164.3, 187.3 (<sup>2</sup>J<sub>13C-31P</sub> = 16 Hz, C=O). Found: C, 54.25; H, 3.98%. Calcd for

C<sub>24</sub>H<sub>21</sub>O<sub>6</sub>PS<sub>3</sub>: C, 54.13; H, 3.97%.

**Tris(4-chlorobenzoylthio)phosphine (5g).** As with **5d**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.8 mL, 0.80 mmol) with potassium 4-chlorothiobenzoate (0.617 g, 2.93 mmol), followed by recrystallization from a mixed solvent of dichloromethane (3.0 mL) and then hexane (3.0 mL), gave tris(4-chlorobenzoylthio)phosphine (**5g**) as colorless crystals (0.328 g, 75%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.91 (d, *J* = 8.5 Hz, 6H), 7.42 (d, *J* = 8.5 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 129.2, 129.7, 134.4, 141.1, 188.0 (<sup>2</sup>*J*<sub>13C-31P</sub> = 17 Hz, C=O). Found: C, 46.38; H, 2.45%. Calcd for C<sub>21</sub>H<sub>12</sub>Cl<sub>3</sub>O<sub>3</sub>PS<sub>3</sub>: C, 46.21; H, 2.22%.

**Diphenyl(thiobenzoylthio)phosphine (6a).** As with **6b**, the reaction of chlorodiphenylphosphine (0.218 g, 0.99 mmol) with piperidinium dithiobenzoate (0.241 g, 1.01 mmol), followed by recrystallization from a solvent of ether (3.0 mL), gave diphenyl(thiobenzoylthio)phosphine (**6a**) as purple crystals (0.117 g, 35%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.32–8.14 (m, 15H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 127.3, 128.6 (<sup>3</sup>*J*<sub>13C-31P</sub> = 6.8 Hz), 128.8, 129.5, 129.7, 130.8, 133.2 (<sup>2</sup>*J*<sub>13C-31P</sub> = 21 Hz), 134.8 (<sup>1</sup>*J*<sub>13C-31P</sub> = 24 Hz), 225.7 (<sup>2</sup>*J*<sub>13C-31P</sub> = 21 Hz, C=S). Found: C, 67.47; H, 4.50%. Calcd for C<sub>19</sub>H<sub>15</sub>PS<sub>2</sub>: C, 67.43; H, 4.47%.

**(4-Methylthiobenzoylthio)diphenylphosphine (6b).** To a solution of chlorodiphenylphosphine (0.212 g, 0.96 mmol) in ether (10 mL) was added piperidinium 4-methyldithiobenzoate (0.247 g, 0.98 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Ether (1.6 mL) was added and this mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave (4-methylthiobenzoylthio)-diphenylphosphine (**6b**) as red crystals (0.318 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 2.35 (s, 3H, CH<sub>3</sub>), 7.15 (d, *J* = 8.4 Hz, 2H), 7.33–7.39 (m, 6H), 7.54–7.58 (m, 4H), 8.06 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 21.6 (CH<sub>3</sub>), 127.3, 128.6 (<sup>3</sup>*J*<sub>13C-31P</sub> = 6.8 Hz), 128.9, 129.7, 133.2 (<sup>2</sup>*J*<sub>13C-31P</sub> = 21 Hz), 134.8 (<sup>1</sup>*J*<sub>13C-31P</sub> = 24 Hz), 142.1, 143.9, 225.5 (<sup>2</sup>*J*<sub>13C-31P</sub> = 20 Hz, C=S). Found: C, 68.20; H, 4.88%. Calcd for C<sub>20</sub>H<sub>17</sub>PS<sub>2</sub>: C, 68.16; H, 4.86%.

**(2-Methoxythiobenzoylthio)diphenylphosphine (6c).** As with **6b**, the reaction of chlorodiphenylphosphine (0.244 g, 1.11 mmol) with piperidinium 2-methoxydithiobenzoate (0.305 g, 1.13 mmol) gave (2-methoxythiobenzoylthio)diphenylphosphine (**6c**) as red oil (0.377 g, 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 3.83 (s, 3H, CH<sub>3</sub>O), 6.89–6.95 (m, 2H), 7.36–7.94 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 56.0 (CH<sub>3</sub>O), 111.8, 120.4, 128.4, 128.6 (<sup>3</sup>*J*<sub>13C-31P</sub> = 6.8 Hz), 129.4, 129.6, 131.8, 133.1 (<sup>2</sup>*J*<sub>13C-31P</sub> = 21 Hz), 134.8 (<sup>1</sup>*J*<sub>13C-31P</sub> = 25 Hz), 155.0, 222.7 (<sup>2</sup>*J*<sub>13C-31P</sub> = 17 Hz, C=S).

**(4-Methoxythiobenzoylthio)diphenylphosphine (6d).** As with **6b**, the reaction of chlorodiphenylphosphine (0.106 g, 0.45 mmol) with sodium 4-methoxydithiobenzoate (0.108 g, 0.52 mmol), followed by recrystallization from a solvent of ether (3.0 mL), gave (4-methoxythiobenzoylthio)diphenylphosphine (**6d**) as vermilion crystals (0.098 g, 61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 3.84 (s, 3H, CH<sub>3</sub>O), 6.83 (d, *J* = 8.8 Hz, 2H), 7.36–7.38 (m, 6H), 7.50–7.56 (m, 4H), 8.20 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 55.6 (CH<sub>3</sub>O), 113.4, 128.6 (<sup>3</sup>*J*<sub>13C-31P</sub> = 6.4 Hz), 129.6, 129.7, 131.9, 133.2 (<sup>2</sup>*J*<sub>13C-31P</sub> = 21 Hz), 134.9, 164.0, 223.5 (<sup>2</sup>*J*<sub>13C-31P</sub> = 19 Hz, C=S). Found: C, 65.44; H, 4.74%. Calcd for C<sub>20</sub>H<sub>17</sub>OPS<sub>2</sub>: C, 65.20; H, 4.65%.

**(4-Chlorothiobenzoylthio)diphenylphosphine (6e).** As with **6b**, the reaction of chlorodiphenylphosphine (0.213 g, 0.97 mmol) with piperidinium 4-chlorodithiobenzoate (0.268

g, 0.98 mmol), followed by recrystallization from a solvent of ether (2.0 mL), gave (4-chlorothiobenzoylthio)diphenylphosphine (**6e**) as red crystals (0.090 g, 25%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 7.32\text{--}7.55$  (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 128.1, 128.5, 128.6$  ( $^3J_{13\text{C}\text{--}31\text{P}} = 6.8$  Hz), 129.7, 133.2 ( $^2J_{13\text{C}\text{--}31\text{P}} = 21$  Hz), 134.8 ( $^1J_{13\text{C}\text{--}31\text{P}} = 25$  Hz), 139.0, 141.6, 224.2 ( $^2J_{13\text{C}\text{--}31\text{P}} = 21$  Hz, C=S). Found: C, 61.24; H, 3.81%. Calcd for  $\text{C}_{19}\text{H}_{14}\text{ClPS}_2$ : C, 61.21; H, 3.78%.

**(2,4,6-Trimethylthiobenzoylthio)diphenylphosphine (6f)**. As with **6b**, the reaction of chlorodiphenylphosphine (0.123 g, 0.56 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.131 g, 0.60 mmol), followed by recrystallization from a solvent of ether (2.0 mL), gave (2,4,6-trimethylthiobenzoylthio)diphenylphosphine (**6f**) as pink crystals (0.114 g, 54%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 2.24$  (s, 3H,  $\text{CH}_3$ ), 2.25 (s, 6H,  $\text{CH}_3$ ), 6.82 (s, 2H), 7.34–7.39 (m, 6H), 7.66–7.73 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 19.3$  ( $\text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 128.5, 128.7 ( $^3J_{13\text{C}\text{--}31\text{P}} = 6.4$  Hz), 129.9, 130.8, 132.2, 133.2 ( $^2J_{13\text{C}\text{--}31\text{P}} = 21$  Hz), 138.0, 144.9, 236.3 ( $^2J_{13\text{C}\text{--}31\text{P}} = 19$  Hz, C=S). Found: C, 69.72; H, 5.58%. Calcd for  $\text{C}_{22}\text{H}_{21}\text{PS}_2$ : C, 69.45; H, 5.56%.

**Phenylbis(thiobenzoylthio)phosphine (7a)**. As with **7b**, the reaction of dichlorophenylphosphine (0.065 mL, 0.48 mmol) with sodium dithiobenzoate (0.180 g, 1.02 mmol) gave phenylbis(thiobenzoylthio)phosphine (**7a**) as reddish purple oil (0.142 g, 71%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 7.40\text{--}7.43$  (m, 6H), 7.55–7.64 (m, 3H), 7.92–7.97 (m, 2H), 8.15–8.17 (m, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 127.0, 128.4$  ( $^3J_{13\text{C}\text{--}31\text{P}} = 6.8$  Hz), 128.8, 129.1, 130.5, 133.3 ( $^1J_{13\text{C}\text{--}31\text{P}} = 21$  Hz), 133.7, 143.7, 226.9 ( $^2J_{13\text{C}\text{--}31\text{P}} = 23$  Hz, C=S).

**Bis(4-methylthiobenzoylthio)phenylphosphine (7b)**. To a solution of dichlorophenylphosphine (0.070 mL, 0.52 mmol) in dichloromethane (10 mL) was added sodium 4-methyldithiobenzoate (0.247 g, 1.31 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaCl) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (6.0 mL) and then hexane (5.0 mL) were added and this mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave bis(4-methylthiobenzoylthio)phenylphosphine (**7b**) as red crystals (0.079 g, 36%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 2.36$  (s, 6H,  $\text{CH}_3$ ), 7.16 (d,  $J = 8.2$  Hz, 4H), 7.36–7.38 (m, 3H), 7.86–7.90 (m, 2H), 8.04 (d,  $J = 8.2$  Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 21.6$  ( $\text{CH}_3$ ), 127.1, 127.2, 128.4 ( $^3J_{13\text{C}\text{--}31\text{P}} = 6.8$  Hz), 129.1, 130.4, 133.7 ( $^1J_{13\text{C}\text{--}31\text{P}} = 20$  Hz), 141.4, 144.5, 226.3 ( $^2J_{13\text{C}\text{--}31\text{P}} = 22$  Hz, C=S). Found: C, 59.92; H, 4.47%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{PS}_4$ : C, 59.70; H, 4.33%.

**Bis(2-methoxythiobenzoylthio)phenylphosphine (7c)**. As with **7b**, the reaction of dichlorophenylphosphine (0.070 mL, 0.52 mmol) with sodium 2-methoxydithiobenzoate (0.213 g, 1.04 mmol), followed by recrystallization from a mixed solvent of dichloromethane (3.0 mL) and then hexane (2.0 mL), gave bis(2-methoxythiobenzoylthio)phenylphosphine (**7c**) as red crystals (0.046 g, 19%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 3.86$  (s, 6H,  $\text{CH}_3\text{O}$ ), 6.90–6.94 (m, 8H), 7.37–7.42 (m, 3H), 7.78–7.85 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 55.9$  ( $\text{CH}_3\text{O}$ ), 112.0, 120.6, 128.6, 128.8 ( $^3J_{13\text{C}\text{--}31\text{P}} = 6.8$  Hz), 130.1, 130.5, 132.7, 133.3 ( $^1J_{13\text{C}\text{--}31\text{P}} = 22$  Hz), 135.6, 155.7, 227.9 ( $^2J_{13\text{C}\text{--}31\text{P}} = 24$  Hz, C=S). Found: C, 55.69; H, 4.09%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{PS}_4$ : C, 55.68; H, 4.03%.

**Bis(4-methoxythiobenzoylthio)phenylphosphine (7d)**. As with **7b**, the reaction of dichlorophenylphosphine (0.100 mL, 0.74 mmol) with sodium 4-methoxydithiobenzoate (0.331 g, 1.60 mmol), followed by recrystallization from a mixed solvent of dichloromethane (3.0 mL) and then hexane (1.0 mL), gave bis(4-methoxythiobenzoylthio)phenylphosphine (**7d**) as red

crystals (0.038 g, 11%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 3.84 (s, 6H,  $\text{CH}_3\text{O}$ ), 6.83 (d,  $J$  = 7.6 Hz, 4H), 7.35–7.36 (m, 3H), 7.87–7.90 (m, 2H), 8.17 (d,  $J$  = 7.6 Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 55.6 ( $\text{CH}_3\text{O}$ ), 113.5, 128.3 ( $^3J_{13\text{C}-31\text{P}}$  = 6.3 Hz), 129.4, 129.5, 130.3, 133.7 ( $^1J_{13\text{C}-31\text{P}}$  = 21 Hz), 137.2, 164.4, 224.2 ( $^2J_{13\text{C}-31\text{P}}$  = 24 Hz, C=S). Found: C, 55.74; H, 4.06%. Calcd for  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{PS}_4$ : C, 55.68; H, 4.03%.

**Bis(2,4,6-trimethylthiobenzoylthio)phenylphosphine (7f).** As with **6b**, the reaction of dichlorophenylphosphine (0.060 mL, 0.44 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.216 g, 0.99 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (1.0 mL), gave bis(2,4,6-trimethylthiobenzoylthio)phenylphosphine (**7f**) as vermilion crystals (0.192 g, 44%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 2.23 (s, 6H,  $\text{CH}_3$ ), 2.27 (s, 12H,  $\text{CH}_3$ ), 6.85 (s, 4H), 7.38–7.41 (m, 3H), 7.78–7.85 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 19.2 ( $\text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 128.5, 128.6, 130.9, 132.0, 132.5, 133.7 ( $^1J_{13\text{C}-31\text{P}}$  = 21 Hz), 138.4, 144.1, 236.5 ( $^2J_{13\text{C}-31\text{P}}$  = 22 Hz, C=S). Found: C, 62.79; H, 5.51%. Calcd for  $\text{C}_{26}\text{H}_{27}\text{PS}_4$ : C, 62.62; H, 5.46%.

**Tris(4-methylthiobenzoylthio)phosphine (8b).** To a suspension of sodium 4-methyldithiobenzoate (0.202 g, 1.06 mmol) in dichloromethane (10 mL) was added tribromophosphine / dichloromethane 1.0 M solution (0.3 mL, 0.30 mmol), and the mixture was stirred at 20 °C for 1 h. The insoluble parts (NaBr) were filtered off by glass filter (G4) in vacuo. The solvents were removed under reduced pressure (23 °C/53 Pa). Dichloromethane (2.0 mL) and then hexane (3.0 mL) were added and this mixture was allowed to stand at -20 °C for 24 h. Filtration of the resulting crystals gave tris(4-methylthiobenzoylthio)phosphine (**8b**) as red crystals (0.061 g, 38%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 2.38 (s, 9H,  $\text{CH}_3$ ), 7.19 (d,  $J$  = 7.3 Hz, 6H), 8.02 (d,  $J$  = 7.3 Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 21.8 ( $\text{CH}_3$ ), 127.1, 129.3, 134.8, 145.8, 227.6 ( $^2J_{13\text{C}-31\text{P}}$  = 25 Hz, C=S). Found: C, 54.27; H, 3.99%. Calcd for  $\text{C}_{24}\text{H}_{21}\text{PS}_6$ : C, 54.11; H, 3.97%.

**Tris(4-chlorothiobenzoylthio)phosphine (8e).** As with **8b**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.4 mL, 0.40 mmol) with sodium 4-chlorodithiobenzoate (0.320 g, 1.52 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (2.0 mL), gave tris(4-chlorothiobenzoylthio)phosphine (**8e**) as red crystals (0.125 g, 53%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 7.41 (d,  $J$  = 8.8 Hz, 6H), 8.06 (d,  $J$  = 8.8 Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 128.3, 18.8, 140.6, 141.3, 227.0 ( $^2J_{13\text{C}-31\text{P}}$  = 26 Hz, C=S). Found: C, 42.52; H, 2.08%. Calcd for  $\text{C}_{21}\text{H}_{12}\text{Cl}_3\text{PS}_6$ : C, 42.46; H, 2.04%.

**Tris(2,4,6-trimethylthiobenzoylthio)phosphine (8f).** As with **8b**, the reaction of tribromophosphine/dichloromethane 1.0 M solution (0.4 mL, 0.40 mmol) with sodium 2,4,6-trimethyldithiobenzoate (0.325 g, 1.40 mmol), followed by recrystallization from a mixed solvent of dichloromethane (2.0 mL) and then hexane (3.0 mL), gave tris(2,4,6-trimethylthiobenzoylthio)phosphine (**8f**) as vermilion crystals (0.176 g, 71%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 2.29 (s, 9H,  $\text{CH}_3$ ), 2.31 (s, 18H,  $\text{CH}_3$ ), 6.88 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 19.4 ( $\text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 128.6, 132.6, 138.8, 143.8, 238.9 ( $^2J_{13\text{C}-31\text{P}}$  = 25 Hz, C=S). Found: C, 58.51; H, 5.44%. Calcd for  $\text{C}_{30}\text{H}_{33}\text{PS}_6$ : C, 58.41; H, 5.39%.

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## Chapter 5

### **Thioacylsulfanylarsines $(\text{RCS}_2)_x\text{AsPh}_{3-x}$ , $x = 1-3$ ]: synthesis, structures, natural bond order analyses and reactions with piperidine**

#### **5.1. Introduction**

The chemistry of arsenic compounds with dithio-carbamato and -carbonato ligands has been investigated in great detail.<sup>1</sup> In contrast, the preparation of arsenic compounds with thio- and dithio-carboxylato ligands was limited to only seven thiocarboxylic<sup>2</sup> and two dithiocarboxylic acid arsenic derivatives<sup>3</sup> when our study began in 1974. Their spectral data and crystal structure analyses have not been described. The reason for this seemed to be the difficulty of purification and of the preparation of the starting compounds such as dithiocarboxylic acids and their alkali metal and ammonium salts. The arsenic compounds with dithio- and thio-carboxylato ligands are considered to be effective precursors for the synthesis of organoarsenic thiolate anion species such as  $\text{R}_2\text{AsS}^-$ ,<sup>4</sup> which can be used easily to introduce the arsenic-sulfur framework into a molecule. It is possible that the reactions of alkali metal diorganoarsenide with elemental sulfur may be used for the synthesis of the organoarsenic thiolates. In Author's research the preparation of  $\text{R}_2\text{As}^- \text{M}^+$  ( $\text{M} =$  alkali metal) appeared to be impractical. Author's laboratory previously developed convenient syntheses of ammonium and alkali metal chalcogeno-carboxylates,<sup>5</sup> and synthesized a variety of their main group element derivatives.<sup>6</sup> In addition, diphenyl(selenocarboxylato)-arsines<sup>7</sup> have been found to be effective precursors for the synthesis of diphenylselenoarsenic(III) ammonium salts.<sup>8</sup> Recently the structure of tris(benzoylsulfanyl)-arsine was reported by Nöth and co-workers.<sup>9</sup> This prompted us to reveal Author's results concerning Group 15 element derivatives of thio- and dithio-carboxylic acids. The Author describe here in detail the synthesis and structural analyses of a series of dithiocarboxyarsines  $[(\text{RCS}_2)_x\text{AsPh}_{3-x}]$ ,  $x = 1-3$  along with a structural comparison with the corresponding thiocarboxyarsines  $[(\text{RCOS})_x\text{AsPh}_{3-x}]$ ,  $x = 1-3$  and in addition reactions with amines, leading to the first isolation of the organotrithioarsonate dianion  $\text{RAsS}_3^{2-}$ .

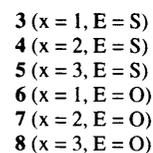
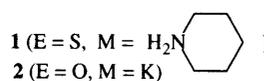
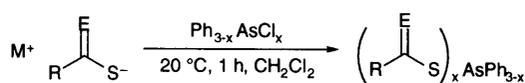
#### **5.2. Results and Discussion**

**Synthesis of complexes.** Initially, the synthesis of diphenyl(dithiocarboxy)arsines **3**, phenyl-bis(dithiocarboxy)arsines **4** and tris(dithiocarboxy)arsines **5** was examined using piperidinium 4-methylbenzenecarbo-dithioate. Under the conditions as shown in Scheme 1 these compounds were obtained in 70–90% yields.<sup>10a</sup> Although small amounts of alkanedithioic acid derivatives are lost during purification, the main reactions (to give **3**, **4** and **5**) proceed quantitatively. In order to compare structure and spectral data, a series of diphenyl-(thiocarboxy)arsines **6**, phenyl-bis(thiocarboxy)arsines **7** and tris(thiocarboxy)arsines **8** were

synthesized in similar yields by treating potassium thiocarboxylates **2** instead of piperidinium dithiocarboxylates **1** (Scheme 1).<sup>10b</sup> The resulting dithio- and thio-carboxylic acid arsenic derivatives (especially aromatic derivatives) are stable both thermally and toward oxygen and water. Upon exposure to air, they do not show any appreciable change for three months.

**Crystal structures.** The structures of (4-methoxythiobenzoylsulfanyl)diphenyl- **3g**, bis(4-methylthiobenzoyl-sulfanyl)phenyl- **4e** and tris(4-methylthiobenzoylsulfanyl)arsine **5e** are shown in Figure 1. The dithiocarboxylato ligand and the

Scheme 1

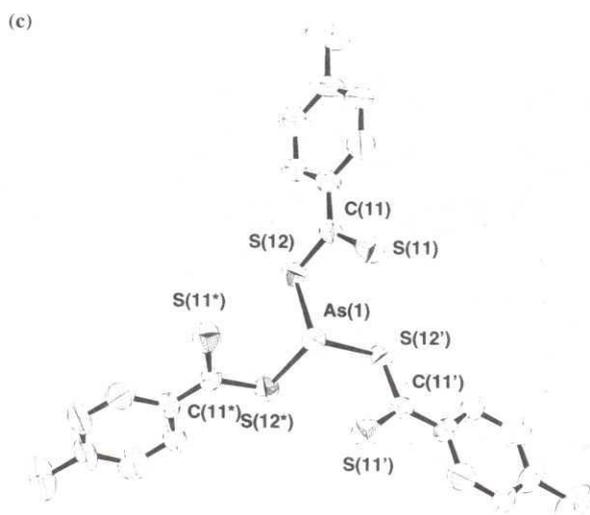
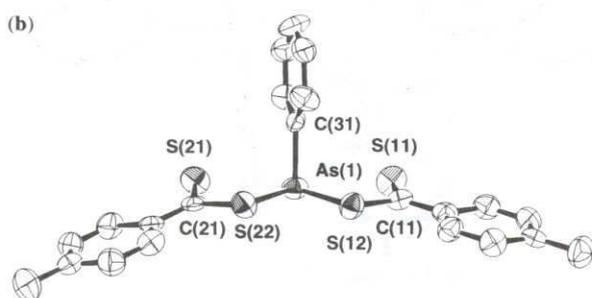
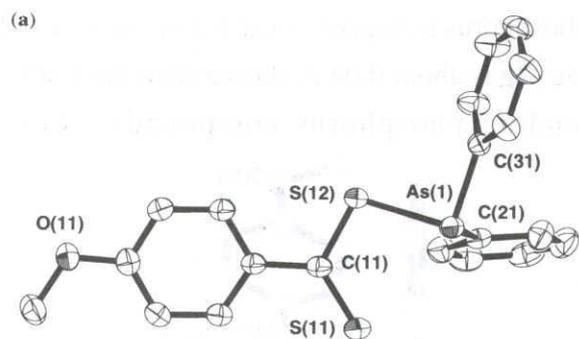


No.	R	No.	R
<b>3, 4, 5a</b>	CH <sub>3</sub>	<b>6, 7, 8a</b>	CH <sub>3</sub>
<b>b</b>	C <sub>2</sub> H <sub>5</sub>	<b>b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
<b>c</b>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<b>c</b>	C <sub>6</sub> H <sub>5</sub>
<b>d</b>	C <sub>6</sub> H <sub>5</sub>	<b>d</b>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>e</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>e</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>f</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>f</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>
<b>g</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>g</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>
<b>h</b>	4-ClC <sub>6</sub> H <sub>4</sub>	<b>h</b>	4-ClC <sub>6</sub> H <sub>4</sub>
<b>i</b>	1-C <sub>10</sub> H <sub>7</sub>	<b>i</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>

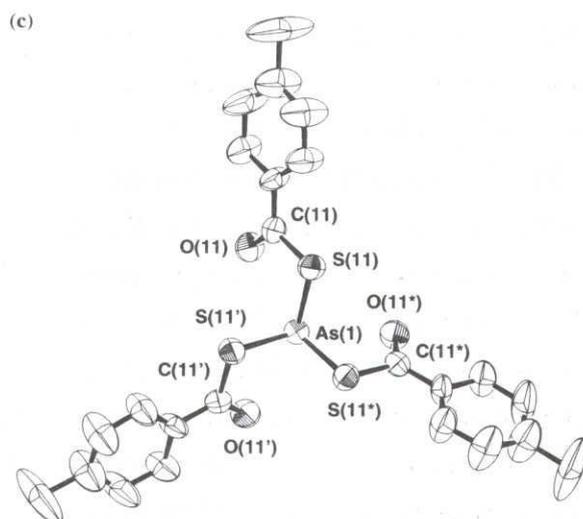
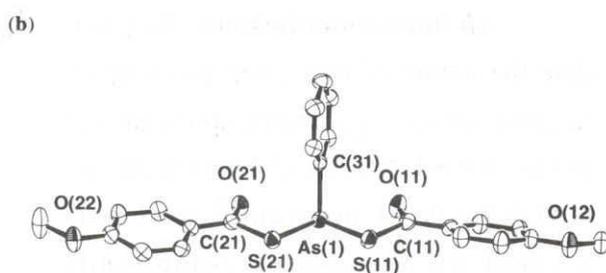
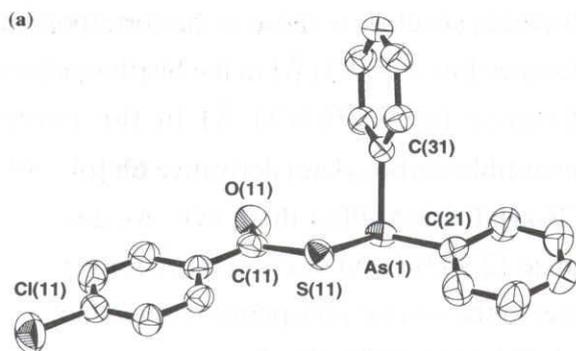
phenyl ring containing C(21) in **3g** are twisted [S(11)–As(1)–C(21)–C(22) 60.0(2)°] (Figure 1a). In **4e**, the two dithiocarboxyl ligands exist in the same plane with the same orientation, where two thiocarbonyl sulfurs are located in the same direction (Figure 1b). In **5e**, the three dithio-carboxylato ligands exist in C<sub>3</sub> symmetry and no two ligands of the three exist in the same plane (Figure 1c). The distances between the central As atom and the thiocarbonyl sulfur [As(1)···S 2.96–3.15 Å] are within the sum of the van der Waals radii of both atoms (3.65 Å),<sup>11</sup> indicating interactions between the unshared electron pair on the thiocarbonyl sulfur and the σ\* orbitals of the As–S and/or As–C<sub>ipso</sub> bonds [S(11)–As(1)–C(31) 155.54(8)°]. It is noted that the two As···S distances in **4e** [As(1)···S(11) 2.958(4), As(1)···S(21) 2.956(4) Å] are shorter than those in the mono **3g** [3.1470(8) Å] and tris derivatives **5e** (2.969(4) Å). This may facilitate interaction because the two dithiocarboxylato ligands of **4e** exist in the same plane. These complexes can be described as having a distorted tetrahedral structure and the bonds around the As atoms can be considered to exhibit a p<sup>3</sup>-type bond.<sup>1b,g</sup>

For comparison, the structure analyses of the corresponding thiocarboxylato complexes were carried out. The ORTEP<sup>12</sup> drawings of (4-chlorobenzoyl-sulfanyl)diphenyl- **6h**, bis(4-methoxybenzoylsulfanyl)phenyl- **7g** and tris(4-methylbenzoylsulfanyl)arsine **8e** are shown in Figure 2. Unlike the dithiocarboxylato complex **3g**, the thiocarboxylato ligand of **6h** exists nearly in the same plane as the phenyl ring containing C(21). Although the crystal system and space group of **7g** are different from those of **4e**, the structures of both compounds resemble one another (Figure 2b). The structure of **8e** is comparable to both that in **5e** and the recently reported tris(benzoylsulfanyl)arsine<sup>9</sup> (Figure 2c). Similarly to dithio-carboxylato complexes, the distances between the central As atom and the carbonyl oxygens (As···O 2.71–2.94 Å) are elongated in the order bis **7g**, tris **8e**, mono **6h**.

**Packing.** The molecular arrangement of compounds **3g** and **6h** is shown in Fig. 3. It is noteworthy that in **3g** two molecules form a pair where the two CSSAs planes [C(11\*)–S(11\*)–



**Figure 1** Molecular structures of (a) 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CS<sub>2</sub>AsPh<sub>2</sub> **3g**, (b) (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CS<sub>2</sub>)<sub>2</sub>AsPh **4e** and (c) (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CS<sub>2</sub>)<sub>3</sub>As **5e**. The thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity.



**Figure 2** Molecular structures of (a) 4-ClC<sub>6</sub>H<sub>4</sub>COSAsPh<sub>2</sub> **6h**, (b) (4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COS)<sub>2</sub>AsPh **7g** and (c) (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COS)<sub>3</sub>As **8e**. Details as in Figure 1.

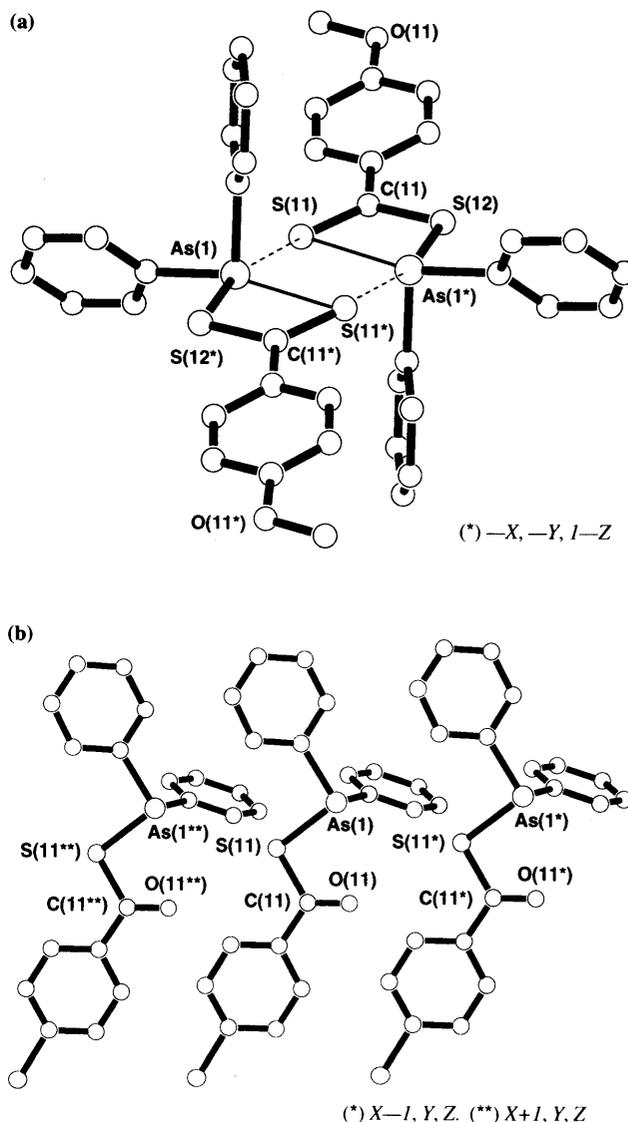
S(12\*)–As(1) and C(11)–S(11)–S(12)–As(1\*)] are parallel, the distance between the planes being 1.37 Å and the distance between As(1\*) and S(11) (or As(1)⋯S(11\*)) is significantly short (3.939 Å), although greater than the sum of the van der Waals radii of both atoms. In contrast such a pairing of the molecules is not observed for the other compounds as shown in Fig. 3 (b) and also for the corresponding phosphorus isologues ((RCES)PPh<sub>2</sub>, E = O or S).<sup>12</sup>

**Structural comparison with the phosphorus isologues.** In Table 1 the distances between the thiocarbonyl sulfur or carbonyl oxygen and the central arsenic atom are collected along with the C=E⋯P (E = O or S) distances of the corresponding phosphorus isologues. Interestingly, despite the large atomic radius of arsenic compared with that of phosphorus, the C=S⋯As

distances are close to those in the corresponding phosphorus isologues. In addition, the C=O...As distance [av. 2.720(3) Å] in the bis(thiocarboxylate) **7g** is about 0.04 Å shorter than the C=O...P distance [av. 2.765(3) Å] in the corresponding phosphorus compounds. In the mono(thio-carboxylate) derivative **6h** [(4-

**ab initio** calculations. To elucidate the nature of these non-bonding attraction, *ab initio* geometry optimizations at the RHF/LANL2DZ level with the GAUSSIAN 94 program<sup>15</sup> were performed on the model compounds (acetylsulfanyl)-dimethyl-phosphine **1'** and -arsine **2'** and dimethyl-(thioacetylsulfanyl)-phosphine **1''** and -arsine **2''** for (RCES)M(CH<sub>3</sub>)<sub>2</sub> (E = O or S; M = P or As) and bis(acetylsulfanyl)-methyl-phosphine **3'** and -arsine **4'** and bis(thioacetylsulfanyl)methyl-phosphine **3''** and -arsine **4''** for (RCES)<sub>2</sub>MCH<sub>3</sub> (E = O or S; M = P or As). The NBO (natural bond orbital) analyses showed that the orbital interactions between the n orbital (n<sub>O</sub>) on the carbonyl oxygen and the σ\*<sub>MC</sub> orbitals in **1'** and **2'** (Figure 4a) are present, but their values are close to each other

(Table 2). Interactions between the n<sub>S</sub> and σ\*<sub>MS</sub> orbitals (Figure 4b) are also appreciable for **1''** and **2''** together with interactions between the n<sub>S</sub> and σ\*<sub>MC</sub> orbitals. The contour maps of the n<sub>E</sub> and σ\*<sub>MS</sub> orbitals in the molecular plane C(=S)–



**Figure 3** Molecular arrangement of (a) 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CS<sub>2</sub>AsPh<sub>2</sub> **3g** and (b) 4-ClC<sub>6</sub>H<sub>4</sub>COSAsPh<sub>2</sub> **6h**.

**Table 1** Distances between the thiocarbonyl sulfur or carbonyl oxygen and As or P in (RCES)<sub>x</sub>AsPh<sub>3-x</sub> and (RCES)<sub>x</sub>PPh<sub>3-x</sub>

No.	R	$(\text{RCES})_x\text{AsPh}_{3-x}$			$(\text{RCES})_x\text{PPh}_{3-x}$			Ref.
		E	x	Distance As...E/Å	E	x	Distance P...E/Å	
	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	S	2	2.956(4)	S	2	2.965(3)	14
				2.958(4)			2.975(3)	
	4-ClC <sub>6</sub> H <sub>4</sub>	O	1	2.943(3)	O	1	2.917(3)	14
<b>7g</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	O	2	2.708(3)	O	2	2.747(3)	14
				2.731(3)			2.784(3)	
<b>8e</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	O	3	2.81(1)	O	3	2.82(1)	14

S–M (E = O or S; M = P or As) for the model compounds were depicted by using the MOLDEN 3.6 program.<sup>14</sup> Indeed, the overlaps between the  $n_S$  and  $\sigma^*_{MS}$  orbitals are present for **1''** and **2''**.

In the case of the bis derivatives (**3'**, **3''**, **4'** and **4''**), the interactions between the  $n_E$  orbitals ( $n_E$ ) on the carbonyl oxygen or thiocarbonyl sulfur and  $\sigma^*_{MC}$  are absent. Instead, the orbital interactions between  $n_{E5}$  and  $\sigma^*_{MS3}$  and between  $n_{E4}$  and  $\sigma^*_{MS3}$  (Figure 4c) are large. Those between  $n_{E5}$  and  $\sigma^*_{MS2}$  and between  $n_{E4}$  and  $\sigma^*_{MS3}$  (Fig. 4d) are also appreciable for **4'**, **3''** and **4''**, but small. The contour maps of the  $n_E$  and  $\sigma^*_{MS}$  orbitals in the molecular planes C(=E)–S–M–S–C(=E) (E = O or S; M = P or As) for **4'**, **3''** and **4''** obtained by using the MOLDEN 3.6 program<sup>14</sup> showed the expected overlaps between the  $n_E$  and  $\sigma^*_{MS}$  orbitals. The stabilization energies of the arsenic compounds **2'**, **2''**, **4'** and **4''** are larger than those of the corresponding phosphorus compounds **1'**, **1''**, **3'** and **3''**, respectively. In addition, the stabilization energies of the dithiocarboxylic acid

derivatives **1''**–**4''** are greater than those of the corresponding thiocarboxylic acid derivatives **1'**–**4'**, respectively. The former tendency may be understood in the terms of their orbital levels: the lower energy level of the  $\sigma^*_{AsS}$  orbitals compared with that of  $\sigma^*_{PS}$ . Also, the latter can also be understood in terms of the lower energy level of the  $n_O$  orbitals (–0.93201, –0.46778 au for **2'**; –0.94975, –0.48359 au for **2''**) compared with that of the  $n_S$  orbitals (–0.66262, –0.31594 au for **4'**; –0.67753, –0.33772 au for **4''**). These non-bonding orbital interactions between  $n_E$  and  $\sigma^*_{MS}$  in the bis derivatives **4** and **7** may facilitate the two dithio- or thio-carboxylate groups being in the same direction (see Fig. 1b and 2b). The atomic charges (0.73) of the As in the arsenic compounds (**2'**, **2''**, **4'** and **4''**) are larger than those in phosphorous compounds (0.63 for **1'** and **1''**; 0.53 for **3'** and **3''**), suggesting that the electrostatic interactions may contribute to the short C=E...As distances.

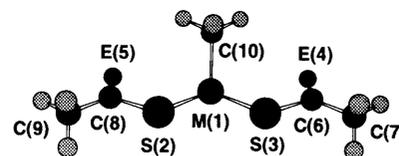
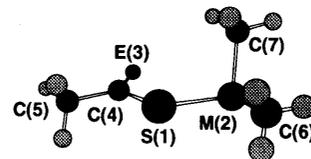
**Table 2** NBO Analysis of  $CH_3CESM(CH_3)_2$  and  $(CH_3CES)_2MCH_3$  (E = O, S; M = P, As) at RHF/LANL2DZ levels of theory

$CH_3CESM(CH_3)_2$			$\Delta E^a/\text{kcal mol}^{-1}$	
No.	E	M	$n_E \rightarrow \sigma^*_{MC6}$	$n_E \rightarrow \sigma^*_{MS}$
<b>1'</b>	O	P	0.55	–
<b>2'</b>	O	As	0.77	–
<b>1''</b>	S	P	1.46	0.62
<b>2''</b>	S	As	2.22	0.84

$(CH_3CES)_2MCH_3$			$\Delta E^a/\text{kcal mol}^{-1}$		
No.	E	M	$n_E \rightarrow \sigma^*_{MC10}$	$n_E \rightarrow \sigma^*_{MS2}$	$n_E \rightarrow \sigma^*_{MS3}$
<b>3'</b>	O	P	–	1.77 (E4)	– (E4)
			–	– (E5)	1.77 (E5)
<b>4'</b>	O	As	–	2.84 (E4)	0.64 (E4)
			–	0.64 (E5)	2.84 (E5)
<b>3''</b>	S	P	–	4.97 (E4)	1.57 (E4)
			–	1.57 (E5)	4.97 (E5)
<b>4''</b>	S	As	–	8.25 (E4)	2.50 (E4)
			–	2.50 (E5)	8.25 (E5)

<sup>a</sup>Stabilization energy associated with delocalization.

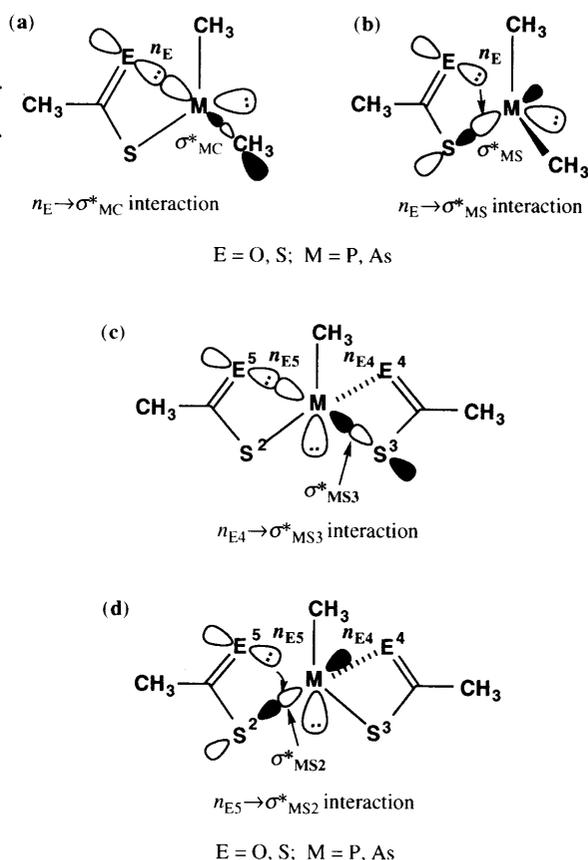


**Spectra.** In Table 3 the thiocarbonyl and carbonyl stretching frequencies, thiocarbonyl and carbonyl carbon chemical shifts and the visible spectra are collected. It is noted that the thiocarbonyl stretching frequencies of compounds **3–5** appear at 1170–1250  $\text{cm}^{-1}$ . The carbonyl stretching frequencies for **6–8** are observed at 1610–1690  $\text{cm}^{-1}$  and show a low frequency shift in the order  $7 < 8 < 6$ , which is consistent with the  $\text{C}=\text{O}\cdots\text{As}$  distance. The thiocarbonyl carbon chemical shifts of **4** and **5** are observed in the region  $\delta$  214–257, and those of **3** show an upfield shift of 3–5 ppm compared with those of **4** and **5**. The carbonyl carbon chemical shifts of **6–8** appear at  $\delta$  190–208, and that of the *t*-C<sub>4</sub>H<sub>9</sub> derivative **6b** shows a downfield shift relative to those of the other derivatives. In the electronic spectra the absorptions of **4** due to the  $n-\pi^*$  transitions of the  $\text{C}=\text{S}$  group show hypsochromic shifts compared with those of the mono **3** and tris derivatives **5**.

#### Reactions of compounds **3–5** or **6–8** with

**piperidine.** Expecting formation of piperidinium diphenylthioarsenate(III) salt  $(\text{H}_2\text{NC}_5\text{H}_{10})^+\text{Ph}_2\text{AsS}^-$ , the reactions of (4-methylthiobenzoylsulfanyl)diphenyl- **3e** and (4-methylbenzoylsulfanyl)diphenyl-arsine **6e** with piperidine were examined (Table 4). When **3e** or **6e** and two equivalents of piperidine were refluxed in ethanol, piperidinium diphenyldithioarsinate **9** was obtained in yields of 38 and 42%, respectively, together with *N*-4-methyl-

thiobenzoylpiperidine **10-S** or *N*-4-methylbenzoylpiperidine **10-O** (entries 2 and 5). The reaction with an equivalent of piperidine in EtOH at 20 °C resulted in a significant decrease in **9**. Instead, the corresponding thioamide **10-S** or amide **10-O** was obtained in good yields along with **11-S** or



**Figure 4** Non-bonding attraction due to (a) the  $n_E \rightarrow \sigma^*_{MC}$  and (b)  $n_E \rightarrow \sigma^*_{MS}$  interactions in  $(\text{CH}_3\text{CES})\text{M}(\text{CH}_3)_2$  (E = O or S; M = P or As) and (c) the  $n_{E4} \rightarrow \sigma^*_{MS3}$  and (d)  $n_{E5} \rightarrow \sigma^*_{MS2}$  interactions in  $(\text{CH}_3\text{CES})_2\text{MCH}_3$  (E = O or S; M = P or As).

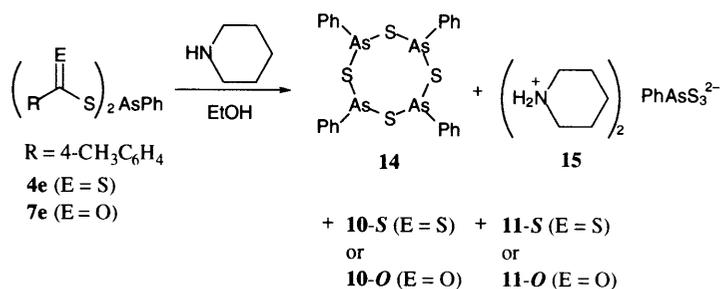
**Table 3** Spectral data of **3, 4, 5, 6, 7** and **8**

R	$\nu(\text{C}=\text{S})^a/\text{cm}^{-1}$			$\delta_{\text{C}=\text{S}}^b$			$\lambda_{\text{max}}^c/\text{nm}$		
	mono- <b>3</b>	bis- <b>4</b>	tris- <b>5</b>	mono- <b>3</b>	bis- <b>4</b>	tris- <b>5</b>	mono- <b>3</b>	bis- <b>4</b>	tris- <b>5</b>
C <sub>6</sub> H <sub>5</sub>	1218	1238	1241	229.0	231.0	234.2	527	506	511
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>				227.8	230.3	234.1			
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>				226.2	228.1	231.0			
4-ClC <sub>6</sub> H <sub>4</sub>				227.0	228.9	232.7	533	507	510
1-Naph				233.4	235.4	239.3	494	495	500
R	$\nu(\text{C}=\text{O})^a/\text{cm}^{-1}$			$\delta_{\text{C}=\text{O}}^b$					
	mono- <b>6</b>	bis- <b>7</b>	tris- <b>8</b>	mono- <b>6</b>	bis- <b>7</b>	tris- <b>8</b>			
C <sub>6</sub> H <sub>5</sub>	1644	1639	1631	192.1	192.8	190.3			
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1644	1626	1639	191.7	192.4	192.5			
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1629	1628	1627	190.5	191.1	191.3			
4-ClC <sub>6</sub> H <sub>4</sub>	1655	1612	1660	190.8	191.6	191.7			

<sup>a</sup> As KBr disc. <sup>b</sup> In CDCl<sub>3</sub>. <sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>.



**Table 5** Reactions of **4e** and **7e** with piperidine

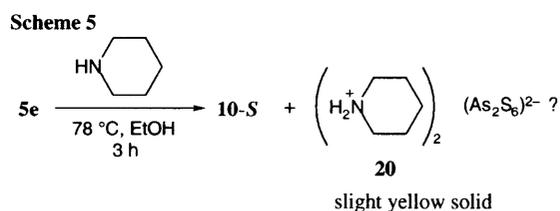
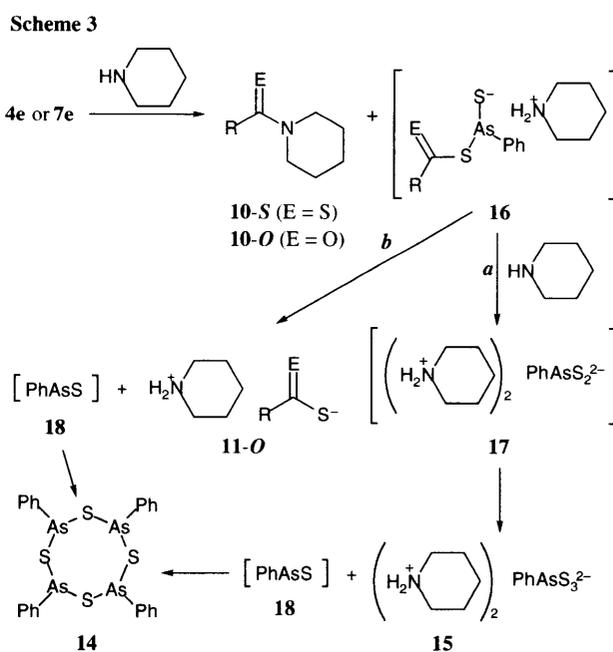
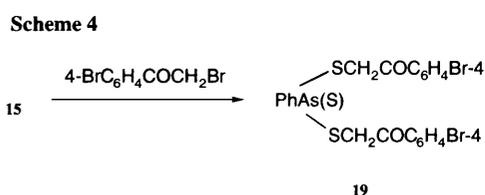


Entry	Compound	4e or 7e: piperidine <sup>a</sup>	t/h	T/°C	Yield <sup>b</sup> (%)			
					10	11	14	15
1	4e	1 : 2	5	20	35 (10-S)	0 (11-S)	0	14
2	4e	1 : 2	2	78	38 (10-S)	0 (11-S)	4	24
3	4e	1 : 4	5	78	84 (10-S)	0 (11-S)	16	65
4	7e	1 : 2	15	60	70 (10-O)	27 (11-O)	63	0
5	7e	1 : 2	3	20	56 (10-O)	40 (11-O)	66	0

<sup>a</sup> Mole ratio. <sup>b</sup> Isolated yields.

and unstable piperidinium salts **16** (E = S or O), respectively. In the case of dithiocarboxylic acid derivative **4e** the thiocarbonyl carbon is further attacked by piperidine to form the dithioarsenate dianion **17** which disproportionates to give **15** and phenylthioarsine **18** which further tetramerizes to give **14** (path *a*). In this reaction, the formation of cyclic trimer of **18** was not observed. In the case of the thiocarboxylic acid derivative **7e** the As–S bond of **16** (E = O) is cleaved to give **11-O** and **18** (path *b*). The processes for the disproportionation of **17** to give **15** and for the tetramerization of **18** to **14** are not clear at this time. The structures of **9**, **14** and **15** were determined by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis and by X-ray structural analysis. In addition, **15** was converted into 4-bromophenacyl ester **19** (Scheme 4).

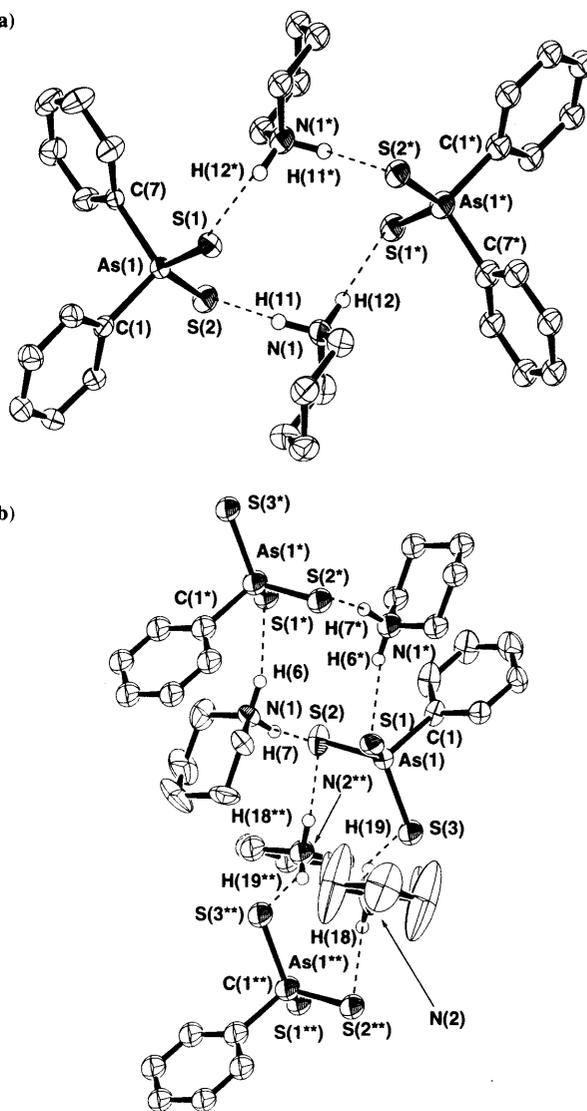
The reaction of tris(4-methylthio-benzoylsulfanyl)arsine **5e** with piperidine under reflux in ethanol gave **10-S** along with traces of a white solid with mp >300 °C and a slight yellow solid **20** with mp 142–145 °C (Scheme 5). The structure of **20** was deduced as (H<sub>2</sub>NC<sub>5</sub>H<sub>10</sub><sup>+</sup>)<sub>2</sub>(As<sub>2</sub>S<sub>6</sub>)<sup>2-</sup> on the basis of elemental analysis and the IR and <sup>1</sup>H NMR



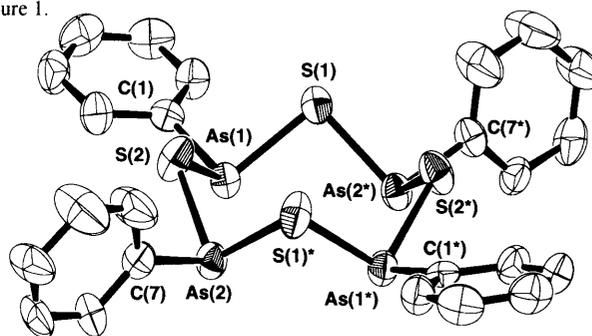
spectra which show characteristic absorption bands of piperidinium salts as observed for **9** and **15**.

**Structures of the salts 9 and 15 and the cyclic tetramer (PhAsS)<sub>4</sub> 14.** The ORTEP drawings of the salts **9** and **15** are shown in Figure 5a and b, respectively. The structure determined for **9** shows that it exists as a dimer in the solid state, in which the distances S(1)⋯N(1\*) 3.225(3) and S(2)⋯N(1) 3.473(3) Å are close to the sum of (a) the van der Waals radii of both atoms (3.26 Å),<sup>11</sup> clearly indicative of the presence of N–H⋯S hydrogen bonding between the molecules. In the dimer a 12-membered ring is formed by the hydrogen bonding (Figure 5a). The two As–S bond lengths (As(1)–S(1) 2.128(1), As(1)–S(2) 2.101(1) Å) are intermediate between the sum of their single (2.25 Å)<sup>18</sup> and double-bond covalent bond radii (2.05 Å),<sup>18</sup> suggesting delocalization of the negative charge on the AsS<sub>2</sub> moiety of **9**. The angles around the As atom (103.3(1)–116.27(4)°) are close to tetrahedral, thus yielding a distorted tetrahedral structure.

In compound **15** the three As–S bond distances are in the range 2.135(3)–2.151(2) Å, indicative of their covalent radii having values intermediate between those of single and double bond,<sup>18</sup> and suggesting delocalization of the negative charges on the AsS<sub>3</sub> group. The bond angles around the central As atom are S(1)–As(1)–S(2) 111.69(9), S(1)–As(1)–C(1) 105.8(2)°, S(1)–As(1)–S(3) 112.0(1)°, S(2)–As(1)–C(1) 106.7(2)°, S(2)–As(1)–S(3) 113.6(1)° and S(3)–As(1)–C(1) 106.5(2)°, indicating a distorted tetrahedron. As in **9**, the distances between S and N (3.195(8)–3.339(8) Å) of **15** are close to the sum of their van der Waals radii (3.35 Å), indicating the presence of N–H⋯S intermolecular hydrogen bonding.<sup>11</sup> Thus, **15** exists as a polymer in which a 12-membered ring was



**Figure 5** Molecular structures of (a) piperidinium diphenyldithioarsinate **9** and (b) di(piperidinium) phenyltrithioarsonate **15**. Details as in Figure 1.



**Figure 6** Molecular structure of 2,4,6,8-tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrasocane **14**. Detail as in Figure 1.

formed by the hydrogen bonding (Figure 5b) and is the first example of an organoarsenic trithionate in which two negative charges are delocalized on the AsS<sub>3</sub> moiety.

The ORTEP drawing of cyclic tetramer **14** is shown in Figure 6. The crown ring structure is similar to that of the tetramer (PhAsS)<sub>4</sub> prepared by treating phenylarsine with thionyl chloride,<sup>19</sup> and closely resembles those in the analogous methyl cyclo-tetramer<sup>20</sup> and *cyclo*-S<sub>8</sub>.

### 5.3. Conclusion.

A series of thioacylsulfanylarsines ((RCS<sub>2</sub>)AsPh<sub>2</sub>, (RCS<sub>2</sub>)<sub>2</sub>AsPh, (RCS<sub>2</sub>)<sub>3</sub>As) were synthesized by treating piperidinium dithio-carboxylates with Ph<sub>2</sub>AsCl, PhAsCl<sub>2</sub> or AsCl<sub>3</sub>, respectively and characterized. Their molecular structures were determined by X-ray crystallography and compared with those of the corresponding acylsulfanyl derivatives ((RCOS)AsPh<sub>2</sub>, (RCOS)<sub>2</sub>AsPh, (RCOS)<sub>3</sub>As). They exist as monomers, and the environment around the arsenic atoms is distorted tetrahedral with one lone pair at the apex. The structure of the mono-(dithiocarboxylate) is different from that of the corresponding thiocarboxylic acid derivative, while the bis and tris derivatives showed similar structure to the corresponding thio-carboxylic acid derivatives ((RCOS)<sub>2</sub>AsPh, (RCOS)<sub>3</sub>As), respectively. The new compounds showed intramolecular interactions between the thiocarbonyl sulfur and the central arsenic atom. The NBO (Natural Bond Orbital) analyses performed on the model compounds, (CH<sub>3</sub>CS<sub>2</sub>)As(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>CS<sup>1</sup><sub>2</sub>)-(CH<sub>3</sub>CS<sup>2</sup><sub>2</sub>)AsCH<sub>3</sub> at the RHF/LANL2DZ level of theory showed the presence of interactions between the nonbonding orbitals on the thiocarbonyl sulfur (n<sub>S</sub>) and the σ\*<sub>MS</sub> orbitals together with that between the n<sub>S</sub> and the σ\*<sub>MC</sub> orbitals for the former compound; for the latter the presence of both orbital interactions between n<sub>S</sub> and σ\*<sub>MS1</sub> and between n<sub>S</sub> and σ\*<sub>MS2</sub> are present. The reactions of the mono(dithiocarboxylate) derivative (R = 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) with piperidine in ethanol gave piperidinium diphenyldithioarsinate along with the corresponding *N*-thioacyl- or *N*-acyl-piperidine. A similar reaction of the bis(dithiocarboxylate) derivative (R = 4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>) gave the novel di(piperidinium) phenyltrithioarsonate in which two anion charges are delocalized on the AsS<sub>3</sub> moiety and a cyclic phenylarsine sulfide tetramer (PhAsS)<sub>4</sub>. The diphenyldithioarsinate and phenyltrithioarsonate salts exist as a dimer and a polymer, respectively, in which 12-membered rings are formed by intermolecular N–H⋯S hydrogen bonds.

### 5.4. Experimental

**General.** Melting points were determined by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on JASCO grating IR-G and Perkin-Elmer FT-IR 1640 spectrophotometers, <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR spectra (100 MHz) on JEOL JNM-α400 spectrometers in CDCl<sub>3</sub> containing Me<sub>4</sub>Si as an internal standard, the <sup>1</sup>H spectrum (60 MHz) of compound **19** on Hitachi R-24 and UV and visible spectra on Hitachi 124 and 330 spectrophotometers. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University and Bernhardt Analytisch Laboratorium.

**Materials.** All solvents were dried and distilled prior to use. Arsenic(III) chloride was obtained from Aldrich. Chlorodiphenylarsine<sup>21</sup> and dichlorophenylarsine<sup>22</sup> were prepared by heating triphenylarsine<sup>23</sup> with arsenic(III) chloride under argon at 250 °C for 5–10 h. Piperidinium carbodithioates<sup>5b</sup> and potassium carbothioates<sup>24</sup> were prepared according to the literature procedures. Piperidine and 4-bromophenacyl bromide were commercial grade.

**X-Ray crystallography.** Measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). All the structures were solved and refined using the TEXSAN<sup>®</sup> crystallographic software package.<sup>25</sup> All crystal samples were cut from the grown crystals, mounted on a glass fiber, and coated with an epoxy resin. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections [ $\Psi$  scans<sup>26</sup> (**3g**, **4e**, **5e**, **6h**, **7g**, **8e** or **14**) and DIFABS<sup>27</sup> (**9** or **15**)] were also applied. The structures were solved by direct method using SHELXS 86<sup>26</sup> for **3g**, **6h**, **7g**, **9**, **14** or **15** and SAPI91<sup>28</sup> for **4e** or **8e** MITHRIL 90<sup>29</sup> for **5e** and expanded using DIRDIF, 94.<sup>30</sup> Scattering factors for neutral atoms were from Cromer and Waber<sup>31</sup> and anomalous dispersion<sup>32</sup> was used. A full-matrix least-squares refinement was executed, with non-hydrogen atoms being anisotropic for **3g**, **4e**, **5e**, **6h**, **7g**, **8e**, **9**, **14** or **15**, and using SHELXL 93 for **8e**.<sup>33</sup> The final least-square 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. Crystal data and data collection parameters are summarized in Table 6. The bond lengths and angles and torsion angles are deposited as ESI supplementary data.

**Preparation of single crystals at 25 °C.** Compound **3g** (0.060 g) from dichloromethane (1.5 mL) and hexane (1.1 mL) for 8 days, **4e** (0.130 g) from dichloromethane (1.0 mL) and hexane (0.6 mL) for 6 days, **5e** (0.095 g) from dichloromethane (4.3 mL) and hexane (3.0 mL) for 6 days, **6h** (0.090 g) from dichloromethane (2.0 mL) and hexane (2.0 mL) for 4 days, **7g** (0.140 g) from dichloromethane (1.5 mL) and hexane (1.1 mL) for 1 week, **8e** (0.070 g) from dichloromethane (0.5 mL) and hexane (2.8 mL) for 4 days, **9** (0.035 g) from dichloromethane (3.5 mL) and hexane (2.8 mL) for 1 week, **14** (0.032 g) from dichloromethane (0.5 mL) and hexane (0.7 mL) for 3 days and **15** (0.051 g) from dichloromethane (1.5 mL) and hexane (3.0 mL) for 5 days.

**Syntheses of thioacylsulfanyl- 3–5 and acylsulfanyl-arsines 6–8.** Typical procedures are described in detail for the preparation of compounds **3e** and **6e**.

**(Thioacetylsulfanyl)diphenylarsine (3a).** Yellow crystals (34%), mp 102–104 °C;  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1196 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.79 (s, 3H, CH<sub>3</sub>), 7.18–7.30 (m, 6H) and 7.39–7.51 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  36.3 (CH<sub>3</sub>), 128.7, 129.1, 133.1, 137.6 and 233.6 (C=S).

**(Thiopropanoysulfanyl)diphenylarsine (3b).** Orange oil (86%),  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1179 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.33 (t,  $J = 7.3$ , 3H, CH<sub>3</sub>), 3.05 (q,  $J = 7.3$ , 2H, CH<sub>2</sub>), 7.27–7.29 (m, 6H) and 7.47–7.49 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  15.4 (CH<sub>3</sub>), 46.6 (CH<sub>2</sub>), 128.7, 129.3, 133.0, 137.6 and 243.0 (C=S).

**(2-Methylthiopropanoysulfanyl)diphenylarsine (3c).** Orange oil (87%),  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1198 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.31 (d,  $J = 6.7$ , 6H, CH<sub>3</sub>), 3.50 (sept,  $J = 6.7$ , 1H, CH), 7.26–7.29 (m, 6H) and 7.46–7.49 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  24.3 (CH<sub>3</sub>), 51.0 (CH), 128.6, 129.2, 132.9,

Table 6 Crystal data and refinement parameters for 3g, 4e, 5e, 6h, 7g, 8e, 9, 14 and 15

	3g	4e	5e	6h	7g	8e	9	14	15
Formula	C <sub>20</sub> H <sub>17</sub> AsOS <sub>2</sub>	C <sub>22</sub> H <sub>19</sub> AsS <sub>4</sub>	C <sub>24</sub> H <sub>21</sub> AsS <sub>6</sub>	C <sub>19</sub> H <sub>14</sub> AsClOS	C <sub>22</sub> H <sub>19</sub> AsO <sub>4</sub> S <sub>2</sub>	C <sub>24</sub> H <sub>21</sub> AsO <sub>3</sub> S <sub>3</sub>	C <sub>17</sub> H <sub>23</sub> AsNS <sub>2</sub>	C <sub>24</sub> H <sub>20</sub> As <sub>4</sub> S <sub>4</sub>	C <sub>16</sub> H <sub>29</sub> AsN <sub>2</sub> S <sub>3</sub>
<i>M</i>	412.40	486.55	576.71	400.75	486.43	528.53	379.41	736.35	420.52
Crystal system	Triclinic	Orthorhombic	Trigonal	Monoclinic	Triclinic	Trigonal	Monoclinic	Tetragonal	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> (#19)	<i>R</i> $\bar{3}$ (#147)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>P</i> $\bar{1}$ (#2)	<i>R</i> 3 <i>c</i> (#161)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)	<i>P</i> 4 <sub>2</sub> / <i>n</i> (#86)	<i>P</i> $\bar{1}$ (#2)
<i>a</i> /Å	10.464(2)	16.458(3)	18.846(1)	5.870(3)	11.304(2)	13.587(1)	9.846(8)	16.4696(5)	10.500(2)
<i>b</i> /Å	11.022(3)	22.083(4)	4.855(1)	8.373(3)	12.119(2)	27.285(2)	12.9809(9)	11.643(3)	11.643(3)
<i>c</i> /Å	8.916(2)	5.947(2)	99.71(1)	35.147(2)	8.725(1)	99.71(1)	14.2520(8)	9.971(1)	9.012(2)
$\alpha$ /°	96.09(2)				101.91(1)		96.757(6)		94.42(2)
$\beta$ /°	92.36(2)			90.44(2)	110.14(1)				108.82(1)
$\gamma$ /°	63.01(1)			1727.3(7)	106.00(3)				73.02(2)
<i>U</i> /Å <sup>3</sup>	911.2(4)	2161.3(9)	1493.4(3)			4362.0(5)			997.2(4)
<i>Z</i>	2	4	2	4	2	8	4	4	2
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	20.98	19.64	15.67	22.44	18.26	18.72	21.04	52.22	20.18
<i>T</i> /K	193	296	296	296	193	296	193	296	193
Total reflections	4424	2867	2674	4352	5114	2396	4381	3512	4802
Unique reflections	4194		2290	3972	4880	1123	4147	3105	4575
No. observations	3432 ( $I > 2\sigma(I)$ )	1243 ( $I > 2\sigma(I)$ )	985 ( $I > 1.4\sigma(I)$ )	2587 ( $I > 2\sigma(I)$ )	3055 ( $I > 2\sigma(I)$ )	607 ( $I > 2\sigma(I)$ )	2774 ( $I > 2\sigma(I)$ )	1051 ( $I > 2\sigma(I)$ )	2344 ( $I > 2\sigma(I)$ )
No. variables	218	246	95	209	262	94	191	146	199
Residuals	<i>R</i> = 0.032 <i>R</i> <sub>w</sub> = 0.035	<i>R</i> = 0.054 <i>R</i> <sub>w</sub> = 0.057	<i>R</i> = 0.084 <i>R</i> <sub>w</sub> = 0.102	<i>R</i> = 0.037 <i>R</i> <sub>w</sub> = 0.040	<i>R</i> = 0.040 <i>R</i> <sub>w</sub> = 0.041	<i>R</i> = 0.067 <sup>d</sup> <i>R</i> <sub>w</sub> = 0.231 <sup>c</sup>	<i>R</i> = 0.037 <sup>d</sup> <i>R</i> <sub>w</sub> = 0.039 <sup>b</sup>	<i>R</i> = 0.037 <sup>d</sup> <i>wR</i> 2 = 0.135 <sup>e</sup>	<i>R</i> = 0.066 <sup>d</sup> <i>R</i> <sub>w</sub> = 0.067 <sup>b</sup>

137.6 and 248.7 (C=S).

**Diphenyl(thiobenzoylsulfanyl)arsine (3d).** Red purple crystals (84%), mp 82–84 °C (Calc. for C<sub>19</sub>H<sub>15</sub>AsS<sub>2</sub>: C, 59.68; H, 3.95. Found: C, 59.59; H, 4.06%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1218 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 307 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  15 900) and 527 (170);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.32–7.49 (m, 8H) and 7.51–7.86 (m, 7H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.1, 128.5, 128.8, 129.4, 133.1, 133.5, 137.9, 138.3 and 229.0 (C=S).

**(4-Methylthiobenzoylsulfanyl)-diphenylarsine (3e).** To a solution of piperidinium 4-methylbenzenecarbodithioate (0.269 g, 1.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added Ph<sub>2</sub>AsCl (0.264 g, 1.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and the mixture stirred at 20 °C for 1 h. After addition of CH<sub>2</sub>Cl<sub>2</sub> (100 mL), the mixture was washed with water (3 x 90 mL), followed by drying over MgSO<sub>4</sub> (*ca.* 2 g) for 1 h. The solvent was removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in diethyl ether (5 mL), and allowed to stand in a refrigerator (–20 °C) for 24 h to give compound 3e as red crystals 0.358g (91%), mp 85–87 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsS<sub>2</sub>: C, 60.60; H, 4.32. Found: C, 60.50; H, 4.36%).  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1227 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 330 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  17 000) and 527 (170);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.22 (s, 3H, CH<sub>3</sub>), 7.03 (d, *J* = 8.1, 2H), 7.24–7.27 (m, 6H), 7.49–7.53 (m, 4H) and 8.06 (d, *J* = 8.1, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.4 (CH<sub>3</sub>), 127.1, 128.6, 128.6, 129.2, 133.0, 137.9, 141.9, 143.6 and 227.8 (C=S).

**(2-Methoxythiobenzoylsulfanyl)-diphenylarsine (3f).** Red crystals (94%), mp 62–65 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsOS<sub>2</sub>: C, 58.25; H, 4.16. Found: C, 58.37; H, 4.22%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1251 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$

3.66 (s, 3H, CH<sub>3</sub>O), 6.77–6.84 (m, 2H), 7.20–7.25 (m, 8H) and 7.50–7.52 (m, 4H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 55.6 (CH<sub>3</sub>O), 111.6, 120.0, 128.5, 128.8, 129.1, 131.4, 132.8, 136.7, 137.6, 154.4 and 230.5 (C=S).

**(4-Methoxythiobenzoylsulfanyl)diphenylarsine (3g).** Red purple crystals (94%), mp 115–117 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsOS<sub>2</sub>: C, 58.25; H, 4.16. Found: C, 58.48; H, 4.27%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1264 (KBr);  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 351 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 20 900) and 518 (300);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 3.80 (s, 3H, CH<sub>3</sub>O), 6.80 (d,  $J$  = 8.9, 2H), 7.28–7.34 (m, 6H), 7.54–7.56 (m, 4H) and 8.22 (d,  $J$  = 8.9, 2H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 55.5 (CH<sub>3</sub>O), 113.3, 128.7, 129.3, 129.6, 133.2, 137.9, 138.2, 163.9 and 226.2 (C=S).

**(4-Chlorothiobenzoylsulfanyl)diphenylarsine (3h).** Red purple crystals (88%), mp 69–72 °C (Calc. for C<sub>19</sub>H<sub>14</sub>AsClS<sub>2</sub>: C, 54.75; H, 3.39. Found: C, 55.01; H, 3.63%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1224 and 1213 (KBr);  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 316 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 24 000) and 533 (200);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.29 (d,  $J$  = 8.7, 2H), 7.34–7.38 (m, 6H), 7.50–7.57 (m, 4H) and 8.09 (d,  $J$  = 8.7, 2H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 128.3, 128.5, 128.9, 129.6, 133.2, 137.8, 139.3, 142.7 and 227.0 (C=S).

**Diphenyl(1-thionaphthoysulfanyl)arsine (3i).** Red crystals (92%), mp 170–175 °C (Calc. for C<sub>23</sub>H<sub>17</sub>AsS<sub>2</sub>: C, 63.88; H, 3.96. Found: C, 64.12; H, 3.66%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1238 (KBr);  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 290 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 20 900) and 494 (450);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.23–7.30 (m, 8H), 7.33–7.41 (m, 1H), 7.52–7.70 (m, 5H), 7.72–7.74 (m, 2H) and 8.22–8.24 (m, 1H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 123.8, 124.5, 125.1, 126.2, 126.8, 128.0, 128.8, 129.5, 129.9, 133.1, 133.5, 133.6, 137.5, 145.8 and 233.4 (C=S).

**Bis(thioacetylsulfanyl)phenylarsine (4a).** Yellow crystals (15%), mp 105–109 °C;  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1178 (KBr);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.88 (s, 6H, CH<sub>3</sub>), 7.31–7.42 (m, 3H) and 7.72–7.74 (m, 2H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 41.0 (CH<sub>3</sub>), 128.3, 129.0, 131.6, 133.6 and 238.7 (C=S).

**Bis(thiopropanoysulfanyl)phenylarsine (4b).** Red orange oil (76%),  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1176 (neat);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.32 (t,  $J$  = 7.3, 6H, CH<sub>3</sub>), 3.03 (q,  $J$  = 7.3, 4H, CH<sub>2</sub>), 7.27–7.33 (m, 3H) and 7.70–7.75 (m, 2H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 15.0 (CH<sub>3</sub>), 46.7 (CH<sub>2</sub>), 128.2, 129.6, 133.4, 139.6 and 245.7 (C=S).

**Bis(2-methylthiopropanoysulfanyl)phenylarsine (4c).** Red oil (84%),  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1197 (neat);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.29 (d,  $J$  = 6.7, 12H, CH<sub>3</sub>), 3.40 (sept,  $J$  = 6.7, 2H, CH), 7.40–7.47 (m, 3H) and 7.72–7.76 (m, 2H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 24.1 (CH<sub>3</sub>), 51.4 (CH), 128.4, 129.6, 133.3, 139.8 and 251.7 (C=S).

**Bis(thiobenzoylsulfanyl)phenylarsine (4d).** Red orange crystals (67%), mp 119–122 °C (Calc. for C<sub>20</sub>H<sub>15</sub>AsS<sub>4</sub>: C, 52.39; H, 3.30. Found: C, 52.18; H, 3.26%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1238 and 1224 (KBr);  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 315 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 34 700), 506 (500);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 7.28–7.31 (m, 3H), 7.36 (t,  $J$  = 7.6, 4H), 7.54 (t,  $J$  = 7.6, 2H), 7.83–7.89 (m, 2H) and 8.16 (d,  $J$  = 7.6, 4H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 127.0, 128.3, 128.4, 129.6, 133.4, 133.8, 140.6, 143.8 and 231.0 (C=S).

**Bis(4-methylthiobenzoylsulfanyl)phenylarsine (4e).** Red crystals (70%), mp 183–185 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsS<sub>4</sub>: C, 54.31; H, 3.94. Found: C, 54.37; H, 4.00%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> (C=S) 1241 (KBr);  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 333 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 40 000) and 505 (660);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.37 (s, 6H, CH<sub>3</sub>), 7.17 (d,  $J$  = 8.3, 4H), 7.29–7.34 (m, 3H), 7.87–7.89 (m, 2H) and 8.10 (d,  $J$  = 8.3, 4H);  $\delta_{\text{C}}$ (CDCl<sub>3</sub>) 21.7 (CH<sub>3</sub>), 127.1, 128.3, 129.0, 129.4, 129.5, 133.8, 141.6, 144.7 and 230.3 (C=S).

**Bis(2-methoxythiobenzoylsulfanyl)phenylarsine (4f).** Red orange crystals (83%), mp 105–107 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>2</sub>S<sub>4</sub>: C, 50.96; H, 3.69. Found: C, 51.14; H, 3.79%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1247 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.81 (s, 6H, CH<sub>3</sub>O), 6.86–6.93 (m, 4H), 7.30–7.38 (m, 5H), 7.66–7.68 (m, 2H) and 7.86–7.88 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.9 (CH<sub>3</sub>O), 112.0, 120.2, 128.2, 129.4, 129.9, 132.7, 133.3, 135.5, 140.1, 155.7 and 231.4 (C=S).

**Bis(4-methoxythiobenzoylsulfanyl)phenylarsine (4g).** Red orange crystals (77%), mp 165–167 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>2</sub>S<sub>4</sub>: C, 50.96; H, 3.69. Found: C, 50.99; H, 3.72%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1265 and 1240 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 352 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  37 000) and 498 (1 000);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.84 (s, 6H, CH<sub>3</sub>O), 6.83 (d,  $J = 8.9$ , 4H), 7.27–7.32 (m, 3H), 7.87–7.90 (m, 2H) and 8.23 (d,  $J = 8.9$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.7 (CH<sub>3</sub>O), 113.4, 128.2, 129.4, 129.6, 133.8, 137.3, 141.5, 164.5 and 228.1 (C=S).

**Bis(4-chlorothiobenzoylsulfanyl)phenylarsine (4h).** Red crystals (64%), mp 150–153 °C (Calc. for C<sub>20</sub>H<sub>13</sub>AsCl<sub>2</sub>S<sub>4</sub>: C, 45.55; H, 2.48. Found: C, 45.62; H, 2.55%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1237 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 326 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  39 000) and 507 (900);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.30–7.32 (m, 3H), 7.34 (d,  $J = 8.7$ , 4H), 7.84–7.87 (m, 2H) and 8.10 (d,  $J = 8.7$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.2, 128.2, 128.4, 128.5, 129.8, 133.8, 140.2, 142.0 and 228.9 (C=S).

**Bis(1-naphthoylsulfanyl)phenylarsine (4i).** Red orange crystals (83%), mp 113–118 °C (Calc. for C<sub>28</sub>H<sub>19</sub>AsS<sub>4</sub>: C, 60.20; H, 3.43. Found: C, 60.29; H, 3.57%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1227 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 292 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  32 000) and 495 (620);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.41–7.49 (m, 9H), 7.61–7.63 (m, 2H), 7.82–7.89 (m, 4H), 7.96–7.98 (m, 2H) and 8.16–8.18 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  124.5, 124.6, 125.2, 126.5, 127.2, 128.3, 128.6, 128.9, 130.1, 130.8, 133.7, 133.9, 139.4, 145.5 and 235.4 (C=S).

**Tris(thioacethylsulfanyl)arsine (5a).** Red crystals (20%), mp 95–97 °C;  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1194 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.87 (s, 9H, CH<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  41.0 (CH<sub>3</sub>) and 239.2 (C=S).

**Tris(thiopropanoylsulfanyl)arsine (5b).** Red oil (56%),  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1174 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.38 (t,  $J = 7.3$ , 9H, CH<sub>3</sub>) and 3.06 (q,  $J = 7.3$ , 6H, CH<sub>2</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.8 (CH<sub>3</sub>), 46.8 (CH<sub>2</sub>) and 250.1 (C=S).

**Tris(2-methylthiopropanoylsulfanyl)arsine (5c).** Yellow crystals (45%), mp 42–44 °C;  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1202 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.35 (d,  $J = 6.4$ , 18H, CH<sub>3</sub>) and 3.41 (sept,  $J = 6.4$ , 3H, CH);  $\delta_{\text{C}}(\text{CDCl}_3)$  24.0 (CH<sub>3</sub>), 50.1 (CH) and 256.2 (C=S).

**Tris(thiobenzoylsulfanyl)arsine (5d).** Red crystals (80%), mp 128–129 °C (Calc. for C<sub>21</sub>H<sub>15</sub>AsS<sub>6</sub>: C, 47.17; H, 2.83. Found: C, 46.86; H, 2.89%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1241 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 313 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  42 000) and 511 (650);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.29 (t,  $J = 7.9$ , 6H), 7.48 (t,  $J = 7.9$ , 3H) and 8.10 (d,  $J = 7.9$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  126.7, 128.1, 133.5, 143.0 and 234.2 (C=S).

**Tris(4-methylthiobenzoylsulfanyl)arsine (5e).** Red crystals (78%), mp 68–70 °C (Calc. for C<sub>24</sub>H<sub>21</sub>AsS<sub>6</sub>: C, 49.98; H, 3.67. Found: C, 50.02; H, 3.74%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1243 and 1228 (KBr);  $\lambda_{\max}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 330 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  42 000) and 511 (800);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.37 (s, 9H, CH<sub>3</sub>), 7.18 (d,  $J = 8.4$ , 6H) and 8.10 (d,  $J = 8.4$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.8 (CH<sub>3</sub>), 127.1, 129.8, 141.4, 145.1 and 234.1 (C=S).

**Tris(2-methoxythiobenzoylsulfanyl)arsine (5f).** Orange crystals (74%), mp 72–74 °C (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>3</sub>S<sub>6</sub>: C, 46.14; H, 3.39. Found: C, 46.44; H, 3.52%);  $\nu_{\max}/\text{cm}^{-1}$  (C=S) 1249 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.83 (s, 9H, CH<sub>3</sub>O), 6.83–6.98 (m, 6H), 7.34–7.43 (m, 3H) and 7.80–

7.88 (m, 3H);  $\delta_{\text{C}}(\text{CDCl}_3)$  56.0 (CH<sub>3</sub>O), 111.9, 120.2, 129.4, 131.4, 135.9, 156.0 and 236.2 (C=S).

**Tris(4-methoxythiobenzoylsulfanyl)arsine (5g).** Red crystals (82%), mp 128–129 °C (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>3</sub>S<sub>6</sub>: C, 46.14; H, 3.39. Found: C, 46.51; H, 3.66%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=S) 1241 (KBr);  $\lambda_{\text{max}}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 355 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  74 000) and 505 (1 300);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.76 (s, 9H, CH<sub>3</sub>O), 6.76 (d,  $J = 9.0$ , 6H) and 8.16 (d,  $J = 9.0$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.5 (CH<sub>3</sub>O), 113.2, 129.2, 136.8, 164.5 and 231.0 (C=S).

**Tris(4-chlorothiobenzoylsulfanyl)arsine (5h).** Orange crystals (86%), mp 140–145 °C (Calc. for C<sub>21</sub>H<sub>12</sub>AsCl<sub>3</sub>S<sub>6</sub>: C, 39.53; H, 1.90. Found: C, 39.46; H, 2.10%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=S) 1229 (KBr);  $\lambda_{\text{max}}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 323 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  47 000) and 510 (700);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.37 (d,  $J = 8.8$ , 6H), 8.11 (d,  $J = 8.8$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.3, 128.6, 129.0, 140.8 and 232.7 (C=S).

**Tris(1-thionaphthoylsulfanyl)arsine (5i).** Orange crystals (74%), mp 156–157 °C (Calc. for C<sub>33</sub>H<sub>21</sub>AsS<sub>6</sub>: C, 57.88; H, 3.09. Found: C, 57.58; H, 2.83%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=S) 1223 (KBr);  $\lambda_{\text{max}}/\text{nm}$  (CH<sub>2</sub>Cl<sub>2</sub>) 292 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  36 300) and 500 (1 200);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.33–7.50 (m, 12H) and 7.68–7.88 (m, 9H);  $\delta_{\text{C}}(\text{CDCl}_3)$  124.6, 124.8, 125.2, 126.0, 126.5, 127.0, 128.2, 131.3, 133.6, 145.1 and 239.3 (C=S).

**(Acetylsulfanyl)diphenylarsine (6a).** Colorless oil (91%),  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1682 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.43 (s, 3H, CH<sub>3</sub>), 7.31–7.34 (m, 6H) and 7.50–7.52 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  32.2 (CH<sub>3</sub>), 128.7, 129.3, 133.0, 138.2 and 195.9 (C=O).

**(2,2-Dimethylpropanoylsulfanyl)diphenylarsine (6b).** Yellow oil (88%),  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1674 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.29 (s, 9H, CH<sub>3</sub>), 7.32–7.35 (m, 6H) and 7.52–7.54 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.8 (CH<sub>3</sub>), 47.6 (CCH<sub>3</sub>), 128.7, 129.2, 133.0, 138.5 and 195.9 (C=O).

**(Benzoylsulfanyl)diphenylarsine (6c).** Colorless crystals (87%), mp 76–78 °C (Calc. for C<sub>19</sub>H<sub>15</sub>AsOS: C, 62.30; H, 4.13. Found: C, 62.67; H, 4.32%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1644 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.34–7.39 (m, 6H), 7.43 (t,  $J = 7.8$ , 2H), 7.56 (t,  $J = 7.8$ , 1H), 7.59–7.62 (m, 4H) and 8.07 (d,  $J = 7.8$ , 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.3, 128.5, 128.8, 129.4, 133.2, 133.5, 137.2, 138.4 and 192.1 (C=O).

**(2-Methylbenzoylsulfanyl)diphenylarsine (6d).** Colorless crystals (87%), mp 63–67 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsOS: C, 63.16; H, 4.51. Found: C, 63.46; H, 4.72%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1642 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.45 (s, 3H, CH<sub>3</sub>), 7.20–7.34 (m, 8H), 7.55–7.59 (m, 4H) and 7.93–7.97 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.0 (CH<sub>3</sub>), 125.7, 128.8, 129.7, 129.9, 130.3, 132.0, 134.0, 136.2, 137.4, 138.1 and 194.7 (C=O).

**(4-Methylbenzoylsulfanyl)diphenylarsine (6e).** To a solution of Ph<sub>2</sub>AsCl (0.271 g, 1.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), potassium 4-methylbenzenecarbothioate (0.196 g, 1.03 mmol) was added and the mixture was stirred at 20 °C for 1 h. After addition of CH<sub>2</sub>Cl<sub>2</sub> (100 mL), the mixture was washed with water (3 x 90 mL), followed by drying over MgSO<sub>4</sub> (ca. 2 g) for 1 h. The solvents were removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and hexane (10 mL) and allowed to stand in a refrigerator (–20 °C) for 24 h to give compound **6e** as colorless crystals (0.358 g, 92%), mp 96–99 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsOS: C, 63.16; H, 4.51. Found: C, 62.95; H, 4.61%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1644 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.39 (s, 3H, CH<sub>3</sub>), 7.21 (d,  $J = 8.1$ , 2H), 7.34–7.38 (m, 6H), 7.56–7.60 (m, 4H) and 7.94 (d,  $J = 8.1$ , 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.7 (CH<sub>3</sub>), 128.4, 128.8,

129.2, 129.4, 133.2, 134.8, 138.5, 144.5 and 191.7 (C=O).

**(2-Methoxybenzoylsulfanyl)diphenylarsine (6f).** Colorless crystals (89%), mp 94–96 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsO<sub>2</sub>S: C, 60.61; H, 4.32. Found: C, 60.73; H, 4.54%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1621 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.82 (s, 3H, CH<sub>3</sub>O), 6.90–6.95 (m, 2H), 7.32–7.33 (m, 6H), 7.38–7.42 (m, 1H), 7.57–7.58 (m, 4H) and 7.78–7.83 (m, 1H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.7 (CH<sub>3</sub>O), 112.0, 120.2, 128.5, 128.6, 129.1, 130.3, 133.1, 133.8, 138.5, 157.8 and 190.8 (C=O).

**(4-Methoxybenzoylsulfanyl)diphenylarsine (6g).** Colorless crystals (87%), mp 42–44 °C (Calc. for C<sub>20</sub>H<sub>17</sub>AsO<sub>2</sub>S: C, 60.61; H, 4.32. Found: C, 60.55; H, 4.17%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1629 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.84 (s, 3H, CH<sub>3</sub>O), 6.89 (d,  $J = 9.0$ , 2H), 7.33–7.36 (m, 6H), 7.60–7.64 (m, 4H) and 8.02 (d,  $J = 9.0$ , 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.5 (CH<sub>3</sub>O), 113.7, 128.8, 129.3, 130.6, 132.4, 133.2, 138.6, 163.9 and 190.5 (C=O).

**(4-Chlorobenzoylsulfanyl)diphenylarsine (6h).** Colorless crystals (91%), mp 94–96 °C (lit.,<sup>2c</sup> 87–88 °C) (Calc. for C<sub>19</sub>H<sub>14</sub>AsClOS: C, 56.95; H, 3.52. Found: C, 56.83; H, 3.58%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1655 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.36–7.38 (m, 6H), 7.39 (d,  $J = 7.8$ , 2H), 7.56–7.60 (m, 4H) and 7.99 (d,  $J = 7.8$ , 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.8, 128.9, 129.5, 129.6, 133.2, 135.6, 138.2, 140.0 and 190.8 (C=O).

**(4-Nitrobenzoylsulfanyl)diphenylarsine (6i).** Yellow crystals (60%), mp 101–103 °C (Calc. for C<sub>19</sub>H<sub>14</sub>AsNO<sub>3</sub>S: C, 55.48; H, 3.43. Found: C, 55.75; H, 3.60%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1655 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.39–7.41 (m, 6H), 7.57–7.59 (m, 4H), 8.18 (d,  $J = 8.0$ , 2H) and 8.27 (d,  $J = 8.0$ , 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  123.8, 129.0, 129.2, 129.8, 133.2, 137.8, 141.7, 150.0 and 190.8 (C=O).

**Bis(acetylsulfanyl)phenylarsine (7a).** Yellow oil (91%),  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1694 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.43 (s, 6H, CH<sub>3</sub>), 7.31–7.34 (m, 3H) and 7.50–7.52 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$   $\delta$  32.1 (CH<sub>3</sub>), 128.7, 130.2, 132.2, 137.4 and 196.3 (C=O).

**Bis(2,2-dimethylpropanoylsulfanyl)phenylarsine (7b).** Yellow crystals (93%), mp 63–67 °C (Calc. for C<sub>16</sub>H<sub>23</sub>AsO<sub>2</sub>S<sub>2</sub>: C, 49.73; H, 6.00. Found: C, 49.82; H, 6.13%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1672 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.23 (s, 18H, CH<sub>3</sub>), 7.26–7.42 (m, 3H) and 7.67–7.80 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.6 (CH<sub>3</sub>), 47.6 (CCH<sub>3</sub>), 128.6, 130.0, 132.1, 138.4 and 207.8 (C=O).

**Bis(benzoylsulfanyl)phenylarsine (7c).** Colorless crystals (95%), mp 130–131 °C (lit.,<sup>2c</sup> 132–132 °C) (Calc. for C<sub>20</sub>H<sub>15</sub>AsO<sub>2</sub>S<sub>2</sub>: C, 56.34; H, 3.55. Found: C, 56.15; H, 3.41%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1639 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.38–7.40 (m, 3H), 7.42 (t,  $J = 7.6$ , 4H), 7.56 (t,  $J = 7.6$ , 2H), 7.88–7.90 (m, 2H) and 8.00 (d,  $J = 7.6$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.3, 128.6, 128.9, 130.3, 132.5, 133.9, 136.6, 138.3 and 192.8 (C=O).

**Bis(2-methylbenzoylsulfanyl)phenylarsine (7d).** Colorless crystals (43%), mp 75–77 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>2</sub>S<sub>2</sub>: C, 58.15; H, 4.21. Found: C, 58.29; H, 4.10%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1641 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.47 (s, 6H, CH<sub>3</sub>), 7.20–7.25 (m, 4H), 7.36–7.47 (m, 5H), 7.88–7.90 (m, 2H) and 7.94–7.96 (m, 2H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.1 (CH<sub>3</sub>), 125.8, 128.8, 130.2, 130.3, 131.8, 132.3, 132.5, 136.7, 137.7, 138.2 and 194.6 (C=O).

**Bis(4-methylbenzoylsulfanyl)phenylarsine (7e).** Colorless crystals (96%), mp 164–167 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>2</sub>S<sub>2</sub>: C, 58.15; H, 4.21. Found: C, 58.03; H, 4.34%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1626 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.38 (s, 6H, CH<sub>3</sub>), 7.21 (d,  $J = 8.2$ , 4H), 7.34–7.40 (m, 3H), 7.87–7.90 (m, 2H) and 7.89 (d,  $J = 8.2$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.7 (CH<sub>3</sub>), 128.4, 128.8, 129.2, 129.4, 133.2, 134.8, 138.5, 144.5 and 192.4 (C=O).

**Bis(2-methoxybenzoylsulfanyl)phenylarsine (7f).** Colorless crystals (89%), mp 93–96 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>4</sub>S<sub>2</sub>: C, 54.32; H, 3.94. Found: C, 54.40; H, 3.96%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1606 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.87 (s, 6H, CH<sub>3</sub>O), 6.92–6.99 (m, 4H), 7.34–7.46 (m, 5H) and 7.80–7.90 (m, 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.8 (CH<sub>3</sub>O), 112.0, 120.3, 126.1, 128.6, 129.8, 130.4, 132.4, 134.4, 138.9, 158.4 and 191.3 (C=O).

**Bis(4-methoxybenzoylsulfanyl)phenylarsine (7g).** Colorless crystals (96%), mp 149–151 °C (Calc. for C<sub>22</sub>H<sub>19</sub>AsO<sub>4</sub>S<sub>2</sub>: C, 54.32; H, 3.94. Found: C, 54.04; H, 3.95%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1628 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.82 (s, 6H, CH<sub>3</sub>O), 6.88 (d,  $J = 8.9$ , 4H), 7.34–7.41 (m, 3H), 7.87–7.90 (m, 2H) and 7.97 (d,  $J = 8.9$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.5 (CH<sub>3</sub>O), 113.7, 128.8, 129.5, 130.1, 130.6, 132.4, 138.7, 164.2 and 191.1 (C=O).

**Bis(4-chlorobenzoylsulfanyl)phenylarsine (7h).** Colorless crystals (91%), mp 158–160 °C (Calc. for C<sub>20</sub>H<sub>13</sub>AsCl<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 48.50; H, 2.65. Found: C, 48.64; H, 2.58%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1612 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.35–7.41 (m, 3H), 7.41 (d,  $J = 7.8$ , 4H), 7.85–7.88 (m, 2H) and 7.94 (d,  $J = 7.8$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.0, 129.0, 129.7, 130.6, 132.5, 135.0, 137.8, 140.5 and 191.6 (C=O).

**Bis(4-nitrobenzoylsulfanyl)phenylarsine (7i).** Yellow crystals (44%), mp 104–106 °C (Calc. for C<sub>20</sub>H<sub>13</sub>AsN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 46.52; H, 2.54. Found: C, 46.82; H, 2.69%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1626 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.44–7.47 (m, 3H), 7.86–7.89 (m, 2H), 8.16 (d,  $J = 8.0$ , 4H) and 8.29 (d,  $J = 8.0$ , 4H);  $\delta_{\text{C}}(\text{CDCl}_3)$  123.9, 129.2, 129.3, 131.0, 132.6, 136.8, 140.8, 150.8 and 191.3 (C=O).

**Tris(acetylsulfanyl)arsine (8a).** Yellow oil (61%),  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1694 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.47 (s, 9H, CH<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  32.1 (CH<sub>3</sub>) and 196.4 (C=O).

**Tris(2,2-dimethylpropanoylsulfanyl)arsine (8b).** Colorless oil (66%),  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1668 (neat);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.26 (s, 27H, CH<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.5 (CH<sub>3</sub>), 47.7 (CCH<sub>3</sub>) and 207.8 (C=O).

**Tris(benzoylsulfanyl)arsine (8c).** Colorless crystals (73%), mp 179–182 °C (lit.,<sup>9</sup> 155–157 °C) (Calc. for C<sub>21</sub>H<sub>15</sub>AsO<sub>3</sub>S<sub>3</sub>: C, 51.85; H, 3.11. Found: C, 51.35; H, 3.08%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1631 (KBr) (lit.,<sup>9</sup> 1630 cm<sup>-1</sup>);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.46 (d,  $J = 7.4$ , 6H), 7.60 (d,  $J = 7.4$ , 3H) and 8.02 (d,  $J = 7.4$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  128.5, 128.7, 134.2, 136.3 and 193.0 (C=O).

**Tris(2-methylbenzoylsulfanyl)arsine (8d).** Colorless crystals (56%), mp 89–92 °C (lit.,<sup>9</sup> 80 °C) (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>3</sub>S<sub>3</sub>: C, 54.54; H, 4.00. Found: C, 54.42; H, 3.97%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1637 (KBr) (lit.,<sup>9</sup> 1637 cm<sup>-1</sup>);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.56 (s, 9H, CH<sub>3</sub>), 7.24–7.28 (m, 6H), 7.40–7.44 (m, 3H) and 7.94–7.96 (m, 3H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.3 (CH<sub>3</sub>), 125.9, 130.5, 131.9, 132.7, 136.2, 138.1 and 194.7 (C=O).

**Tris(4-methylbenzoylsulfanyl)arsine (8e).** Colorless crystals (98%), mp 137–139 °C (lit.,<sup>9</sup> 128–130 °C) (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>3</sub>S<sub>3</sub>: C, 54.54; H, 4.00. Found: C, 54.29; H, 4.07%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1639 (KBr) (lit.,<sup>9</sup> 1620 cm<sup>-1</sup>);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.40 (s, 9H, CH<sub>3</sub>), 7.23 (d,  $J = 8.2$ , 6H) and 7.80 (d,  $J = 8.2$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.8 (CH<sub>3</sub>), 128.6, 129.4, 133.9, 145.3 and 192.5 (C=O).

**Tris(2-methoxybenzoylsulfanyl)arsine (8f).** Colorless crystals (66%), mp 150–155 °C (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>6</sub>S<sub>3</sub>: C, 50.00; H, 3.67. Found: C, 50.28; H, 3.89%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1611 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.87 (s, 9H, CH<sub>3</sub>O), 6.95 (t,  $J = 7.6$ , 6H), 7.46 (t,  $J = 7.6$ , 3H) and 7.86 (d,  $J = 7.6$ , 3H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.7 (CH<sub>3</sub>O), 112.0, 120.2, 125.3, 130.3, 134.8, 158.7 and

191.4 (C=O).

**Tris(4-methoxybenzoylsulfanyl)arsine (8g).** Colorless crystals (86%), mp 94–96 °C (Calc. for C<sub>24</sub>H<sub>21</sub>AsO<sub>6</sub>S<sub>3</sub>: C, 50.00; H, 3.67. Found: C, 49.70; H, 3.84%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1627 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  3.86 (s, 9H, CH<sub>3</sub>O), 6.90 (d,  $J = 8.7$ , 6H) and 7.98 (d,  $J = 8.7$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  55.6 (CH<sub>3</sub>O), 113.9, 129.3, 130.8, 164.4 and 191.3 (C=O).

**Tris(4-chlorobenzoylsulfanyl)arsine (8h).** Colorless crystals (83%), mp 161–164 °C (Calc. for C<sub>21</sub>H<sub>12</sub>AsCl<sub>3</sub>O<sub>3</sub>S<sub>3</sub>: C, 42.77; H, 2.05. Found: C, 42.99; H, 1.92%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1660 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.43 (d,  $J = 8.8$ , 6H) and 7.94 (d,  $J = 8.8$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.1, 129.8, 134.5, 141.0 and 191.7 (C=O).

**Tris(4-nitrobenzoylsulfanyl)arsine (8i).** Yellow crystals (99%), mp 101–103 °C (Calc. for C<sub>21</sub>H<sub>12</sub>AsN<sub>3</sub>O<sub>9</sub>S<sub>3</sub>: C, 40.59; H, 1.95. Found: C, 41.72; H, 2.04%);  $\nu_{\max}/\text{cm}^{-1}$  (C=O) 1625 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  8.19 (d,  $J = 8.0$ , 6H) and 8.34 (d,  $J = 8.0$ , 6H);  $\delta_{\text{C}}(\text{CDCl}_3)$  124.1, 129.5, 140.3, 151.1 and 191.6 (C=O).

**Reaction of compound 3e with piperidine (Table 4, entry 2).** A suspension of compound 3e (0.198 g, 0.50 mmol) in ethanol (40 mL) was added dropwise to a solution of piperidine (0.085 g, 1.00 mmol) in ethanol (20 mL). This suspension was stirred at 78 °C for 9 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitates gave piperidinium diphenyldithioarsinate 9 as colorless needles (0.072 g, 38%). *N*-4-Methylthiobenzoylpiperidine 10-S was obtained from this filtrate as yellow crystals (0.076 g, 69%). <sup>1</sup>H and <sup>13</sup>C NMR spectra were exactly consistent with those of authentic samples prepared by heating piperidinium 4-methylbenzenecarbodithioate. Piperidinium diphenyldithioarsinate 9: mp 155–157 °C (Calc. for C<sub>17</sub>H<sub>22</sub>AsNS<sub>2</sub>: C, 53.82; H, 5.84; N, 3.69. Found: C, 53.44; H, 5.70; N, 3.82%);  $\nu_{\max}/\text{cm}^{-1}$  3014, 2885, 1603, 1609, 1491, 1456, 1410, 1324, 1178, 1098, 1043, 1019, 961, 948, 881, 772, 718 and 699 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.41–1.46 (m, 2H), 1.60–1.66 (m, 4H), 3.04–3.06 (m, 4H), 7.33–7.41 (m, 6H), 8.04–8.06 (m, 4H) and 9.02 (br, 2H, NH<sub>2</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  22.3, 22.5, 44.2, 128.4, 129.7, 130.0 and 143.5.

**Reaction of compound 6e with piperidine (Table 4, entry 3).** A suspension of compound 6e (0.380 g, 1.00 mmol) in ethanol (40 mL) was added dropwise to a solution of piperidine (0.086 g, 1.01 mmol) in ethanol (20 mL). This suspension was stirred at 20 °C for 3 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitates gave piperidinium 4-methylbenzenecarbothioate 11-O as a colorless solid (0.040 g, 17%). To the filtrate was added toluene (10 mL) and the mixture allowed to stand in a refrigerator (–20 °C) for 48 h. Filtration of the resulting precipitate gave 9 as colorless needles (0.019 g, 5%). *N*-4-Methylbenzoylpiperidine 10-O was obtained from this filtrate as colorless oil (0.168 g, 83%).

**Reaction of compound 4e with piperidine (Table 5, entry 1).** A suspension of compound 4e (0.487 g, 1.00 mmol) in ethanol (80 mL) was added dropwise to a solution of piperidine (0.173 g, 2.03 mmol) in ethanol (40 mL), and this suspension was stirred at 20 °C for 5 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitate gave di(piperidinium) phenyltrithioarsonate 15 as a colorless solid (0.057 g, 14%). Evaporation of the filtrate under reduced pressure gave 10-S (0.149 g, 35%). Di(piperidinium) phenyltrithioarsonate 15: mp 154–157 °C (Calc. for C<sub>16</sub>H<sub>29</sub>AsN<sub>2</sub>S<sub>3</sub>: C, 45.70; H, 6.95; N, 6.66. Found: C, 45.54; H, 6.87; N, 6.51%);  $\nu_{\max}/\text{cm}^{-1}$

2950, 2710, 2500, 1579, 1455, 1441, 1308, 1078, 1039, 938, 872, 754, 703 and 651 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.59–1.65 (m, 4H), 1.82–1.88 (m, 8H), 3.23–3.25 (m, 8H), 7.33–7.35 (m, 3H), 7.42–7.44 (m, 2H) and 8.23 (br, 4H,  $\text{NH}_2$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  22.6, 22.9, 44.8, 128.3, 129.8, 131.0 and 133.0.

**Reaction of compound 7e with piperidine (Table 5, entry 5).** A suspension of compound **7e** (0.454 g, 1.00 mmol) in ethanol (80 mL) was added dropwise to a solution of piperidine (0.173 g, 2.03 mmol) in ethanol (40 mL), and this suspension was stirred at 20 °C for 3 h. The solvent was evaporated under reduced pressure (20 °C/53 Pa), followed by addition of ether (20 mL). Filtration of the resulting precipitate gave **11-O** as a colorless solid (0.190 g, 40%). The filtrate was added to ethanol (20 mL), and filtration of the resulting precipitate gave 0.162 g, (66%) of 2,4,6,8-tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14** as a colorless solid which was recrystallized from dichloromethane-hexane. The compound **10-O** was obtained from this filtrate as colorless oil (0.227 g, 56%). 2,4,6,8-Tetraphenyl-1,3,5,7,2,4,6,8-tetrathiatetrarsocane **14**: mp 174–175 °C (lit.,<sup>20</sup> 175–176 °C) (Calc. for  $\text{C}_{24}\text{H}_{20}\text{As}_4\text{S}_4$ : C, 39.15; H, 2.74. Found: C, 39.32; H, 2.66%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3042, 1571, 1475, 1429, 1179, 1062, 1019, 998, 728, 687 and 468 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  7.34–7.45 (m, 12H) and 7.77–7.87 (m, 8H);  $\delta_{\text{C}}(\text{CDCl}_3)$  129.0, 130.0, 131.6 and 142.3.

**Reaction of di(piperidinium) phenyltrithioarsonate 15 with 4-bromophenacyl bromide (Scheme 4).** A two molar amount of 4-bromophenacyl bromide (0.139 g, 0.50 mmol) in ethanol (5.0 mL) was added to a suspension of compound **15** (0.105 g, 0.25 mmol) in ethanol (20 mL) and refluxed for 10 min. The solvent was evaporated and ether (50 mL) was added, followed by washing with water (3 x 90 mL) and drying over  $\text{Na}_2\text{SO}_4$  (ca. 2 g) for 1 h. The solvents were removed under reduced pressure by use of a rotary evaporator (30 °C/2.7 kPa). The resulting residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (2.0 mL) and hexane (0.5 mL) and allowed to stand in a refrigerator (–20 °C) for 24 h to give di(4-bromophenacyl) phenyltrithioarsonate **19** as colorless crystals (0.027 g, 18%): mp 134–137 °C (Calc. for  $\text{C}_{22}\text{H}_{17}\text{AsBr}_2\text{O}_2\text{S}_3$ : C, 41.01; H, 2.66. Found: C, 41.35; H, 2.66%);  $\nu_{\text{max}}/\text{cm}^{-1}$  (C=O) 1685 (KBr);  $\delta_{\text{H}}(\text{CDCl}_3)$  4.1 (s, 4H,  $\text{CH}_2$ ) and 7.2–8.0 (m, 13H).

**Reaction of compound 5e with piperidine (Scheme 5).** Tris(4-methylthiobenzoylsulfanyl)arsine **5e** (0.288 g, 0.50 mmol) and piperidine (0.128 g, 1.50 mmol) were refluxed in ethanol (50 mL) for 3 h. Filtration of the precipitates gave 0.006 g of a white solid (mp > 300 °C) ( $\text{As}_x\text{S}_y$ ?). The ethanol from the filtrate was removed under reduced pressure. To the residue ether (30 mL) was added. Filtration of the ether insoluble part gave 0.088 g of slightly yellow solid **20** [mp 142–145 °C (decomp.)] (Calc. for  $\text{C}_{10}\text{H}_{24}\text{As}_2\text{N}_2\text{S}_8$ : C, 20.76; H, 4.18; N 4.84. Found: C, 20.43; H, 4.06; N 4.92%);  $\delta_{\text{H}}(\text{DMSO}-d_6)$  1.1–3.2]. Removal of the ether from the filtrate under reduced pressure gave **10-S** in 48% yield.

**Table S1** Selected bond lengths (Å), angles (deg.) and torsion angles (deg.) of **3g**, **4e** and **5e**

Diphenyl(4-methoxythiobenzoylthio)arsine <b>3g</b>									
Bond lengths					Angles				
As(1)···S(11)	3.1470(8)	As(1)–C(21)	1.966(3)	S(11)···As(1)–S(12)	64.08(2)	S(12)–As(1)–C(21)	91.47(8)		
As(1)–S(12)	2.2651(8)	As(1)–C(31)	1.965(3)	S(11)–C(11)–S(12)	121.0(2)	S(12)–As(1)–C(31)	99.44(8)		
C(11)–S(11)	1.655(3)	O(11)–C(18)	1.431(4)	As(1)···S(11)–C(11)	73.27(9)	C(21)–As(1)–C(31)	96.0(1)		
C(11)–S(12)	1.753(3)			As(1)–S(12)–C(11)	100.44(9)	C(18)–O(11)–C(15)	117.4(2)		
				S(11)···As(1)–C(21)	155.55(8)		89.20(8)		
Torsion angles									
S(12)–C(11)–C(12)–C(17)	175.7(2)	C(11)–S(12)–As(1)–C(21)	173.1(1)						
C(18)–O(11)–C(15)–C(14)	2.8(4)	C(11)–S(12)–As(1)–C(31)	90.7(1)						
S(12)–As(1)–C(21)–C(22)	60.0(2)								
Bis(4-methylthiobenzoylthio)phenylarsine <b>4e</b>									
Bond lengths					Angles				
As(1)···S(11)	2.958(4)	As(1)···S(21)	2.956(4)	S(11)···As(1)···S(21)	143.1(1)	S(12)–As(1)–S(22)	83.8(1)		
As(1)–S(12)	2.299(4)	As(1)–S(22)	2.315(4)	S(11)···As(1)–S(12)	66.5(1)	S(21)···As(1)–S(22)	66.5(1)		
C(11)–S(11)	1.64(1)	C(21)–S(21)	1.65(1)	S(11)–C(11)–S(12)	119.8(7)	S(21)–C(21)–S(22)	120.3(8)		
C(11)–S(12)	1.75(1)	C(21)–S(22)	1.74(1)	As(1)···S(11)–C(11)	77.0(5)	As(1)···S(21)–C(21)	76.1(5)		
As(1)–C(31)	1.97(1)			As(1)–S(12)–C(11)		As(1)–S(22)–C(21)	95.1(5)		
				S(12)–As(1)–C(31)	99.0(4)	S(22)–As(1)–C(31)	99.1(4)		
Torsion angles									
S(12)–As(1)–S(22)–C(21)	170.3(4)								
S(12)–C(11)–C(12)–C(17)	0(1)	S(22)–C(21)–C(22)–C(27)	1(1)						
C(11)–S(12)–As(1)–C(31)		C(21)–S(22)–As(1)–C(31)	91.6(5)						
Tris(4-methylthiobenzoylthio)arsine <b>5e</b>									
Bond lengths					Angles				
As(1)···S(11)	2.969(4)	C(11)–S(11)	1.68(1)	S(11)···As(1)–S(12)	66.0(1)	As(1)···S(11)–C(11)	77.1(4)		
	2.316(4)	C(11)–S(12)	1.73(1)	S(11)–C(11)–S(12)	118.8(7)	As(1)–S(12)–C(11)	97.6(4)		
				S(12)–As(1)–S(12*)	88.3(1)				
Torsion angles									
S(12)–C(11)–C(12)–C(17)	172.4(10)	S(12)–As(1)–S(12*)–C(11*)	87.4(4)						

\*1-Y, X-Y, Z

**Table S3** Selected bond lengths (Å) and angles (deg.) of **9** and **15**

Piperidinium diphenyldithioarsinate <b>9</b>				Di(piperidinium) phenyltrithioarsonate <b>15</b>			
Bond lengths				Bond lengths			
As(1)–S(1)	2.128(1)	As(1)–C(1)	1.938(3)	As(1)–S(1)	2.146(2)	N(1)–H(6)	0.97
As(1)–S(2)	2.101(1)	As(1)–C(7)	1.939(4)	As(1)–S(2)	2.151(2)	N(1)–H(7)	0.96
S(1)···N(1*)	3.226(3)	S(2)···N(1)	3.473(3)	As(1)–S(3)	2.135(3)	N(2)–H(18)	0.97
S(1)···H(12*)	2.25	S(2)···H(11)	2.72	As(1)–C(1)	1.929(8)	N(2)–H(19)	0.95
N(1)–H(11)	1.02	N(1)–H(12)	0.98	S(1)···N(1*)	3.226(7)	S(1)···H(6*)	2.28
				S(2)···N(1)	3.339(8)	S(2)···H(7)	2.48
Angles				Angles			
S(1)–As(1)–S(2)	116.27(4)	S(2)–As(1)–C(1)	96.1(1)	S(2)···N(2*)	3.195(8)	S(2)···H(18**)	2.30
S(1)–As(1)–C(1)	107.6(1)	S(2)–As(1)–C(7)	100.1(1)	S(3)···N(2)	3.264(9)	S(3)···H(19)	2.36
S(1)–As(1)–C(7)	109.1(1)	C(1)–As(1)–C(7)	98.7(1)				
N(1)–H(11)···S(2)	130.453	N(1)–H(12)···S(1*)	119.8(3)	S(1)–As(1)–S(2)	111.69(9)	S(1)–As(1)–C(1)	105.8(2)
				S(1)–As(1)–S(3)	112.0(1)	S(2)–As(1)–C(1)	106.7(2)
				S(2)–As(1)–S(3)	113.6(1)	S(3)–As(1)–C(1)	106.5(2)
				N(1)–H(6)···S(1*)	164.965	N(2)–H(19)···S(3)	146.196
				N(1)–H(7)···S(2)	148.528	N(2)–H(18)···S(2**)	171.881

\* -X, 1-Y, 2-Z.

\* 1-X, 1-Y, 1-Z. \*\* 1-X, -Y, 1-Z.

**Table S2** Selected bond lengths (Å), angles (deg.) and torsion angles (deg.) of **6h**, **7g** and **8e**

(4-Chlorobenzoylthio)diphenylarsine <b>6h</b>									
Bond lengths					Angles				
As(1)–S(11)	2.270(1)	As(1)–C(21)	1.959(4)	S(11)–As(1)···O(11)	58.99(6)	S(11)–As(1)–C(21)	96.1(1)		
As(1)···O(11)	2.943(3)	As(1)–C(31)	1.953(3)	S(11)–C(11)–O(11)	121.3(3)	S(11)–As(1)–C(31)	100.1(1)		
C(11)–S(11)	1.793(4)	Cl(11)–C(15)	1.731(4)	As(1)–S(11)–C(11)	95.9(1)	C(21)–As(1)–C(31)	98.7(1)		
C(11)–O(11)	1.210(4)			As(1)···O(11)–C(11)	82.6(2)	Cl(11)–C(15)–C(14)	119.8(3)		
				O(11)···As(1)–C(21)	155.0(1)				
Torsion angles									
S(11)–C(11)–C(12)–C(17)	6.5(4)	C(11)–S(11)–As(1)–C(21)	176.3(1)						
Cl(11)–C(15)–C(14)–C(13)	179.3(3)	C(11)–S(11)–As(1)–C(31)							
Bis(4-methoxybenzoylthio)phenylarsine <b>7g</b>									
Bond lengths					Angles				
As(1)–S(11)	2.286(1)	As(1)–S(21)	2.280(1)	S(11)–As(1)–S(21)	88.46(4)	O(11)···As(1)···O(21)	146.57(8)		
As(1)···O(11)	2.708(3)	As(1)–O(21)	2.731(3)	S(11)–As(1)···O(11)	62.28(7)	S(21)–As(1)···O(21)	62.08(6)		
C(11)–S(11)	1.776(4)	C(21)–S(21)	1.796(4)	S(11)–C(11)–O(11)	119.7(3)	S(21)–C(21)–O(21)	119.1(3)		
C(11)–O(11)	1.223(5)	C(21)–O(21)	1.217(5)	As(1)–S(11)–C(11)	90.9(1)	As(1)–S(21)–C(21)	91.5(1)		
As(1)–C(31)	1.956(4)	O(12)–C(18)	1.413(6)	As(1)···O(11)–C(11)	87.2(3)	As(1)···O(21)–C(21)	87.4(2)		
		O(22)–C(28)	1.429(6)	S(11)–As(1)–C(31)	97.6(1)	S(21)–As(1)–C(31)	98.8(1)		
				C(18)–O(12)–C(15)	118.6(4)	C(28)–O(22)–C(25)	117.6(4)		
Torsion angles									
S(11)–As(1)–S(21)–C(21)	176.1(1)								
S(11)–C(11)–C(12)–C(17)	15.8(5)	S(21)–C(21)–C(22)–C(27)	4.9(5)						
C(11)–S(11)–As(1)–C(31)		C(21)–S(21)–As(1)–C(31)	78.7(2)						
Tris(4-methylbenzoylthio)arsine <b>8e</b>									
Bond lengths					Angles				
As(1)–S(11)	2.264(5)	C(11)–S(11)	1.80(1)	S(11)–As(1)···O(11)	60.4(3)	As(1)–S(11)–C(11)	93.4(6)		
As(1)···O(11)	2.81(1)		1.18(2)	S(11)–C(11)–O(11)	119(1)	As(1)···O(11)–C(11)	86.1(9)		
				S(11)–As(1)–S(11*)	92.9(2)				
Torsion angles									
S(11)–C(11)–C(12)–C(17)	5(2)	S(11)–As(1)–S(11*)–C(11*)	88.8(6)						
*1-Y, -1+X-Y, Z									

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## Chapter 6

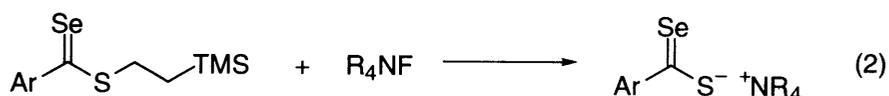
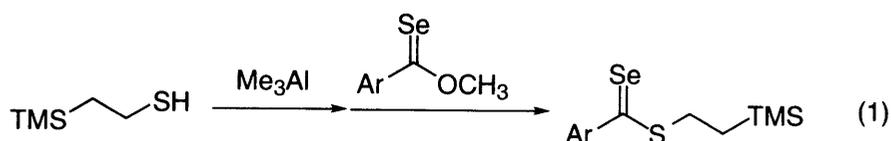
# Ammonium Diselenoates: Stable Heavy Congeners of Carboxylic Acid Salts

### 6.1. Introduction

Since the first synthesis of aromatic dithioic acids and their salts in 1868,<sup>1</sup> tremendous amounts of studies on their synthesis and applications have been reported.<sup>2</sup> In contrast, the selenium isologues, i.e., diselenoic acids and their salts have been totally ignored species until very recently. As their aliphatic derivatives, Jensen noted that the reaction of dialkylzinc with carbon diselenide zinc diselenoates were proposed as a putative unstable intermediate in the reaction.<sup>3</sup> Very recently, the inner salts having diselenocarboxyl group was isolated as stable compounds and characterized.<sup>4</sup> Nevertheless, no example of aromatic diselenoic acids and their salts has been reported.<sup>5</sup>

### 6.2. Results and Discussion

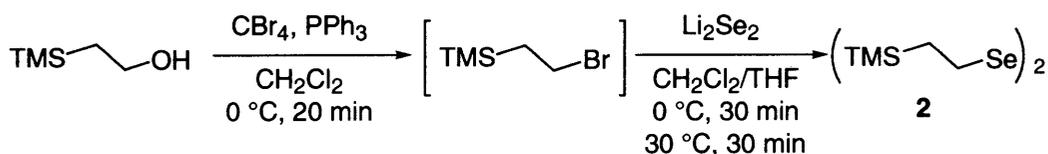
**Synthesis.** During the course of our studies on a series of chalcogenocarboxylic acid salts, ammonium selenothioates were synthesized by reacting *S*- $\beta$ -trimethylsilylethyl selenothioates with ammonium fluorides for the first time (eqs 1 and 2).<sup>6</sup> A similar approach might be possible to the synthesis of ammonium diselenoates.



However,  $\beta$ -trimethylsilylethylselenol **1**,  $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{SeH}$ , which was the key starting material when the reactions of eqs 1 and 2 were applied to the diselenoates, has not yet been known. Furthermore, the selenol **1** was expected to be easily oxidized even though **1** was isolated. The use of bis( $\beta$ -trimethylsilylethyl) diselenide **2** was envisaged as an equivalent to selenol **1**. Initially, a variety of metal diselenides ( $\text{Se/LiBEt}_3\text{H}$ ,<sup>7</sup>  $\text{Se/LiAlH}_4$ ,<sup>8</sup>  $\text{Se/Li}$ <sup>9</sup>) were generated and reacted with *in situ* generated  $\beta$ -trimethylsilylethyl bromide from carbon tetrabromide, triphenylphosphine and  $\beta$ -trimethylsilylethanol. As a result, the reaction of lithium diselenide gave the desired diselenide **2** in 30–57% yields (Scheme 1).

Then, aluminum selenolate,  $\text{TMSCH}_2\text{CH}_2\text{SeAlBu}_2$ , was generated *in situ* from bis( $\beta$ -trimethylsilylethyl) diselenide **2** and DIBAL-H, and reacted with *O*-methyl esters **3** in toluene at

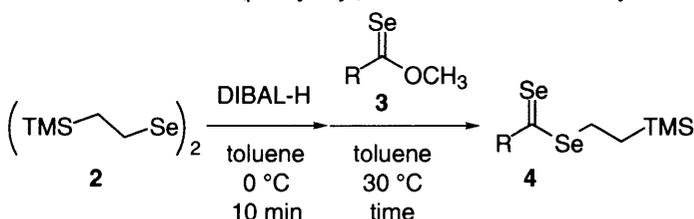
**Scheme 1**



room temperature for 3–16 h. The mixture gradually changed from red to green. The purification by the column chromatography on silica gel successfully gave diselenoic acid  $\beta$ -trimethylsilylethyl esters **4** as a blue-green or green oil in low to good yields (Table 1). These diselenoesters **4** in oil state are unstable, which decomposed to the corresponding selenoic acid esters (RCOSeCH<sub>2</sub>CH<sub>2</sub>TMS) under Ar even at –20 °C within 12 h except for 2-methylphenyl derivative **4b**.

**Table 1.** Reaction of di( $\beta$ -ethylsilyl)diselenides **2** with *O*-methyl esters **3**

Similarly to the synthesis of ammonium selenothioates the ester **4a** was initially reacted with Bu<sub>4</sub>NF. The reaction mixture turned yellow green from green but the NMR spectra of the concentrated residue showed the mixture of ammonium diselenoate **5** along with ammonium selenoate **6** (Scheme 2).

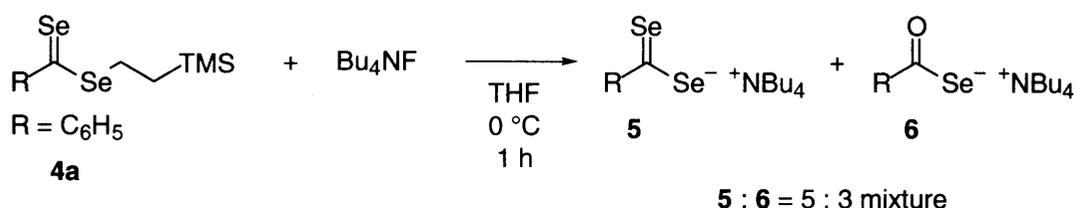


entry	No.	R	time (h)	yield (%)	color
1	<b>4a</b>	C <sub>6</sub> H <sub>5</sub>	3	39 <sup>a</sup>	green
2	<b>4b</b>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	16	59 <sup>a</sup>	blue-green
3	<b>4c</b>	4-BrC <sub>6</sub> H <sub>4</sub>	6	8 <sup>b</sup>	green
4	<b>4d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	12	27 <sup>b</sup>	green

<sup>a</sup> Purification was carried out with chromatography on silica gel.

<sup>b</sup> Purification was carried out with HPLC.

**Scheme 2**



In contrast, the reaction of **4** with Me<sub>4</sub>NF afforded the corresponding ammonium diselenoates **7** with high purity (Table 2). For example, a CH<sub>3</sub>CN solution of **4a** was added to a CH<sub>3</sub>CN suspension of Me<sub>4</sub>NF. After stirring at 0 °C for 1 h, the solvent was removed under reduced pressure. Washing of the residue with Et<sub>2</sub>O afforded tetramethylammonium diselenobenzoate **7a** as green crystalline solid in 59% yield (Table 2). Similarly, other ammonium salts **7b–d** were isolated as green crystalline solids in 47–78% yields, respectively.

The salt **7a** was handled under the air without any appreciable change, whereas the salt **7a** decomposed when it was dissolved in CH<sub>3</sub>CN and THF. On the other hand, the introduction of the methyl group to the ortho position of aromatic ring increased the stability of the salt **7b**, no appreciable change was observed for the salt **7b** even when it was dissolved in CH<sub>3</sub>CN at –20 °C.

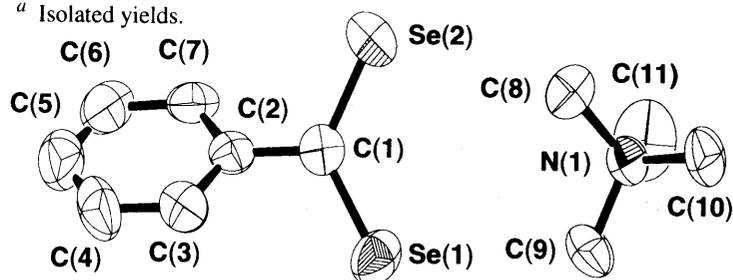
**Structure.** The molecular structure of **7a** was determined by X-ray crystallography. The ORTEP drawing of **7a** is shown in Figure 1. The crystal data are collected in Table 3. Selected bond lengths and angles are shown in Table 4. This is the first example of X-ray molecular analysis of aromatic diselenoic acid salts. Several characteristic features are as follows. First, the distances between the selenium atoms and the hydrogen atoms of the ammonium ion are longer than the sum of the van der Waals radii of both atoms,<sup>10</sup> and no interaction was observed between diselenocarboxylate group and ammonium ion. Second, the diselenoate salt **7a** is monomeric in the solid state. Third, the dihedral angle of the phenyl group and diselenocarboxyl group was 46.0(5)°, and the phenyl group does not seem to resonate diselenocarboxyl group. Fourth, the average bond lengths of the two C–Se bonds are 1.830(4) Å and closer to the bond lengths of the ordinary C–Se double bonds (1.74–1.80 Å)<sup>11</sup> than those of the C–Se single bonds (~1.94 Å).<sup>12</sup>

**Spectra.** Representative spectroscopic data of **4** and **7** are listed in Table 5. In the <sup>13</sup>C NMR spectra, the signals due to the selenocarbonyl carbon atom in **4** were observed at 237±5 ppm, whereas the corresponding signals of diselenoates **7** were shifted to lower fields by 22.5±0.5 ppm. Two resonances at about 900 and 1800 ppm in <sup>77</sup>Se NMR spectra were observed for the selenium atoms of the C–Se single and C=Se double bonds in the case of **4**.

**Table 2.** Reaction of diselenoesters **4** with Me<sub>4</sub>NF

entry	No.	R	time (h)	yield (%) <sup>a</sup>
1	<b>7a</b>	C <sub>6</sub> H <sub>5</sub>	1	59
2	<b>7b</b>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	68
3	<b>7c</b>	4-BrC <sub>6</sub> H <sub>4</sub>	1	47
4	<b>7d</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	1	78

<sup>a</sup> Isolated yields.



**Figure 1.** The ORTEP drawing of C<sub>6</sub>H<sub>5</sub>CS<sub>2</sub><sup>−</sup> + NMe<sub>4</sub> **7a**. Hydrogen atoms have been omitted for clarity.

**Table 3.** Crystallographic Data

7a	
formula	C <sub>11</sub> H <sub>17</sub> NSe <sub>2</sub>
fw	321.18
color	green
crystal size (mm)	0.20 × 0.17 × 0.06
<i>T</i> (K)	296
crystal system	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	8.756(4)
<i>b</i> (Å)	9.679(4)
<i>c</i> (Å)	15.748(7)
<i>V</i> (Å <sup>3</sup> )	1334.5(10)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> (g cm <sup>−3</sup> )	1.598
<i>μ</i> (mm <sup>−1</sup> )	5.509
<i>F</i> (000)	632.00
no. of reflns measured/unique	3045/1764
no. of observations, ( <i>I</i> > 2σ( <i>I</i> ))	1535
R1; wR2	0.033; 0.063
goodness-of-fit	0.68
final max., min., (Δρ, e Å <sup>−3</sup> )	1.39; -0.60

**Table 4.** Selected bond lengths and angles and torsion angle of **7a**

Se(1)–C(1)	1.831(4)	Se(1)–C(1)–Se(2)	124.3(2)
Se(2)–C(1)	1.828(4)	Se(1)–C(1)–C(2)	117.7(3)
C(1)–C(2)	1.482(5)	Se(2)–C(1)–C(2)	118.0(3)
		Se(1)–C(1)–C(2)–C(3)	46.0(5)

The typical coupling constants of the C–Se bond ( $172\pm 3$  Hz) and the C=Se bond ( $224\pm 1.2$  Hz) were also detected.

On the other hand, only one signal appeared at 1360–1493 ppm when the esters **4** were converted to diselenoates **7**. Interestingly, the linear relationship was observed between the signals of the selenium atom forming the double bond in **4** and those of the selenium atom in **7** (Figure 2). Furthermore, the  $^{77}\text{Se}$  signals in **4** were in the region of

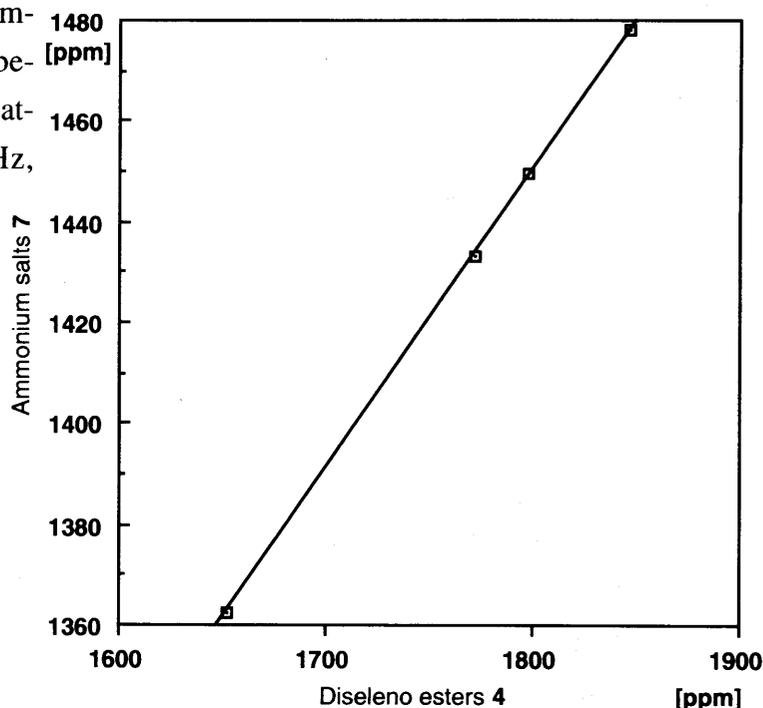
those of the C=Se bonds. More importantly, the coupling constants between the selenium and the carbon atoms in **7** were larger than 200 Hz, which indicates that both the carbon-selenium bond in **7** possesses the double bond character in great depth. In other words, the electrons are highly efficiently delocalized on the diselenocarboxyl group in **7** (eq 3). UV-visible spectra of **7** further support the double bonding between the carbon atom and selenium atoms in **7**. As for **4**, the absorptions ascribed to  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transitions were at 366–394 and at 609–627 nm, respectively. The corresponding absorptions of **7** were substantially shifted to the longer wavelength.

**Calculations.** To further explore the properties of the bonding between the selenium atoms and the carbon atom of **7**, ab initio molecular orbital calculation of the diselenoate ion **7a** was performed by using Gaussian 98 programs.<sup>13</sup> Geometry optimizations for **7a** were carried out with the 6-311+G(d,p) basis set at the B3LYP level. The bond lengths, angles, and torsion angles of the optimized structure are shown in Table 6. The results of Mulliken population analyses are also shown in Table 7. In the diselenoate ion the negative charge is distributed not

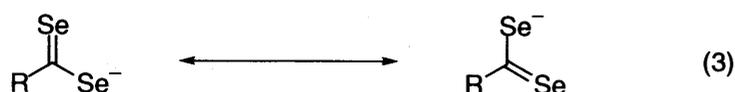
**Table 5.** Spectroscopic Data of Compounds **4** and **7**

No.	$^{13}\text{C}$ NMR <sup>a</sup> $\delta$ [ppm]	$^{77}\text{Se}$ NMR <sup>a</sup> $\delta$ [ppm]	$^1J_{\text{Se-C}}$ <sup>b</sup> [Hz]	UV-Vis [nm] <sup>c</sup>	
				$\pi\text{-}\pi^*$	$n\text{-}\pi^*$
<b>4a</b>	236.9	897.9, 1772.0	171.9, 223.3	391	622
<b>4b</b>	241.5	901.3, 1846.7	174.5, 225.2	375	627
<b>4c</b>	234.2	863.4, 1798.1	171.6, 222.8	394	618
<b>4d</b>	233.6	954.6, 1652.4	169.2, 222.8	366	609
<b>7a</b>	259.3	1433.3	213.5	447 (423) <sup>d</sup>	684 (654) <sup>d</sup>
<b>7b</b>	263.6	1493.0	208.7	417 (385) <sup>d</sup>	670 (671) <sup>d</sup>
<b>7c</b>	256.1	1449.4	214.9	453 (433) <sup>d</sup>	690 (692) <sup>d</sup>
<b>7d</b>	256.6	1362.6	211.6	452 (448) <sup>d</sup>	634 (611) <sup>d</sup>

<sup>a</sup>  $\text{CDCl}_3$  was used as a solvent for **4**, whereas  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$  were used for **7**. <sup>b</sup> The coupling constants were determined in the  $^{13}\text{C}$  NMR spectra. <sup>c</sup> THF was used as a solvent. <sup>d</sup> The UV-Vis spectra were measured in the solid state.



**Figure 2.** Correlation in  $^{77}\text{Se}$  NMR spectra between **4** and **7**.  
 $\delta(^{77}\text{Se NMR in 7}) = 379.29 + 0.59502 \delta(^{77}\text{Se NMR in 4})$ ,  $R^2 = 1.000$



only to two selenium atoms but also to the central carbon atom. In the aromatic ring the electrons are fairly deficient at the ipso-carbon C2. This is compensated by the distribution of the electrons to other carbon atoms in the aromatic ring. On the basis of molecular orbital calculations three molecular orbitals, i.e., LUMO, HOMO, HOMO of  $\pi$ -orbitals (HOMO-1) and next HOMO of  $\pi$ -orbitals (HOMO-3) of **7a** are visualized in Figure 3.<sup>14</sup> Interestingly, the next HOMO of  $\pi$ -orbitals is extended to one side of C(1)–Se(1) bond and to the other side of C(1)–C(2) bond. As a result, the atomic orbital of the central carbon atom highly contributed to the next HOMO of  $\pi$ -orbitals. The LUMO is extended over the C(1)–C(2) bond.

To compare the bonding of diselenoate ion, bond orders of three model compounds calculated by B3LYP/6-311+G(d,p) are shown in Table 8. The polar nature of the C=O group in **8** is clearly seen since the value is on the order of 1.25 for C=O. In contrast, the values are on the order of 1.81 for C=S in **9** and that of 1.78 for C=Se in **10**. This result suggests that the double bond

character of two carbon-selenium bonds in diselenoate ions is more important than that of the carbon-oxygen bonds in carboxylate ions.

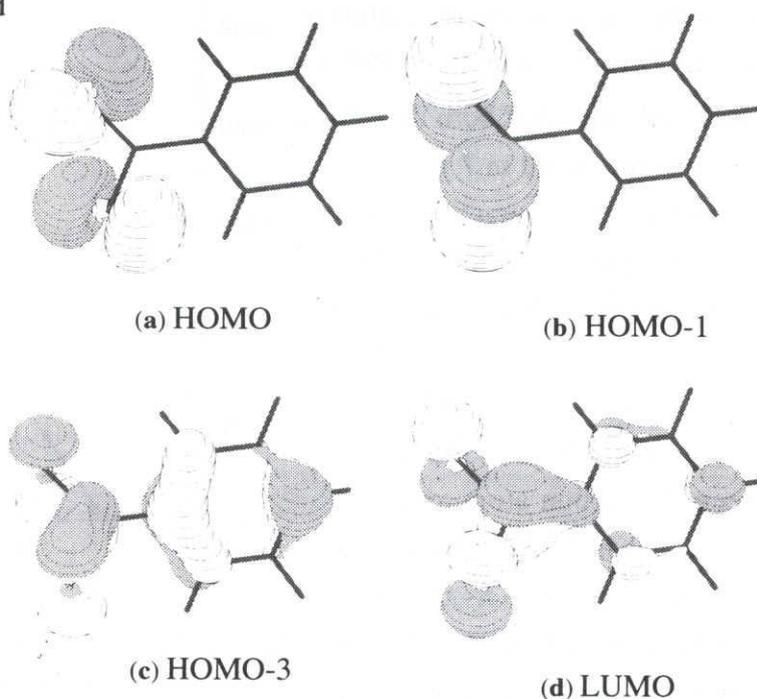
**Reaction.** Finally, the usefulness of ammonium diselenoates **7** as a key starting material leading to a variety of compounds bearing diselenocarboxyl group was proved by the following reaction. First, alkylation of **7b** with *p*-phenylphenacyl bromide gave the corresponding phenacyl ester **11** as stable blue needles (Scheme 3). Second, to generate diselenoic acids, the CF<sub>3</sub>SO<sub>3</sub>H

**Table 6.** Selected bond lengths and angles and torsion angle of **7a** and optimized **7a**

	<b>7a</b>	optimized <b>7a</b>
Se(1)–C(1)	1.831(4)	1.851141
Se(2)–C(1)	1.828(4)	1.851146
C(1)–C(2)	1.482(5)	1.494882
Se(1)–C(1)–Se(2)	124.3(2)	125.3320
Se(1)–C(1)–C(2)	117.7(3)	117.3338
Se(2)–C(1)–C(2)	118.0(3)	117.3342
Se(1)–C(1)–C(2)–C(3)	46.0(5)	41.7644

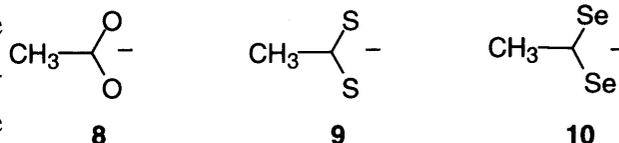
**Table 7.** Mulliken charges of optimized **7a**

Se(1)	–0.430450	C(2)	0.996622	H(1)	0.141512
Se(2)	–0.430694	C(3)	–0.618517	H(2)	0.098859
C(1)	–0.211397	C(4)	–0.217103	H(3)	0.095713
		C(5)	–0.158581	H(4)	0.098781
		C(6)	–0.264551	H(5)	0.141827
		C(7)	–0.242022		



**Figure 3.** The molecular orbital of HOMO (a), HOMO-1 (b), HOMO-3 (c) and LUMO (d) in optimized structure of **7a**.

or HCl/Et<sub>2</sub>O solution was added to a d<sub>8</sub>-THF suspension of **7b** in a NMR tube at -70 °C. As a result, insoluble salt **7b** quickly dissolved in d<sub>8</sub>-THF, and the light green suspension quickly changed to green, which was indicative of the formation of diselenoic acid **12**, but low temperature NMR spectra of the reaction mixture



did not show the signals which could be ascribed to **12**. Then, to the homogeneous reaction mixture of CF<sub>3</sub>SO<sub>3</sub>H with **7b** in Et<sub>2</sub>O was added methyl vinyl ketone at -70 °C, and stirred for 30 min at 30 °C to afford  $\gamma$ -oxabutyl diselenoate **13** as a blue oil in 21% yield. These results suggest that diselenoic acid **12** is generated by the protonation of **7b**, but it easily decomposes.

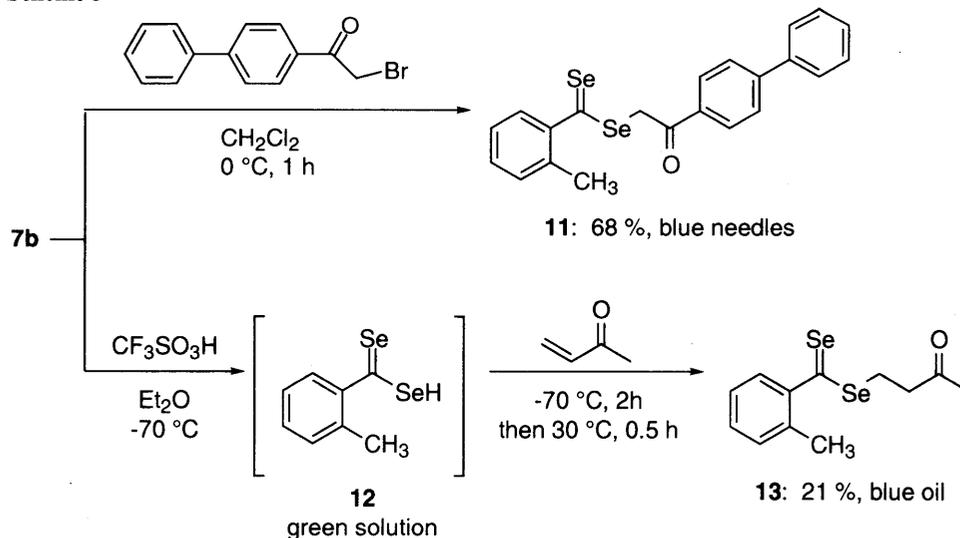
**Table 8.** Selected bond lengths and angles and Mulliken charges and Bond orders of dichalcogenoate ions CH<sub>3</sub>CE<sub>2</sub><sup>-</sup>

	<b>8</b> (E = O)	<b>9</b> (E = S)	<b>10</b> (E = Se)
<b>8</b> (E = O) <b>9</b> (E = S) <b>10</b> (E = Se)			
Bond lengths (Å)			
E(1)-C(3)	1.255345	1.700155	1.847229
E(2)-C(3)	1.256110	1.700155	1.847247
C(3)-C(4)	1.564930	1.528309	1.520342
Bond angles (°)			
E(1)-C(3)-E(2)	128.9159	126.7373	126.4363
E(1)-C(3)-C(4)	116.2398	116.6168	116.7673
E(2)-C(3)-C(4)	114.8444	116.6168	116.7670
Mulliken charges (e)			
E(1)	-0.507466	-0.722472	-0.465435
E(2)	-0.491307	-0.722472	-0.465184
C(3)	0.152473	0.743714	0.116927
C(4)	-0.484200	-0.706945	-0.588831
H(5)	0.109997	0.133992	0.134212
H(6)	0.110005	0.137091	0.134212
H(7)	0.110499	0.137091	0.134212
BondOrders			
E(1)-C(3)	1.25835	1.81031	1.78137
E(2)-C(3)	1.25445	1.81031	1.78156
C(3)-C(4)	0.92779	1.04157	1.05658

### 6.3. Conclusion.

In summary, we have succeeded in the first synthesis and structure analysis of diselenoic acid salts. The selenocarboxyl group in ammonium salts **7** was close to the double bond by various NMR spectra, molecular and electronic analysis.

**Scheme 3**



## 6.4. Experimental

**General Procedures.** Melting points were measured by a Yanagimoto micromelting point apparatus (uncorrected). IR spectra were measured on JASCO FT/IR-410 Fourier Transform Infrared Spectrometer. The  $^1\text{H}$  NMR spectra were measured on a JEOL  $\alpha$ -400 (399.6 MHz) in  $\text{CDCl}_3$ ,  $d_8$ -THF and  $\text{CD}_3\text{CN}$ . Chemical shifts of protons are reported in  $\delta$  values referred to  $\text{CHCl}_3$ , THF and  $\text{CH}_3\text{CN}$  as an internal standard, and the following abbreviation were used as following: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet. The  $^{13}\text{C}$  NMR spectra (100.4 MHz),  $^{77}\text{Se}$  NMR (76.2 MHz) spectra were obtained from the same spectrometer as  $^1\text{H}$  NMR ones. The  $^{77}\text{Se}$  chemical shifts were expressed in  $\delta$  values deshielded with respect to neat  $\text{Me}_2\text{Se}$ . UV-visible spectra were measured on a JASCO U best 55 or HITACHI U-4000. HPLC performed using a Japan Analytical Industry LC-908 recycling preparative HPLC apparatus coupled to an RI indicator and a UV detector (264 nm). HRMS was measured on a JEOL GCmate II. The mass spectra (MS) were taken on SHIMADZU GCMS QP1000 (EI mode). Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

**Materials.** Diethyl ether ( $\text{Et}_2\text{O}$ ) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl prior to use. Acetonitrile ( $\text{CH}_3\text{CN}$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were distilled over diphosphorus pentoxide after refluxing for 5 h. Toluene was distilled from calcium hydride. Hexane was distilled from sodium metal. Selenobenzoic acid *O*-methyl ester<sup>15</sup> was prepared according to the literature. Anhydrous tetramethylammonium fluoride was obtained from the tetramethylammonium fluoride tetrahydrate by removal of the water under reduced pressure (150 °C/1.0 mmHg) with stirring for about 1 h. Lithium (pole), *p*-phenylphenacyl bromide, selenium powder, tetrabromomethane and triphenylphosphine were purchased from Nacalai Tesque Inc. DIBAL-H (1.0 M toluene solution) was purchased from KANTO Chemical Co., Inc. Tetramethylammonium fluoride tetrahydrate, trifluoromethanesulfonic acid and 2-(trimethylsilyl)ethanol were purchased from Aldrich Chemical Company. Methyl vinyl ketone was purchased from Merck KGaA. Silica gel used on column chromatography was run on silica gel 60 of KANTO Chemical Co., Inc. All manipulations were carried under argon atmosphere.

**X-ray crystallography.** Crystal samples were cut from the grown crystals and mounted on a glass fiber. The crystals were coated with an epoxy resin because they were air sensitive. Measurements were carried out on a Rigaku/MSC Mercury CCD using a graphite-monochromator with Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The data were collected at 296K. The structure was solved by a direct method using SHELXS86<sup>16</sup> and expanded using DIRDIF94.<sup>17</sup> Neutral atom scattering factors for neutral atoms were from Cromer and Waber<sup>18</sup> and anomalous dispersion effects<sup>19</sup> were used. A full-matrix least-squares refinement was executed with non-hydrogen atoms. The final least square cycle included fixed hydrogen atoms at calculated positions for which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

**Bis(2-Trimethylsilylethyl) diselenide (2).** In a 100 mL schlenk tube, lithium (0.160 g, 23.1 mmol) and selenium powder (1.801 g, 22.8 mmol) was stirred at -70 °C in liq. NH<sub>3</sub>. After stirring at this temp. for 4 h, the removal of the solvent gave 1.991 g (purity: 75%) of Li<sub>2</sub>Se<sub>2</sub> as a black brown solid. In a 50 mL two-necked round bottom flask, triphenylphosphine (3.294 g, 12.6 mmol) was slowly added to a CH<sub>2</sub>Cl<sub>2</sub> (10 mL) solution of (2-trimethylsilyl)ethanol (1.5 mL, 10.5 mmol) and CBr<sub>4</sub> (4.165 g, 12.6 mmol) at 0 °C over 2 min, and it was stirred at this temp. for 20 min. This solution was added to a CH<sub>2</sub>Cl<sub>2</sub> (5 mL) suspension of Li<sub>2</sub>Se<sub>2</sub> (1.991 g, purify: 75%) in a 100 mL schlenk tube at 0 °C through a canula taking over 5 min. Into this, THF (10 mL) was added dropwise to this mixture by 10 mL syringe at 0 °C over 1.5 min, and it was stirred at 0 °C for 30 min and then at 30 °C for 30 min. The reaction mixture was poured onto water, and extracted with ether (100 mL). The organic layer was dried over MgSO<sub>4</sub> and concentrated *in vacuo*. After addition of hexane (200 mL), the insoluble parts (triphenylphosphine oxide) were filtered, and the mixture was concentrated *in vacuo*. The residue was purified by distillation under reduced pressure (118–124 °C / 0.3 mmHg) to give 1.074 g (57%) of **2** as a orange oil. Bp: 126–128 °C / 0.3 mmHg; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.00 (s, 9H, SiMe<sub>3</sub>), 0.86–1.02 (m, 2H, SiCH<sub>2</sub>), 2.90–2.95 (m, 2H, CH<sub>2</sub>Se); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.80 (<sup>1</sup>J<sub>13C-29Si</sub> = 51.3 Hz, SiMe<sub>3</sub>), 19.4 (<sup>1</sup>J<sub>13C-29Si</sub> = 48.0 Hz, SiCH<sub>2</sub>), 25.0 (CH<sub>2</sub>Se); <sup>77</sup>Se NMR (CDCl<sub>3</sub>, Me<sub>2</sub>Se): δ 352.6; Anal. Calcd for C<sub>10</sub>H<sub>26</sub>Se<sub>2</sub>Si<sub>2</sub>: C, 33.33; H, 7.27. Found: C, 33.32; H, 7.27.

**Diselenobenzoic acid Se-2-(trimethylsilyl)ethyl ester (4a).** In a 30 mL two-necked round bottom flask, a toluene solution of 1.0 M DIBAL-H (1.2 mL, 1.2 mmol) was added to a toluene solution (1 mL) of **2** (0.216 g, 0.60 mmol) at 0 °C, and it was stirred at 30 °C for 10 min. Then, a toluene solution (2 mL) of selenobenzoic acid *O*-methyl ester (0.199 g, 1.00 mmol) was added to the resulting mixture at 0 °C, and the mixture was stirred at 30 °C for 3 h. The reaction mixture was poured onto ice/water mixture, and extracted with hexane. The organic layer was dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane (R<sub>f</sub> = 0.48) as an eluent to give 0.136 g (39%) of **4a** as a green oil. IR (neat): 3037, 3023, 2951, 1587, 1440, 1410, 1246, 1179, 1154, 1010, 941, 858, 841, 754, 686, 610, 585. 544 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.10 (s, 9H, SiMe<sub>3</sub>), 1.16–1.21 (m, 2H, CH<sub>2</sub>), 3.40–3.44 (m, 2H, CH<sub>2</sub>), 7.30 (t, *J* = 7.9 Hz, 2H, Ar), 7.57 (t, *J* = 7.9 Hz, 1H, Ar), 7.95 (d, *J* = 7.9 Hz, 2H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.72 (SiMe<sub>3</sub>), 15.9 (CH<sub>2</sub>), 34.8 (CH<sub>2</sub>), 125.5, 128.6, 131.6, 154.5 (*Cipso*), 236.9 (C=Se: <sup>1</sup>J<sub>13C-77Se</sub> = 171.9 Hz, C–Se: <sup>1</sup>J<sub>13C-77Se</sub> = 223.3 Hz); <sup>77</sup>Se NMR (CDCl<sub>3</sub>, Me<sub>2</sub>Se): δ 897.9 (C–Se, <sup>1</sup>J<sub>77Se-13C</sub> = 170.9 Hz), 1772.0 (C=Se); UV-Vis (THF) λ<sub>max</sub> (log ε): 218 (4.20), 246 (3.71), 323 (3.89), 391 (3.63), 622 (2.15); HRMS Calcd for C<sub>12</sub>H<sub>18</sub>Se<sub>2</sub>Si: 349.9578. Found: 349.94931.

**2-Methyldiselenobenzoic acid Se-2-(trimethylsilyl)ethyl ester (4b).** In a 50 mL two-necked round bottom flask, a toluene solution of 1.0 M DIBAL-H (3.2 mL, 3.2 mmol) was added to a toluene solution (5 mL) of **2** at 0 °C, and it was stirred at 30 °C for 10 min. Then, a toluene solution (5 mL) of 2-methylselenobenzoic acid *O*-methyl ester (0.642 g, 3.01 mmol) was added to the resulting mixture at 0 °C, and the mixture was stirred at 30 °C for 16 h. The reaction mixture was poured onto ice/water mixture, and extracted with hexane. The organic layer was dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane (R<sub>f</sub> = 0.30) as an eluent to give 0.638 g (59%) of **4b** as a blue green oil. IR (neat): 3060, 3014, 2951, 1594, 1453, 1412, 1378, 1246, 1154, 1112,

1010, 950, 933, 845, 744, 695, 621, 571, 495, 441  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.10 (s, 9H,  $\text{SiMe}_3$ ), 1.16–1.20 (m, 2H,  $\text{CH}_2$ ), 2.35 (s, 3H,  $\text{CH}_3$ ), 3.36–3.41 (m, 2H,  $\text{CH}_2$ ), 7.13–7.24 (m, 4H, Ar);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.76 ( $\text{SiMe}_3$ ), 15.9 ( $\text{CH}_2$ ), 19.7 ( $\text{CH}_3$ ), 34.6 ( $\text{CH}_2$ ), 123.2, 125.1, 128.6, 130.1, 130.9, 155.8 (*Cipso*), 241.5 ( $\text{C}=\text{Se}$ :  $^1J_{13\text{C}-77\text{Se}} = 174.5$  Hz,  $\text{C}-\text{Se}$ :  $^1J_{13\text{C}=77\text{Se}} = 225.2$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_2\text{Se}$ ):  $\delta$  954.6 ( $\text{C}-\text{Se}$ ), 1846.7 ( $\text{C}=\text{Se}$ ); UV-Vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 220 (4.30), 252 (3.75), 324 (3.51), 375 (4.01), 609 (2.50); Anal. Calcd for  $\text{C}_{13}\text{H}_{20}\text{Se}_2\text{Si}$ : C, 43.10; H, 5.56. Found: C, 43.37; H, 5.51.

**4-Bromodiselenobenzoic acid Se-2-(trimethylsilyl)ethyl ester (4c).** In a 50 mL two-necked round bottom flask, a toluene solution of 1.0 M DIBAL-H (1.3 mL, 1.3 mmol) was added to a toluene solution (2 mL) of **2** at 0 °C, and it was stirred at 30 °C for 10 min. Then, a toluene solution (2 mL) of 4-bromoselenobenzoic acid *O*-methyl ester (0.280 g, 1.01 mmol) was added to the resulting mixture at 0 °C, and the mixture was stirred at 30 °C for 3 h. The reaction mixture was poured onto ice/water mixture, and extracted with hexane. The organic layer was dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane ( $R_f = 0.48$ ) as an eluent to give 0.110 g (26%) of the mixture containing **4c** as a green oil. The ester **4c** was finally purified by HPLC and isolated in 0.034 g (8%) as green oil. IR (neat): 2952, 1573, 1475, 1391, 1247, 1177, 1073, 1007, 934, 848, 816, 695, 624, 606, 541, 432, 403  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.10 (s, 9H,  $\text{SiMe}_3$ ), 1.15–1.19 (m, 2H,  $\text{CH}_2$ ), 3.39–3.43 (m, 2H,  $\text{CH}_2$ ), 7.43 (d,  $J = 6.8$  Hz, 2H, Ar), 7.82 (d,  $J = 6.8$  Hz, 2H, Ar);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.74 ( $\text{SiMe}_3$ ), 15.9 ( $\text{CH}_2$ ), 35.1 ( $\text{CH}_2$ ), 126.5, 126.8, 131.8, 153.0 (*Cipso*), 234.2 ( $\text{C}=\text{Se}$ :  $^1J_{13\text{C}-77\text{Se}} = 171.6$  Hz,  $\text{C}-\text{Se}$ :  $^1J_{13\text{C}=77\text{Se}} = 222.8$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_2\text{Se}$ ):  $\delta$  901.3 ( $\text{C}-\text{Se}$ ), 1798.1 ( $\text{C}=\text{Se}$ ); UV-Vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 233 (4.14), 332 (4.15), 394 (3.82), 627 (2.29); FAB-MS:  $m/z$  427 ( $\text{M}^+$ ); HRMS Calcd for  $\text{C}_{12}\text{H}_{17}\text{BrSe}_2\text{Si}$ : 427.86129. Found: 427.86295.

**4-Methoxydiselenobenzoic acid Se-2-(trimethylsilyl)ethyl ester (4d).** In a 50 mL two-necked round bottom flask, a toluene solution of 1.0 M DIBAL-H (1.6 mL, 2.5 mmol) was added to a toluene solution (2 mL) of **2** (0.254 g, 0.70 mmol) at 0 °C, and it was stirred at 30 °C for 10 min. Then, a toluene solution (3 mL) of 4-methoxyselenobenzoic acid *O*-methyl ester (0.313 g, 1.37 mmol) was added to the resulting mixture at 0 °C, and the mixture was stirred at 30 °C for 5 h. The reaction mixture was poured onto ice/water mixture, and extracted with hexane. The organic layer was dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The residue was separated by column chromatography on silica gel [solvent gradient: hexane, hexane/ $\text{Et}_2\text{O}$  (20 : 1) to hexane/ $\text{Et}_2\text{O}$  (10 : 1);  $R_f = 0.50$  (hexane/ $\text{Et}_2\text{O} = 10 : 1$ )] to give 0.274 g of the mixture containing **4d** as a green oil. The ester **4d** was finally purified by HPLC and isolated in 0.140 g (27%) as green oil. IR (neat): 2952, 2836, 1656, 1595, 1501, 1460, 1440, 1416, 1304, 1259, 1170, 1116, 1031, 931, 852, 773, 695, 632, 561, 462, 412  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.10 (s, 9H,  $\text{SiMe}_3$ ), 1.15–1.20 (m, 2H,  $\text{CH}_2$ ), 3.40–3.44 (m, 2H,  $\text{CH}_2$ ), 3.80 (s, 3H,  $\text{CH}_3\text{O}$ ), 6.79 (d,  $J = 9.0$  Hz, 2H, Ar), 8.08 (d,  $J = 9.0$  Hz, 2H, Ar);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -1.79 ( $\text{SiMe}_3$ ), 16.0 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 55.5 ( $\text{CH}_3\text{O}$ ), 113.8, 128.1, 147.1 (*Cipso*), 163.2, 233.6 ( $\text{C}=\text{Se}$ :  $^1J_{13\text{C}-77\text{Se}} = 169.2$  Hz,  $\text{C}-\text{Se}$ :  $^1J_{13\text{C}=77\text{Se}} = 222.8$  Hz);  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_2\text{Se}$ ):  $\delta$  863.4 ( $\text{C}-\text{Se}$ ,  $^1J_{77\text{Se}-13\text{C}} = 170.9$  Hz), 1652.4 ( $\text{C}=\text{Se}$ ); UV-Vis (THF)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 219 (4.42), 244 (4.25), 366 (4.32), 618 (2.79); EIMS ( $m/z$ ): 378 ( $\text{M}^+$ ); HRMS Calcd for  $\text{C}_{13}\text{H}_{20}\text{OSe}_2\text{Si}$ : 379.96135. Found: 379.96072; Anal. Calcd for  $\text{C}_{13}\text{H}_{20}\text{OSe}_2\text{Si}\cdot 0.1\text{CHCl}_3$ : C, 40.32; H, 5.19. Found: C, 40.39; H, 5.17.

**Tetrabutylammonium diselenobenzoate (5).** In a 20 mL two-necked round bottom flask, tetrabutylammonium fluoride (0.36 mL, 0.36 mmol) was added to a THF (1.5 mL) solution of **4a** (0.127 g, 0.36 mmol) at 0 °C. After stirring at this temp. for 1 h, the removal of the solvent under reduced pressure gave 5 : 3 mixture of tetrabutylammonium diselenobenzoate **5** and tetrabutylammonium selenobenzoate **6** as a brown oil. <sup>1</sup>H NMR (d<sub>8</sub>-THF): δ 1.13 (t, *J* = 7.3 Hz, 12H, CH<sub>3</sub>), 1.54 (sex, *J* = 7.3 Hz, 8H, CH<sub>2</sub>), 1.83 (qui, *J* = 7.6 Hz, 8H, CH<sub>2</sub>), 3.52–3.57 (m, 8H, CH<sub>2</sub>), 7.18 (t, *J* = 7.8 Hz, 2H, Ar), 7.37 (t, *J* = 7.8 Hz, 1H, Ar), 8.64 (d, *J* = 7.8 Hz, 2H, Ar); <sup>13</sup>C NMR (d<sub>8</sub>-THF): δ 14.1 (CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 59.2 (NCH<sub>2</sub>), 126.4, 126.8, 128.2, 163.0 (*Cipso*), 256.1 (C=Se, <sup>1</sup>*J*<sub>13C-77Se</sub> = 214.7 Hz); <sup>77</sup>Se NMR (d<sub>8</sub>-THF, Me<sub>2</sub>Se): δ 1437.5.

**Tetrabutylammonium selenobenzoate (6).** <sup>1</sup>H NMR (d<sub>8</sub>-THF): δ 1.13 (t, *J* = 7.3 Hz, 12H, CH<sub>3</sub>), 1.54 (sex, *J* = 7.3 Hz, 8H, CH<sub>2</sub>), 1.83 (qui, *J* = 7.6 Hz, 8H, CH<sub>2</sub>), 3.52–3.57 (m, 8H, CH<sub>2</sub>), 7.31 (t, *J* = 7.3 Hz, 2H, Ar), 7.36 (t, *J* = 7.3 Hz, 1H, Ar), 8.43 (d, *J* = 7.3 Hz, 2H, Ar); <sup>13</sup>C NMR (d<sub>8</sub>-THF): δ 14.1 (CH<sub>3</sub>), 20.3 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 59.2 (NCH<sub>2</sub>), 126.9, 129.4, 130.3, 169.8 (*Cipso*), 210.5 (C–Se); <sup>77</sup>Se NMR (d<sub>8</sub>-THF, Me<sub>2</sub>Se): δ 442.2.

**Tetramethylammonium diselenobenzoate (7a).** In a 20 mL two-necked flask, CH<sub>3</sub>CN (2 mL) solution of **4a** (0.178 g, 0.51 mmol) was added to a CH<sub>3</sub>CN (3 mL) suspension of tetramethylammonium fluoride (0.057 g, 0.61 mmol) at 0 °C. After stirring at this temp. for 1 h, the reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts and the solvent was removed under reduced pressure. To this was added ether (5 mL) at 30 °C. Filtration of the resulting deposits with a glass filter (G4) gave 0.097 g (59%) of **7a** as a green solid. mp. (dec.) 115 °C; IR (KBr) 3047, 2996, 1526, 1482, 1435, 1404, 1285, 1258, 1216, 1173, 1153, 1072, 949, 920, 894, 884, 844, 752, 692, 613 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 3.07 (s, 12H, NMe<sub>4</sub>), 7.11 (t, *J* = 7.3 Hz, 2H, Ar), 7.30 (t, *J* = 7.3 Hz, 1H, Ar), 8.10 (d, *J* = 7.3 Hz, 2H, Ar); <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 56.2 (m, NMe<sub>4</sub>), 125.7, 127.4, 128.7, 165.3 (*Cipso*), 259.3 (C=Se, <sup>1</sup>*J*<sub>13C-77Se</sub> = 213.5 Hz); <sup>77</sup>Se NMR (CD<sub>3</sub>CN, Me<sub>2</sub>Se): δ 1433.3; UV-Vis (THF) λ<sub>max</sub> (log ε): 220 (4.35), 267 (3.85), 309 (3.86), 447 (3.73), 684 (2.23); UV-Vis (solid state, MgO) λ<sub>max</sub>: 223, 237, 260, 303, 324, 364, 423, 654; FAB-MS (nitrobenzyl alcohol matrix): *m/z* 247 (M–NMe<sub>4</sub>) (C<sub>7</sub>H<sub>5</sub>Se<sub>2</sub> requires 247); Anal. Calcd for C<sub>11</sub>H<sub>17</sub>NSe<sub>2</sub>•1.5H<sub>2</sub>O: C, 37.94; H, 5.79. Found: C, 37.98; H, 5.25.

**Tetramethylammonium 2-methyldiselenobenzoate (7b).** In a 20 mL two-necked flask, CH<sub>3</sub>CN (10 mL) solution of **4b** (0.638 g, 1.76 mmol) was added to a CH<sub>3</sub>CN (10 mL) suspension of tetramethylammonium fluoride (0.170 g, 1.83 mmol) at 0 °C. After stirring at this temp. for 3 h, the reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts and the solvent was removed under reduced pressure. To this was added Et<sub>2</sub>O (5 mL) at 30 °C. Filtration of the resulting deposits with a glass filter (G4) gave 0.463 g (78%) of **7b** as a green solid. mp. (dec.) 135 °C; IR (KBr) 3008, 2943, 1636, 1523, 1481, 1404, 1235, 1108, 1038, 948, 891, 744, 669, 622, 579, 530, 515, 455, 418 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 2.33 (s, 3H, CH<sub>3</sub>), 3.08 (s, 12H, NMe<sub>4</sub>), 6.90–7.02 (m, 4H, Ar); <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 19.6 (CH<sub>3</sub>), 56.1 (m, NMe<sub>4</sub>), 122.2, 125.0, 125.3, 127.2, 130.6, 170.0 (*Cipso*), 263.6 (C=Se); <sup>77</sup>Se NMR (CD<sub>3</sub>CN, Me<sub>2</sub>Se): δ 1478.2; <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): δ 2.27 (s, 3H, CH<sub>3</sub>), 3.09 (s, 12H, NMe<sub>4</sub>), 6.89–6.96 (m, 4H, Ar); <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): δ 19.1 (CH<sub>3</sub>), 54.3 (m, NMe<sub>4</sub>), 120.9, 123.7, 124.0, 126.3, 129.3, 168.4 (*Cipso*), 263.6 (C=Se, <sup>1</sup>*J*<sub>13C-77Se</sub> = 208.7 Hz); <sup>77</sup>Se NMR (d<sub>6</sub>-DMSO, Me<sub>2</sub>Se): δ 1493.0; UV-Vis (THF) λ<sub>max</sub> (log ε): 219 (4.03), 242 (3.84), 299 (sh), 417 (3.64), 634 (2.32);

UV-Vis (solid state, MgO)  $\lambda_{\max}$ : 228, 250, 321, 385, 611; Anal. Calcd for  $C_{12}H_{19}NSe_2 \cdot 0.25H_2O$ : C, 42.43; H, 5.71. Found: C, 42.26; H, 5.65.

**Tetramethylammonium 4-bromodiselenobenzoate (7c).** In a 20 mL two-necked flask,  $CH_3CN$  (2 mL) solution of **4c** (0.053 g, 0.12 mmol) was added to a  $CH_3CN$  (1 mL) suspension of tetramethylammonium fluoride (0.012 g, 0.13 mmol) at 0 °C. After stirring at 30 °C for 1 h, the reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts and the solvent was removed under reduced pressure. To this was added  $Et_2O$  (5 mL) at 30 °C. Filtration of the resulting deposits with a glass filter (G4) gave 0.034 g (68%) of **7c** a green solid. mp. (dec.) 105 °C; IR (KBr) 3004, 2924, 1589, 1572, 1543, 1481, 1471, 1403, 1384, 1282, 1259, 1209, 1167, 1096, 1071, 1004, 948, 899, 866, 819, 706, 627, 554, 469, 424  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3CN$ ):  $\delta$  3.09 (s, 12H,  $NMe_4$ ), 7.26 (d,  $J = 8.3$  Hz, 2H, Ar), 8.09 (d,  $J = 8.3$  Hz, 2H, Ar);  $^{13}C$  NMR ( $CD_3CN$ ):  $\delta$  56.1 (m,  $NMe_4$ ), 127.6, 130.1, 132.1, 163.7 (*Cipso*), 256.1 (C=Se,  $^1J_{13C-77Se} = 214.9$  Hz);  $^{77}Se$  NMR ( $CD_3CN$ ,  $Me_2Se$ ):  $\delta$  1449.4; UV-Vis (THF)  $\lambda_{\max}$  (log  $\epsilon$ ): 230 (4.19), 276 (4.15), 358 (sh), 453 (3.46), 670 (2.12); UV-Vis (solid state, MgO)  $\lambda_{\max}$ : 224, 234, 297, 327, 433, 671.

**Tetramethylammonium 4-methoxydiselenobenzoate (7d).** In a 20 mL two-necked flask,  $CH_3CN$  (2 mL) solution of **4d** (0.127 g, 0.33 mmol) was added to a  $CH_3CN$  (2 mL) suspension of tetramethylammonium fluoride (0.032 g, 0.34 mmol) at 0 °C. After stirring at this temp. for 1.5 h, the reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts and the solvent was removed under reduced pressure. To this was added  $Et_2O$  (5 mL) at 0 °C. Filtration of the resulting deposits with a glass filter (G4) gave 0.056 g (47%) of **7d** a yellow green solid. mp. (dec.) 95 °C; IR (KBr) 2996, 1591, 1488, 1288, 1250, 1165, 1110, 1028, 948, 888, 828, 632, 556, 488, 453, 425  $cm^{-1}$ ;  $^1H$  NMR ( $CD_3CN$ ):  $\delta$  3.10 (s, 12H,  $NMe_4$ ), 3.76 (s, 3H,  $CH_3O$ ), 6.66 (d,  $J = 9.0$  Hz, 2H, Ar), 8.38 (d,  $J = 9.0$  Hz, 2H, Ar);  $^{13}C$  NMR ( $CD_3CN$ ):  $\delta$  56.0 ( $CH_3O$ ), 56.0 (m,  $NMe_4$ ), 112.4, 128.2, 156.5 (*Cipso*), 162.0, 256.6 (C=Se,  $^1J_{13C-77Se} = 211.6$  Hz);  $^{77}Se$  NMR ( $CD_3CN$ ,  $Me_2Se$ ):  $\delta$  1362.6; UV-Vis (THF)  $\lambda_{\max}$  (log  $\epsilon$ ): 234 (4.64), 342 (4.24), 452 (3.96), 690 (2.45); UV-Vis (solid state, MgO)  $\lambda_{\max}$ : 240, 350, 448, 692.

**2-Methyldiselenobenzoic acid *p*-phenylphenacyl ester (11).** In a 20 mL two-necked flask, *p*-phenylphenacyl bromide (0.102 g, 0.37 mmol) was added to  $CH_2Cl_2$  (10 mL) suspension of **7b** (0.124 g, 0.37 mmol) at 0 °C and this mixture was stirred at this temp. for 1 h. To this was added hexane (10 mL) at 0 °C and the insoluble parts was filtered off. After removal of the solvent from the filtrate under reduced pressure, the residue was purified by column chromatography on silica gel using  $CH_2Cl_2$ /hexane (1:1) ( $R_f = 0.55$ ) to give 0.115 g (68%) of **11** as blue needles. mp. (dec.) 102 °C; IR (KBr) 2920, 2851, 1680 (C=O), 1602, 1559, 1484, 1449, 1350, 1314, 1273, 1186, 1114, 991, 952, 933, 846, 816, 760, 743, 693, 558, 442  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ ,  $Me_4Si$ ):  $\delta$  2.36 (s, 3H,  $CH_3$ ), 4.90 (s, 2H,  $CH_2$ ), 7.15–8.10 (m, 13H, Ar);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  19.8 ( $CH_3$ ), 45.6 ( $CH_2$ ), 123.4, 125.3, 127.2, 127.4, 128.4, 129.0, 129.2, 130.6, 131.1, 134.3, 139.5, 146.4, 154.2, 193.0 (C=O), 238.0 (C=Se);  $^{77}Se$  NMR ( $CDCl_3$ ,  $Me_2Se$ ):  $\delta$  872.9 (C–Se), 1870.7 (C=Se); UV-Vis (THF)  $\lambda_{\max}$  (log  $\epsilon$ ): 221 (4.50), 289 (4.42), 371 (4.05), 601 (2.34); Anal. Calcd for  $C_{22}H_{18}OSe_2$ : C, 57.91; H, 3.98. Found: C, 57.65; H, 4.11.

**2-Methyldiselenobenzoic acid  $\gamma$ -oxobutyl ester (13).** In a 20 mL two-necked flask, trifluoromethanesulfonic acid (92  $\mu$ l, 1.04 mmol) was added to a degassed Et<sub>2</sub>O (7 mL) suspension of **7b** (0.116 g, 0.35 mmol) at -70 °C. The green suspension was immediately changed to green solution. After addition of methyl vinyl ketone (0.3 mL, 3.64 mmol), the stirring was continued for 2 h at -70 °C and 0.5 h at 30 °C. The green solution was gradually changed from green to blue. The reaction mixture was poured onto water, and extracted with Et<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using Et<sub>2</sub>O/hexane (1:10) [R<sub>f</sub> = 0.53 (hexane/Et<sub>2</sub>O = 1 : 1)] to give 0.024 g (21%) of **13** as blue oil. IR (neat) 3413, 3059, 2963, 1714 (C=O), 1477, 1451, 1401, 1362, 1262, 1113, 1035, 951, 935, 867, 848, 801, 748, 704, 666, 621, 555, 505 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  2.21 (s, 3H, CH<sub>3</sub>CO), 2.35 (s, 3H, CH<sub>3</sub>), 3.11 (t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>), 3.56 (t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>Se), 7.15–7.26 (m, 4H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  19.8 (CH<sub>3</sub>), 29.8 (CH<sub>2</sub>), 30.8 (CH<sub>3</sub>CO), 42.1 (CH<sub>2</sub>), 123.2, 125.3, 128.9, 130.3, 131.0, 155.3 (*Cipso*), 206.9 (C=O), 241.1 (C=Se); <sup>77</sup>Se NMR (CDCl<sub>3</sub>, Me<sub>2</sub>Se):  $\delta$  912.3 (C–Se), 1842.6 (C=Se); EIMS (*m/z*): 332 (M<sup>+</sup>); HRMS Calcd for C<sub>12</sub>H<sub>14</sub>OSe<sub>2</sub>: 333.93747. Found: 333.93812.

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## Chapter 7

# Acyl Carbamoyl Selenides and Related Sulfur Isologues: Synthesis and X-Ray Structural Analyses

### 7.1. Introduction

In general, the isolation of carbamic carboxylic mixed acid anhydrides **I** (E = E' = O) is difficult due to the easy equilibrium between the starting compounds (RCOOH and R'NCO) and product [RC(=O)OC(=O)NHR']<sup>1,2</sup> (Figure 1). Previously, Author's laboratory reported the isolation of a series of dithiocarboxylic carbamic mixed acid anhydrides **I** (E = E' = S) as crystals by reacting dithiocarboxylic acids with aryl isocyanates.<sup>3</sup> Since then, several carbamic thiocarboxylic mixed acid anhydrides **I** (E = O, E' = S) have been reported by Motoki et al.<sup>4</sup> However, the synthesis of other carbamic chalcogenocarboxylic mixed acid anhydrides have not been reported in the literature. This is most likely due to the difficulty of synthesizing chalcogenocarboxylic acids themselves.<sup>5</sup> Author's laboratory successful isolation of selenocarboxylic acids<sup>6</sup> prompted the author to synthesize carbamic selenocarboxylic mixed acid anhydrides. The Author report here the first isolation of carbamic selenocarboxylic mixed acid anhydrides and their structures which were determined by X-ray structural analyses.

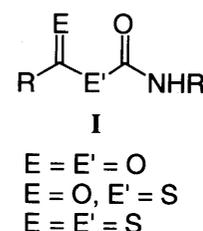
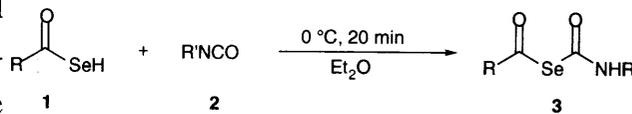


Figure 1

### 7.2. Results and discussion

When a diethyl ether solution of phenyl isocyanate was added to an equimolar amount of 4-methoxybenzenecarbonyl selenide in the same solvent at room temperature, the orange solution of the selenocarboxylic acid quickly

changed to a colorless suspension. Removal of the solvent and recrystallization of the resulting residue from dichloromethane/hexane



gave the expected 4-methoxybenzoyl *N*-phenylcarbamoyl selenide **3h** in 95% yield as colorless crystals. Similarly, the reactions of other selenocarboxylic acids with aryl isocyanates gave the corresponding acyl carbamoyl selenides (**3a–g, k–n**) in isolated yields of 35–99% (Scheme 1). In addition, the reactions with benzoyl and *p*-tosyl isocyanates proceeded more quickly to give the corresponding *N*-benzoyl- **3i** and *N*-(*p*-

RC(O)SeC(O)NHR'			
No.	R	R'	Yield [%]
<b>3a</b>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	35
<b>3b</b>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	95
<b>3c</b>	1-Adamantyl	C <sub>6</sub> H <sub>5</sub>	78
<b>3d</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	99
<b>3e</b>	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	93
<b>3f</b>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	93
<b>3g</b>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	92
<b>3h</b>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	95
<b>3i</b>		C <sub>6</sub> H <sub>5</sub> CO	61
<b>3j</b>		4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	97
<b>3k</b>	2,6-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	100
<b>3l</b>	3-Cl-2,6-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	97
<b>3m</b>	4-C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	92
<b>3n</b>	1-C <sub>10</sub> H <sub>7</sub>	C <sub>6</sub> H <sub>5</sub>	93

tosyl)carbamoyl selenides **3j**. The structures of the products reported herein were established by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and by elemental and X-ray structural analyses.

The resulting mixed acid anhydrides **3** are colorless crystals or colorless oils and are relatively stable thermally and insensitive toward oxygen. The aliphatic derivatives (**3a–c**) appear to be more labile than the aromatic derivatives (**3d–n**). Acetyl *N*-phenylcarbamoyl selenide **3a** decomposed at room temperature even under an argon atmosphere. Therefore, these aliphatic derivatives were not subjected to elemental analysis.

**Spectra.** Previously, we reported that the NH proton chemical shifts in thioacyl carbamoyl sulfides (**I**,  $\text{E} = \text{E}' = \text{S}$ ) appeared at unusually low fields, below  $\delta$  12, indicating the presence of an intramolecular  $\text{C}=\text{S}\cdots\text{HN}$  hydrogen bond.<sup>3</sup> As shown in Table 1, the chemical shifts of the NH proton appear in the range of  $\delta$  9–12, indicative of an intramolecular hydrogen bond between the carbonyl oxygen and the NH hydrogen. The carbonyl and carbamoyl carbon chemical shifts are observed in the ranges of  $\delta$  194–216 and  $\delta$  156–160, respectively. The  $^{77}\text{Se}$  NMR signals appear at  $\delta$  630–730. Thus, these spectral data indicate that **3** exists as structure **IIa** (Figure 2).

However, in the  $^1\text{H}$  NMR spectrum of **3a**, two broad signals at  $\delta$  9.15 and  $\delta$  9.91 (proton ratio = 1:10) was observed, which are attributable to OH and NH protons, respectively. No appreciable change in the proton ratio was observed in the range 20 °C to -60 °C. The  $^{13}\text{C}$  NMR spectra, except for the signals at  $\delta$  156.2 (CONH) and  $\delta$  202.7 (COSe) in **IIaa** (Table 2), also show small signals at  $\delta$  160.9 and  $\delta$  194.6, which are attributable to the  $\text{C}=\text{N}$  and COSe groups, respectively. In addition, in  $^{77}\text{Se}$  NMR spectroscopy, a small sharp signal is observed at  $\delta$  835. These results apparently indicate the existence of a tautomer (**IIab**) of **IIaa**. In the  $^1\text{H}$  NMR spectra of other selenides (**3b, d, h–l**), small or negligible signals of the corresponding tautomers **IIb** are observed. Table 2 shows the proton ratios of NH in **IIa** and OH in **IIb**. We also

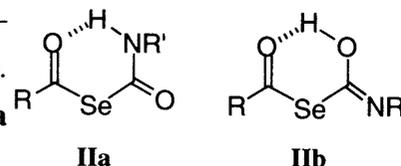


Figure 2

Table 1 Spectral Data of Acyl Carbamoyl Selenides **3**

No.	$\text{RC(O)SeC(O)NHR}'$		NMR ( $\text{CDCl}_3$ ) [ $\delta$ ]			
	<i>R</i>	<i>R'</i>	$^1\text{H}$ (NH)	$^{13}\text{C}$ (O)N	$^{13}\text{C}$ (O)Se	$^{77}\text{Se}$
<b>3a</b>	$\text{CH}_3$	$\text{C}_6\text{H}_5$	9.91	156.2	202.7	687.5
<b>3b</b>	$t\text{-C}_4\text{H}_9$	$\text{C}_6\text{H}_5$	10.05	156.4	215.6	639.1
<b>3c</b>	1-Adamantyl	$\text{C}_6\text{H}_5$	10.10	156.8	215.3	—
<b>3d</b>	$\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5$	10.41	156.0	199.7	648.4
<b>3e</b>	2- $\text{CH}_3\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5$	10.27	157.0	201.8	678.4
<b>3f</b>	4- $\text{CH}_3\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5$	10.45	156.3	198.9	642.6
<b>3g</b>	2- $\text{CH}_3\text{OC}_6\text{H}_4$	$\text{C}_6\text{H}_5$	10.61	159.3	197.4	708.1
<b>3h</b>	4- $\text{CH}_3\text{OC}_6\text{H}_4$	$\text{C}_6\text{H}_5$	10.51	156.4	197.1	632.7
<b>3i</b>		$\text{C}_6\text{H}_5\text{CO}$	10.51	157.4	197.6	—
<b>3j</b>		4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$	11.54	157.3	194.8	—
<b>3k</b>	2,6- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$	4- $\text{CH}_3\text{C}_6\text{H}_4$	10.07	156.5	199.9	—
<b>3l</b>	3-Cl-2,6- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2$	$\text{C}_6\text{H}_5$	10.05	157.6	199.3	726.1
<b>3m</b>	4- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5$	10.46	156.1	198.9	—
<b>3n</b>	1- $\text{C}_{10}\text{H}_7$	$\text{C}_6\text{H}_5$	10.36	157.1	201.9	—

Table 2 Ratio of Tautomers **IIa** and **IIb**

No.	$\text{RC(O)SeC(O)NHR}'$		Ratio	
	<i>R</i>	<i>R'</i>	<b>IIa</b>	<b>IIb</b>
<b>3a</b>	$\text{CH}_3$	$\text{C}_6\text{H}_5$	8 ( <b>IIaa</b> )	1 ( <b>IIab</b> )
<b>3b</b>	$t\text{-C}_4\text{H}_9$	$\text{C}_6\text{H}_5$	12 ( <b>IIba</b> )	1 ( <b>IIbb</b> )
<b>3d</b>	$\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5$	20 ( <b>IIda</b> )	1 ( <b>IIdb</b> )
<b>3e</b>	2- $\text{CH}_3\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5$	9 ( <b>IIea</b> )	1 ( <b>IIeb</b> )
<b>3f</b>	4- $\text{CH}_3\text{C}_6\text{H}_4$	$\text{C}_6\text{H}_5$	30 ( <b>IIfa</b> )	1 ( <b>IIfb</b> )
<b>3g</b>	2- $\text{CH}_3\text{OC}_6\text{H}_4$	$\text{C}_6\text{H}_5$	50 ( <b>IIga</b> )	1 ( <b>IIgb</b> )
<b>3h</b>	4- $\text{CH}_3\text{OC}_6\text{H}_4$	$\text{C}_6\text{H}_5$	30 ( <b>IIha</b> )	1 ( <b>IIhb</b> )
<b>3i</b>	3-Cl-2,6- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$	$\text{C}_6\text{H}_5$	12 ( <b>IIia</b> )	1 ( <b>IIib</b> )

obtained  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which indicate the existence of the tautomers **IIIb** and **IVb** for the previously reported sulfur isologues (**I**,  $E = \text{O}$ ,  $E' = \text{S}^4$  and  $E, E' = \text{S}^3$ ):

4-methoxybenzoyl **4** and 4-methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfides **5** (Figure 3). 4-methoxybenzoyl **4** and 4-methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfides **5** (Figure 3). The proton ratios of **IIIa** and **IIIb** in **4** and **IVa** and **IVb** in **5** were 4:1 and 20:1, respectively.

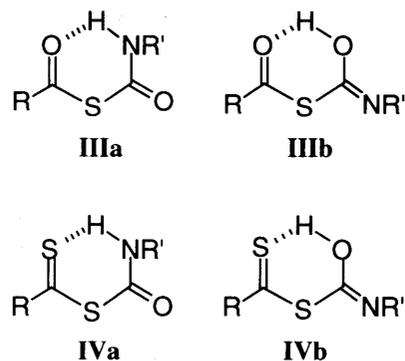


Figure 3

**X-Ray structure.** To confirm the intramolecular hydrogen bond, the X-ray structural analysis of **3** was carried out. To our knowledge, no structural analysis of acyl or thioacyl carbamoyl chalcogenides has been described in the literature. After several attempts to obtain acyl carbamoyl selenides **3** as single crystals, 2,6-dimethoxybenzoyl *N*-(4-methylphenyl)carbamoyl selenide **3k** afforded suitable crystals for X-ray analysis. The molecular structure is shown in Figure 4. The final atomic positional parameters are listed in Table 3. Selected bond distances and angles are shown in Table 4. The C1–O1 [1.204(10) Å] and C11–O2 [1.20(1) Å] distances indicate double bonds. The C11–N1 [1.34(1) Å], C12–N1 [1.436(9) Å], C1–Se1 [1.935(10) Å], and C11–Se1 distances [1.965(9) Å] are normal, indicating single

Table 3 Crystal Data and Experimental Crystallographic Details for Compounds **3k**, **4**, and **5**

Compound	<b>3k</b>	<b>4</b>	<b>5</b>
Empirical formula	$\text{C}_{17}\text{H}_{17}\text{NO}_4\text{Se}$	$\text{C}_{16}\text{H}_{15}\text{NO}_3\text{S}$	$\text{C}_{16}\text{H}_{15}\text{NO}_2\text{S}_2$
<i>M</i>	378.29	301.36	317.42
Crystal Ssize	0.34 X 0.13 X 0.13	0.20 X 0.20 X 0.30	0.34 X 0.13 X 0.13
Color/shape	colorless/needle	colorless/needle	orange/needle
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$\text{Pna}2_1$	$P-1$	$\text{P}2_1/n$
<i>a</i> /Å	13.976(1)	12.389(3)	4.101(4)
<i>b</i> /Å	8.520(1)	15.489(3)	21.076(3)
<i>c</i> /Å	13.753(2)	4.132(2)	17.731(3)
$\alpha^\circ$		91.19(3)	
$\beta^\circ$		90.80(3)	94.65(4)
$\gamma^\circ$		112.89(1)	
<i>V</i> /Å <sup>3</sup>	1637.6(3)	730.1(4)	1527(1)
<i>Z</i>	4	2	4
<i>F</i> (000)	768.00	316.00	664.00
$D_c/\text{g cm}^{-3}$	1.534	1.371	1.380
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	23.12	2.31	3.51
Temp (°C)	23 ± 1	23 ± 1	23 ± 1
$2\theta$ max (°)	55.0	55.0	55.0
Scan Rate (° min <sup>-1</sup> )	16.0	16.0	16.0
Data Collected	+h, +k, +l	+h, ±k, ±l	+h, +k, ±l
Total data collected, unique, observed	2170, 1954, 1170 ( $l > 2\sigma(l)$ )	3502, 3344, 1681 ( $l > 2\sigma(l)$ )	4112, 3624, 1158 ( $l > 2\sigma(l)$ )
No. of variable	209	190	190
Residuals: <i>R</i> 1; <i>wR</i> <sup>a</sup>	0.086, 0.125	0.060, 0.086	0.092, 0.220
Goodness of Fit	1.02	1.28	1.09
Final diff. map max, min (e Å <sup>-3</sup> )	-0.60, 0.55	-0.24, 0.23	-0.58, 0.58

<sup>a</sup> $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  (for  $l > 2\sigma(l)$  data),  $wR = [(\sum w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}$ , where  $w = 1/\sigma^2(F_o^2)$ .

**Table 4** Selected bond lengths (Å) and bond angles (°) of **3k**, **4**, and **5**

<b>3k</b>					
Bond lengths					
Se1-C1	1.935(10)	N1-H1	0.88		
Se1-C11	1.965(9)	N1...O1	2.76(2)		
O1-C1	1.204(10)	O1...H1	1.89		
O2-C11	1.20(1)	Se1...O4	2.959(7)		
N1-C11	1.34(1)	O1...O3	2.722(7)		
N1-C12	1.436(9)				
Angles					
Se1-C1-O1	121.9(6)	O2-C11-N1	127.8(8)		
C1-Se1-C11	106.0(4)	C11-N1-C12	124.7(8)		
Se1-C11-N1	116.2(6)	N1-H1...O1	173.0		
Torsion angles					
Se1-C1-C2-C7	48(1)	O1-C1-C2-C3	42(1)		
N1-C11-Se1-C1	3.2(8)	O2-C11-N1-C12	0(1)		
O1-C1-Se1-C11	0.5(9)	Se1-C11-N1-H1	8		

<b>4</b>				<b>5</b>			
Bond lengths				Bond lengths			
S1-C1	1.791(3)	N1-C11	1.334(4)	S1-C1	1.744(6)	N1-C11	1.322(8)
S1-C11	1.817(4)	N1-C12	1.422(4)	S1-C11	1.844(6)	N1-C12	1.448(8)
O1-C1	1.218(4)	N1-H1	0.85	S2-C1	1.632(7)	N1-H1	0.95
O2-C11	1.202(4)	N1...O1	2.705(3)	O1-C11	1.197(7)	N1...S2	3.062(5)
		O1...H1	1.95			S2...H1	2.58
Angles				Angles			
S1-C1-O1	122.8(3)	O2-C11-N1	128.4(3)	S1-C1-S2	128.0(4)	O1-C11-N1	130.3(6)
C1-S1-C11	109.3(2)	C11-N1-C12	127.5(3)	C1-S1-C11	114.5(3)	C11-N1-C12	126.6(6)
S1-C11-N1	117.2(3)	N1-H1...O1	146.0	S1-C11-N1	117.3(5)	N1-H1...S2	111.8
Torsion angles				Torsion angles			
S1-C1-C2-C7	5.0(5)	O1-C1-C2-C3	4.8(5)	S1-C1-C2-C7	20.6(8)	S2-C1-C2-C3	19.6(9)
N1-C11-S1-C1	3.9(3)	O2-C11-N1-C12	2.2(6)	N1-C11-S1-C1	2.4(7)	O1-C11-N1-C12	5(1)
O1-C1-S1-C11	2.0(4)	S1-C11-N1-H1	10	S2-C1-S1-C11	6.3(6)	S1-C11-N1-H1	54

bond. The O1–N1, N1–H1, and O1–H1 distances are 2.76(2) Å, 0.88 Å, and 1.89 Å, respectively, and the O1–H1–N1 bond angle is 173.0°, indicating the presence of a hydrogen bond between the carbonyl oxygen (O1) and the NH hydrogen (H1). Torsion angles [3.2(9)° for N1–C11–Se1–C1, 0.5(9)° for O1–C1–Se1–C11 and 8° for Se1–C11–N1–H1] indicate that the selenocarboxyl group and carbamoyl group are in approximately the same plane to give a planar intramolecular six-membered ring. In addition, the O3–O1 [2.722(7) Å] and O4–Se1 [2.959(7) Å] distances are remarkably short compared with the sum [3.04 Å for O–O; 3.42 Å for O–Se<sup>7</sup>] [7]) of the van der Waals radii of both the atoms, respectively, suggesting the presence of nonbonded repulsion and nonbonded attraction.

For comparison with the structures of previously isolated sulfur isologues [RC(=O/S)SC(=O)R'], the X-ray structural analyses of 4-methoxybenzoyl **4** and 4-methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfides **5** were carried out. Their molecular structures are shown in Figure 4 (b and c). Selected bond lengths and angles are shown in Table 3. As expected, they have an intramolecular six-membered ring structure formed by a hydrogen bond between the carbonyl oxygen or thiocarbonyl sulfur and the NH hydrogen atoms, respectively. Presumably, this might contribute to the overall stability of the molecules. Attempts to obtain single crystals

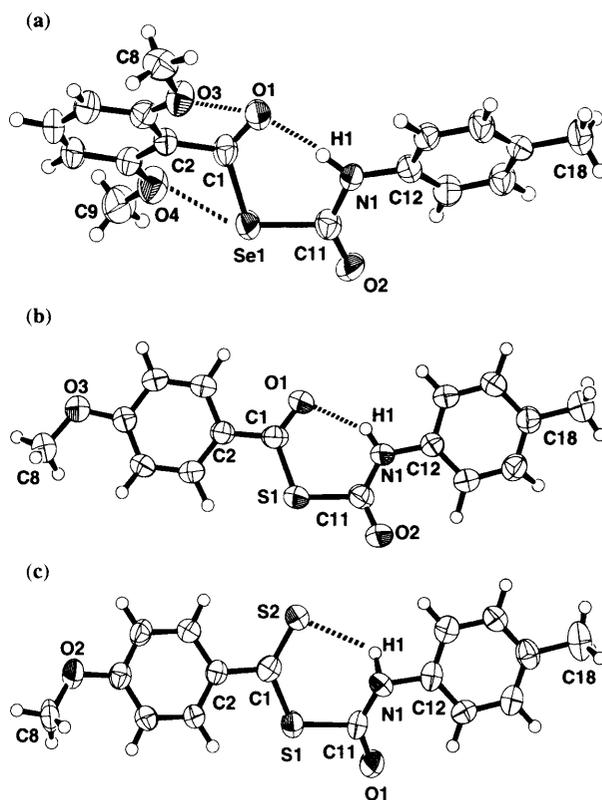
of the tautomers, **Ib**, **IIIb**, and **IVb** failed.

**Reactions.** The reaction of **3h** with sodium methoxide in diethyl ether readily proceeded at room temperature to give sodium 4-methoxybenzenecarboxoselenoate **6** and methyl *N*-phenylcarbamate **7** in good yields (Scheme 2). The reaction with two equimolar amounts of *p*-toluidine under similar conditions gave *N*-4-methylphenyl 4-methoxybenzamide **8** and *N*-4-methylphenyl *N'*-phenyl urea **9** in moderate yields (Scheme 2). Compound **8** may be formed by decomposition of 4-methoxyseleno-carboxylic acid 4-methylphenylammonium salt [4-MeOC<sub>6</sub>H<sub>4</sub>C(=O)Se<sup>-</sup>+NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4]. These results indicate that nucleophiles, such as alkoxides and amines, preferentially attack the carbamoyl carbon rather than the carbonyl carbon in **3**.

### 7.3. Conclusion

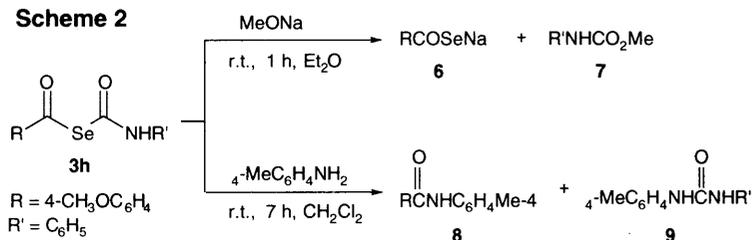
Selenocarboxylic acids [RC(=O)SeH] were found to readily react with aryl, acyl, and arenesulfonyl isocyanates to give the corresponding acyl carbamoyl selenides **3** [RC(=O)Se-

C(=O)NHR', R' = aryl, C<sub>6</sub>H<sub>5</sub>CO, and 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>] in good yields. Their tautomers [RC(=O)Se-C(=NR')OH] were also detected by <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se NMR spectroscopies. The structure of **3** [R = 2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R' = 4-MeC<sub>6</sub>H<sub>4</sub>] was characterized by X-ray crystallography, which showed that this molecule is stabilized by an intramolecular hydrogen bond between the carbonyl oxygen and the NH hydrogen to form a planar six-membered ring and by nonbonded interaction of the ortho methoxy oxygen with the carbonyl oxygen or the selenium atoms. 4-Methoxybenzoyl and 4-methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfides (**4** and **5**) were showed by X-ray crystallography to similarly have a planar intramolecular six-membered ring formed by a hydrogen bond between the carbonyl oxygen or thiocarbonyl sulfur and NH hydrogen atoms. The tautomers [RC(=E)SC(=NR')OH; E = O or S] of **4** and **5** also were detected spectroscopically. The reactions of **3h** (R = 4-MeOC<sub>6</sub>H<sub>4</sub>, R' = Ph) with sodium methoxide and *p*-toluidine gave sodium selenocarboxylate and the corresponding amides and urea as main products, respectively.



**Figure 4** The structures of 2,6-dimethoxybenzoyl *N*-(4-methylphenyl)carbamoyl selenide **3k**, 4-methoxybenzoyl *N*-(4-methylphenyl)carbamoyl sulfide **4** and 4-methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfide **5**. The atoms are drawn with 50% probability thermal ellipsoids.

**Scheme 2**



## 7.4. Experimental

The melting points were determined by a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a PERKIN ELMER FT-IR 1640 instrument. The  $^1\text{H}$  NMR spectra were recorded on JEOL JNM-GX-270 (270 MHz) and JEOL  $\alpha$ -400 (399.7 MHz) instruments with  $\text{Me}_4\text{Si}$  as an internal standard. The  $^{13}\text{C}$  NMR spectra were obtained by use of JEOL JNM-GX-270 (68 MHz) and JEOL  $\alpha$ -400 (100.4 MHz) instruments with  $\text{CDCl}_3$  as an internal standard. The  $^{77}\text{Se}$  NMR spectra were obtained by use of JEOL  $\alpha$ -400 (76.2 MHz) instrument with  $\text{Me}_2\text{Se}$  as an external standard. Elemental analyses were performed by the Elemental Center of Kyoto University.

**Materials.** The following reagents were of commercial grade and used without further purification: phenyl, 4-methylphenyl, and *p*-toluenesulfonyl isocyanates, and *p*-toluidine (from Tokyo Kasei) and hydrogen chloride (1.0 M solution in diethyl ether) (from Aldrich). Benzoyl isocyanate,<sup>8</sup> selenocarboxylic acids,<sup>5,6</sup> 4-methoxybenzenecarbothioic acid,<sup>9</sup> and 4-methoxybenzenecarbodithioic acid<sup>10</sup> were prepared according to the literatures. Dichloromethane was distilled from diphosphorus pentoxide and degassed. Diethyl ether was distilled from sodium diphenylketyl and degassed. Hexane was distilled from sodium metal prior to use and degassed. All of the manipulations were carried out under argon.

**3-Chloro-2,6-dimethoxybenzenecarboseleoic Acid (11).** Yellow oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.29 (br, 1H, SeH), 3.85 (s, 3H,  $\text{CH}_3\text{O}$ ), 3.91 (s, 3H,  $\text{CH}_3\text{O}$ ), 6.67 (d,  $J = 8.1$  Hz, 1H), 7.35 (d,  $J = 8.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  56.3 ( $\text{CH}_3\text{O}$ ), 62.5 ( $\text{CH}_3\text{O}$ ), 108.1, 119.8, 128.4, 132.2, 152.0, 154.4, 189.7 (CO).

**4-Biphenylcarboseleoic Acid (1m).** Red solid; IR (KBr): 2290 (SeH)  $\text{cm}^{-1}$ ,<sup>15</sup> dec.: 54–56°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.85 (br, 1H, SeH), 7.38–8.24 (m, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  127.8, 127.9, 128.0, 128.9, 129.1, 129.7, 129.8, 131.1, 203.2 (CO).

**X-ray Structure Analysis.** All measurement were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71069$  Å). All of the structures were solved and refined using the teXsan crystallographic software package. The cell dimensions were determined by a least-squares refinement of the diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections, and no decay was detected. An empirical absorption correction ( $\Psi$  Scan) was applied. The structures were solved by direct methods (SHELXS86)<sup>11</sup> and expanded using DIRDIF94.<sup>12</sup> Scattering factors for neutral atoms were from Cromer and Waber,<sup>13</sup> and anomalous dispersion<sup>14</sup> was used. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. Crystal data and measurement description are summarized in Table 3.

**Preparation of Single Crystals.** 2,6-Dimethoxybenzoyl *N*-(4-methylphenyl)carbamoyl selenide **3k** was crystallized from diethyl ether/hexane (1:1) at 18°C during a period of four days. 4-Methoxybenzoyl *N*-(4-methylphenyl)carbamoyl sulfide **4** was crystallized from  $\text{CH}_2\text{Cl}_2$ /hexane (1:5) at 23°C for three days. 4-Methoxythiobenzoyl *N*-(4-methylphenyl)carbamoyl sulfide **5** was crystallized from  $\text{CHCl}_3$ /hexane (1:2) at 23°C for two days. These crystal samples were cut from grown crystals, coated with an epoxy resin, and mounted on a glass fiber.

**Synthesis of Acyl Carbamoyl Selenides (3).** The synthesis of 4-methoxybenzoyl *N*-phenylcarbamoyl selenide **3h** is described in detail as typical procedures.

To a solution of sodium 4-methoxybenzenecarboxoselenoate (0.89 g, 3.0 mmol) in diethyl ether (10 mL), contained in a 20 mL two necked round bottom flask, 1.0 M hydrogen chloride in diethyl ether (2.6 mL) was added. The mixture was stirred at 0°C for 10 minutes. Filtration of the precipitates (NaCl and excess of sodium 4-methoxybenzenecarboxoselenoate) and removal of the solvent under reduced pressure (22°C/53.3Pa) gave 0.56 g (2.6 mmol) of 4-methoxybenzenecarboxoselenoic acid as yellow solid [5]. The solid was dissolved into diethyl ether (10 mL). A solution of phenylisothiocyanate (0.30 g, 2.6 mmol) in diethyl ether (5.0 mL) was added and stirred at 20°C for 10 min (The color of the solution changed from red to colorless). Removal of the solvent under reduced pressure (22°C/53.3Pa) gave 0.81 g (95%) of crude 4-methoxybenzoyl *N*-phenylcarbamoyl selenide **3h** as colorless solid. Recrystallization of the solid from a mixed solvent of dichloromethane (3 mL) and hexane (1 mL) at -20°C during 1 hour yielded 0.46 g (59%) of **3h** as colorless needles.

**Acetyl N-Phenylcarbamoyl Selenide (3a).** Colorless needles (35% yield); dec.: 81°C; IR (KBr): 3252 (NH), 1715 (COSe), 1682 (CONH), 1557 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Ilaa**, δ 2.50 (s, 3H, CH<sub>3</sub>), 7.15 (t, *J* = 7.6 Hz, 1H, NHPh), 7.35 (t, *J* = 7.6 Hz, 2H, NHPh), 7.53 (d, *J* = 7.6 Hz, 2H, NHPh), 9.91 (br, 1H, NH); **Ilab**, δ 2.54 (s, 3H, CH<sub>3</sub>), 9.15 (br, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Ilaa**, δ 35.0 (CH<sub>3</sub>), 119.9, 125.0, 129.2, 137.1, 156.2 (CONH), 203.7 (COSe); **Ilab**, δ 35.8 (CH<sub>3</sub>), 119.9, 124.8, 129.6, 137.4, 160.9 (C=N), 194.6 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Ilaa**, δ 687.5; **Ilab**, δ 835.9. This compound is too unstable to subject in elemental analysis.

**1,1-Dimethylethanecarbonyl N-Phenylcarbamoyl Selenide (3b).** Colorless oil (95% yield); IR (Neat): 3246 (NH), 1718 (COSe), 1670 (CONH), 1549 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Iiba**, δ 1.30 (s, 9H, CH<sub>3</sub>), 7.14 (t, *J* = 7.9 Hz, 1H, NHPh), 7.34 (t, *J* = 7.9 Hz, 2H, NHPh), 7.53 (d, *J* = 7.9 Hz, 2H, NHPh), 10.05 (br, 1H, NH); **Iibb**, δ 1.32 (s, 9H, CH<sub>3</sub>), 7.07 (t, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Iiba**, δ 26.0 (CH<sub>3</sub>C), 50.8 (CH<sub>3</sub>C), 119.8, 124.9, 129.1, 137.1, 156.4 (CONH), 215.6 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Iiba**, δ 639.1. This compound is too unstable to subject in elemental analysis.

**1-Adamantanecarbonyl N-Phenylcarbamoyl Selenide (3c).** Colorless crystals (78% yield); dec.: 103–105°C; IR (KBr): 3229 (NH), 1715 (COSe), 1664 (CONH), 1555 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.75 (br, 6H, Ad), 1.97 (br, 6H, Ad), 2.11 (br, 3H, Ad), 7.14 (t, *J* = 7.7 Hz, 1H, NHPh), 7.34 (t, *J* = 7.7 Hz, 2H, NHPh), 7.55 (d, *J* = 7.7 Hz, 2H, NHPh), 10.10 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 28.0 (Ad), 36.2 (Ad), 38.9 (Ad), 53.1 (Ad), 119.9, 124.9, 129.2, 137.2, 156.8 (CONH), 215.3 (COSe). This compound is too unstable to subject in elemental analysis.

**Benzoyl N-Phenylcarbamoyl Selenide (3d).** Colorless crystals (99% yield); dec.: 97–99°C; IR (KBr): 3222 (NH), 1728 (COSe), 1645 (CONH), 1554 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Iida**, δ 7.18 (t, *J* = 7.6 Hz, 1H, NHPh), 7.38 (t, *J* = 7.6 Hz, 2H, NHPh), 7.53 (t, *J* = 7.9 Hz, 2H, PhCO), 7.61 (d, *J* = 7.6 Hz, 2H, NHPh), 7.69 (t, *J* = 7.9 Hz, 1H, PhCO), 7.94 (d, *J* = 7.9 Hz, 2H, PhCO), 10.41 (br, 1H, NH); **Iidb**, δ 7.31 (t, *J* = 7.3 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Iida**, δ 120.0, 125.1, 127.6, 129.2, 129.3, 135.2, 137.2, 138.0, 156.0 (CONH), 199.7 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Iida**, δ 648.4. Anal. calcd for C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>Se: C, 55.28; H, 3.64. Found: C, 55.20; H, 3.57.

**2-Methylbenzoyl N-Phenylcarbamoyl Selenide (3e).** Colorless crystals (93% yield); dec.: 65–66°C; IR (KBr): 3225 (NH), 1718 (COSe), 1662 (CONH), 1549 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Ilea**, δ 2.55 (s, 3H, CH<sub>3</sub>), 7.10–7.80 (m, 9H), 10.27 (br, 1H, NH); **Iieb**: δ 2.51 (s, 3H, CH<sub>3</sub>), 9.04 (br, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Ilea**, δ 20.9 (CH<sub>3</sub>), 120.0, 124.8, 125.1, 126.4, 129.2, 129.6, 132.3, 133.4, 137.0, 137.1, 157.0 (CONH), 201.8 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Ilea**, δ 678.7. Anal. calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub>Se: C, 56.61; H, 4.12. Found: C, 56.36; H, 4.21.

**4-Methylbenzoyl N-Phenylcarbamoyl Selenide (3f).** Colorless crystals (93% yield); dec.: 97–99°C; IR (KBr): 3219 (NH), 1693 (COSe), 1645 (CONH), 1547 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Iifa**, δ 2.43 (s, 3H, CH<sub>3</sub>), 7.17 (t, *J* = 7.9 Hz, 1H, NHP*h*), 7.31 (d, *J* = 8.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 7.37 (t, *J* = 7.9 Hz, 2H, NHP*h*), 7.61 (d, *J* = 7.9 Hz, 2H, NHP*h*), 7.83 (t, *J* = 8.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 10.45 (br, 1H, NH); **Iifb**, δ 2.42 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Iifa**, δ 21.9 (CH<sub>3</sub>), 120.0, 125.0, 127.7, 129.2, 130.0, 135.5, 137.2, 146.7, 156.3 (CONH), 198.9 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Iifa**, δ 642.6. Anal. calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub>Se: C, 56.61; H, 4.12. Found: C, 56.60; H, 3.90.

**2-Methoxybenzoyl N-Phenylcarbamoyl Selenide (3g).** Colorless crystals (92% yield); dec.: 95–97°C; IR (KBr): 3257 (NH), 1707 (COSe), 1614 (CONH), 1556 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Iiga**, δ 4.00 (s, 3H, CH<sub>3</sub>O), 7.04 (d, *J* = 7.7 Hz, 1H, C<sub>6</sub>H<sub>4</sub>CO), 7.08 (t, *J* = 7.7 Hz, 1H, C<sub>6</sub>H<sub>4</sub>CO), 7.15 (t, *J* = 7.5 Hz, 1H, NHP*h*), 7.36 (t, *J* = 7.5 Hz, 2H, NHP*h*), 7.59 (t, *J* = 7.7 Hz, 1H, C<sub>6</sub>H<sub>4</sub>CO), 7.63 (d, *J* = 7.5 Hz, 2H, NHP*h*), 7.87 (d, *J* = 7.7 Hz, 1H, C<sub>6</sub>H<sub>4</sub>CO), 10.61 (br, 1H, NH); **Iigb**, δ 3.93 (s, 3H, CH<sub>3</sub>O); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Iiga**, δ 55.7 (CH<sub>3</sub>O), 112.4, 120.1, 121.1, 124.8, 126.7, 129.2, 129.4, 135.9, 137.4, 159.3 (CONH), 160.2, 197.4 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Iiga**, δ 708.1. Anal. calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>Se: C, 53.90; H, 3.92. Found: C, 53.98; H, 4.08.

**4-Methoxybenzoyl N-Phenylcarbamoyl Selenide (3h).** Colorless crystals (95% yield); dec.: 106–108°C; IR (KBr): 3224 (NH), 1728 (COSe), 1645 (CONH), 1572 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **Iiha**, δ 3.90 (s, 3H, CH<sub>3</sub>O), 6.98 (d, *J* = 9.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 7.16 (t, *J* = 7.8 Hz, 1H, NHP*h*), 7.37 (t, *J* = 7.8 Hz, 2H, NHP*h*), 7.60 (d, *J* = 7.8 Hz, 2H, NHP*h*), 7.91 (d, *J* = 9.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 10.51 (br, 1H, NH); **Iihb**, δ 3.86 (s, 3H, CH<sub>3</sub>O); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **Iiha**, δ 55.8 (CH<sub>3</sub>O), 114.5, 119.9, 124.9, 129.2, 130.2, 130.6, 137.3, 156.4 (CONH), 165.3, 197.1 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **Iiha**, δ 632.7. Anal. calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>Se: C, 53.90; H, 3.92. Found: C, 53.65; H, 4.02.

**4-Methoxybenzoyl N-(Benzoyl)carbamoyl Selenide (3i).** Colorless crystals (61% yield); dec.: 81–83°C; IR (KBr): 3373 (NH), 1769 (COSe), 1642 (CONH), 1574 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.91 (s, 3H, CH<sub>3</sub>O), 7.00 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 7.45 (t, *J* = 7.8 Hz, 1H, NHP*h*), 7.58 (t, *J* = 7.8 Hz, 2H, NHP*h*), 7.93 (d, *J* = 7.8 Hz, 2H, NHP*h*), 8.15 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 10.51 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 55.8 (CH<sub>3</sub>O), 114.7, 128.3, 128.6, 130.0, 130.5, 131.1, 133.5, 157.4 (SeCONH), 162.7 (PhCONH), 165.8, 197.6 (COSe).

**4-Methoxybenzoyl N-(Tosyl)carbamoyl Selenide (3j).** Colorless crystals (97% yield); dec.: 99–100°C; IR (KBr): 3365 (NH), 1719 (COSe), 1646 (CONH), 1509 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.44 (s, 3H, CH<sub>3</sub>), 3.90 (s, 3H, CH<sub>3</sub>O), 6.98 (d, *J* = 8.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 7.35 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 7.84 (d, *J* = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 8.00 (d, *J* = 8.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>CO), 11.54 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.7 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>O), 114.7, 128.5, 128.6, 129.7, 129.8, 135.5, 145.5, 157.3 (CONH), 165.9, 194.8 (COSe). Anal. calcd for

C<sub>16</sub>H<sub>15</sub>NO<sub>5</sub>SSe: C, 46.61; H, 3.67. Found: C, 46.74; H, 3.46.

**2,6-Dimethoxybenzoyl N-(4-Methylphenyl)carbamoyl Selenide (3k).** Colorless needles (100% yield); dec.: 118–122°C; IR (KBr): 3231 (NH), 1695 (COSe), 1654 (CONH), 1593, 1523 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.33 (s, 3H, CH<sub>3</sub>), 3.83 (s, 6H, CH<sub>3</sub>O), 6.58 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 6.7 Hz, 2H), 7.35 (t, *J* = 6.7 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 10.08 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 20.9 (CH<sub>3</sub>), 56.2 (CH<sub>3</sub>O), 104.3, 120.0, 129.6, 133.1, 134.4, 134.9, 156.5, 158.3 (CONH), 199.9 (COSe). Anal. calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>4</sub>Se: C, 53.98; H, 4.53. Found: C, 53.84; H, 4.41.

**3-Chloro-2,6-dimethoxybenzoyl N-Phenylcarbamoyl Selenide (3l).** Colorless crystals (97% yield); dec.: 84–86°C; IR (KBr): 3240 (NH), 1714 (COSe), 1655 (CONH), 1547 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **IIIa**, δ 3.86 (s, 3H, CH<sub>3</sub>O), 3.95 (s, 3H, CH<sub>3</sub>O), 6.70 (d, *J* = 9.3 Hz, 1H, C<sub>6</sub>H<sub>2</sub>CO), 7.18 (t, *J* = 7.8 Hz, 1H, NHPh), 7.38 (t, *J* = 7.8 Hz, 2H, NHPh), 7.43 (d, *J* = 7.8 Hz, 1H, C<sub>6</sub>H<sub>2</sub>CO), 7.61 (d, *J* = 7.8 Hz, 2H, NHPh), 10.05 (br, 1H, NH); **IIIb**, δ 3.87 (s, 3H, CH<sub>3</sub>O), 3.96 (s, 3H, CH<sub>3</sub>O); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **IIIa**, δ 56.5 (CH<sub>3</sub>O), 62.7 (CH<sub>3</sub>O), 108.3, 119.9, 120.0, 125.1, 125.5, 129.2, 133.4, 137.2, 152.6, 155.0, 157.6 (CONH), 199.3 (COSe); <sup>77</sup>Se NMR (CDCl<sub>3</sub>): **IIIa**, δ 726.1. Anal. calcd for C<sub>16</sub>H<sub>14</sub>ClNO<sub>4</sub>Se: C, 48.20; H, 3.54. Found: C, 48.29; H, 3.56.

**4-Biphenylcarbonyl N-Phenylcarbamoyl Selenide (3m).** Colorless crystals (92% yield); dec.: 106–108°C; IR (KBr): 3223 (NH), 1693 (COSe), 1655 (CONH), 1517 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.17–7.99 (m, 14H), 10.46 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 120.0, 125.0, 127.2, 127.3, 127.8, 128.2, 128.8, 129.0, 129.1, 137.1, 139.2, 148.0, 156.1 (CONH), 198.9 (COSe).

**1-Naphthalenecarbonyl N-Phenylcarbamoyl Selenide (3n).** Colorless crystals (93% yield); dec.: 87–90°C; IR (KBr): 3234 (NH), 1725 (COSe), 1655 (CONH), 1555 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.20–8.57 (m, 12H), 10.36 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 120.0, 124.5, 124.7, 125.1, 127.2, 128.2, 128.7, 129.0, 129.3, 129.4, 134.0, 134.9, 135.5, 137.2, 157.1 (CONH), 201.9 (COSe). Anal. calcd for C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>Se: C, 61.03; H, 3.70. Found: C, 61.02; H, 3.92.

**4-Methoxybenzoyl N-(4-Methylphenyl)carbamoyl Sulfide (4).** Colorless crystals; dec.: 136–142°C; IR (KBr): 3209 (NH), 1714 (COS), 1705 (CONH), 1542 (NH) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **IIIa**, δ 2.34 (s, 3H, CH<sub>3</sub>), 3.90 (s, 3H, CH<sub>3</sub>O), 6.98 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 10.82 (br, 1H, NH); **IIIb**, δ 2.32 (s, 3H, CH<sub>3</sub>), 3.87 (s, 3H, CH<sub>3</sub>O), 6.94 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 2H), 8.05 (d, *J* = 7.7 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **IIIa**, δ 21.0 (CH<sub>3</sub>), 55.7 (CH<sub>3</sub>O), 114.4, 120.2, 124.5, 128.5, 129.7, 130.2, 134.7, 158.3 (CONH), 165.2, 191.9 (COS).

**4-Methoxythiobenzoyl N-(4-Methylphenyl)carbamoyl Sulfide (5).** Orange needles; dec.: 120–121°C [3]; IR (KBr): 3282 (NH), 1712 (CO), 1541 (NH), 1248 (CS) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): **IVa**, δ 2.34 (s, 3H, CH<sub>3</sub>), 3.88 (s, 3H, CH<sub>3</sub>O), 6.91 (d, *J* = 9.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 8.05 (d, *J* = 9.3 Hz, 2H), 11.51 (br, 1H, NH); **IVb**, δ 2.31 (s, 3H, CH<sub>3</sub>), 3.86 (s, 3H, CH<sub>3</sub>O), 6.85 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): **IVa**, δ 21.0 (CH<sub>3</sub>), 55.7 (CH<sub>3</sub>O), 114.0, 120.3, 124.4, 129.5, 129.8, 130.1, 135.1, 158.2 (CONH), 165.0, 224.8 (CSS); **IVb**, δ 20.8 (CH<sub>3</sub>), 55.7 (CH<sub>3</sub>O), 113.5, 120.1, 129.4, 129.5, 134.3, 138.2.

**Reaction of 4-Methoxybenzoyl N-Phenylcarbamoyl Selenide(3h) with Sodium Methoxide.** 4-Methoxybenzoyl *N*-phenylcarbamoyl selenide **3h** (0.17 g, 0.5 mmol) and sodium methoxide (0.03 g, 0.5 mmol) were stirred in diethyl ether (5 mL) at 24°C for 1 h. The solvent was evaporated under reduced pressure to give yellow solid containing *sodium 4-methoxybenzenecarbosenoate* **6**. To the solid iodomethane (1 mL) was added and the mixture was stirred at 24°C for 1 h. To the reaction mixture was added diethyl ether (3 mL). The resulting precipitates (NaI containing methyl *N*-phenylcarbamate **7**) was filtered out. Evapoartion of the solvent from the filtrate under reduced pressure gave 0.11g (98%) of *Se*-methyl 4-methoxybenzenecarbosenoate, which was identified by comparison of the IR and <sup>1</sup>H NMR spectra with those of the authentic sample.

**Methyl N-phenylcarbamate 7.** m.p.: 43–45°C; IR (KBr): 3321 (NH), 1714 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.72 (s, 3H, CH<sub>3</sub>), 7.02 (t, *J* = 7.8 Hz, 1H), 7.02 (br, 1H, NH), 7.25 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 52.1 (CH<sub>3</sub>), 123.3, 129.5, 128.8, 137.9, 154.3 (CO).

**Reaction of 3h with p-Toluidine.** To a solution of 4-methoxybenzoyl *N*-phenylcarbamoyl selenide **3h** (0.26 g, 0.8 mmol) in dichloromethane (10 mL) *p*-toluidine (0.17 g, 1.6 mmol) was added and the mixture was stirred at room temperature for 7 h. After evaporation of the sovent under reduced pressure, diethyl ether (5 mL) was added. Filtration of the resulting precipitates gave 0.16 g (85% yield) *N*-4-methylphenyl *N'*-phenyl urea **9** as colorless needles. Removal of the diethyl ether from the filtrate under reduced pressure gave 0.11 g (57% yield) of *N*-4-methylphenyl 4-methoxybenzamide **8** as colorless crystals.

**N-4-Methylphenyl 4-Methoxybenzamide (8).** Colorless crystals; m.p.: 156–157°C; IR (KBr): 3340 (NH), 1651 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.31 (s, 3H, CH<sub>3</sub>), 3.83 (s, 3H, CH<sub>3</sub>O), 6.90 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.95 (br, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 20.9 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>O), 113.8, 120.4, 127.2, 128.9, 129.5, 133.9, 135.6, 162.3 (CO), 165.3.

**N-4-Methylphenyl N'-Phenyl Urea (9).** Colorless needles; m.p.: 204–205°C; IR (KBr): 3303 (NH), 1635 (CO) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>+DMSO-d<sub>6</sub>): δ 2.27 (s, 3H, CH<sub>3</sub>), 6.94 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 8.42 (br, 1H, NH), 8.49 (br, 1H, br); <sup>13</sup>C NMR (CDCl<sub>3</sub>+DMSO-d<sub>6</sub>): δ 20.4 (CH<sub>3</sub>), 118.1, 118.3, 121.5, 128.5, 129.0, 130.6, 137.0, 139.7, 152.6 (CO).

## 7.5. Reference

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## Conclusion

The synthesis and structure of Group 14 and 15 element derivatives of chalcogenocarboxylic acid are described in this thesis. The synthesis, structure, and reactivity of hitherto diselenocarboxylic acid salts is also described. The important results described in each chapter are summarized as follows.

In chapter 1 and 2, Group 14 element derivatives of chalcogenocarboxylic acid were synthesized, and their structures were determined by X-ray crystallography. The nonbonded distances between the carbonyl oxygen and the tin atom are the shortest in all derivatives. Natural bond orbital analyses showed that the interactions between the nonbonding orbitals on the carbonyl oxygen ( $n_O$ ) and the  $\sigma^*_{MS}$  orbitals have an influence on the attenuation of the  $M\cdots O$  distances ( $M = \text{Ge, Sn, Pb}$ ) in thiocarboxylate derivatives. A similar interaction weakens in selenocarboxylates and even more in tellurocarboxylate derivatives. In tellurocarboxylate derivatives, the interaction between the nonbonding orbitals on the carbonyl oxygen ( $n_O$ ) and the  $\sigma^*_{MC}$  orbitals ( $C = ipso\text{-benzene carbon}$ ) play the important role in the shortening of  $M\cdots O$  distances ( $M = \text{Ge, Sn, Pb}$ ).

In chapter 3, the structures of Group 14 element derivatives of dithiocarboxylates determined by X-ray crystallography are shown. The dithiocarboxylato ligand in mono derivatives  $\text{RCSSMPh}_3$  is bound to Group 14 elements as monodentate ligand, but those of bis- and tris-dithiocarboxylato derivatives were bound to Group 14 elements as anisobidentate ligand. Therefore, the structures around the Group 14 elements in mono derivatives showed a distorted tetrahedral, those in bis and tri derivatives showed a skew trapezoidal bipyramidal and pentagonal bipyramidal, respectively.

Chapter 4 and 5 described the synthesis and structure of Group 15 element derivatives of thio and dithiocarboxylic acid. In Both derivatives, the distances between the carbonyl oxygen or thiocarbonyl sulfur and the Group 15 elements ( $\text{P, As}$ ) is shorter than the sum of the van der Waals radii of both atoms. In arsenic derivatives, the reaction of the bis thio- and dithio carboxylate derivatives with piperidine gave the cyclic tetramer  $(\text{PhAsS})_4$  and the phenyltrithioarsonate dianion species  $\text{PhAsS}_3^{2-}$ .

In chapter 6, the synthesis pathway to the diselenocarboxylic acid salts and their spectroscopic properties, reactivity and structures are shown. Initially, the synthetic methods for diselenocarboxylic acid  $\beta$ -silylethyl esters as a key starting materials are outlined. Diselenocarboxylic acid  $\beta$ -silylethyl esters were synthesized by the reaction of aluminum selenolate, generated from the reduction of bis( $\beta$ -silylethyl) diselenide with DIBAL, with selenocarboxylic acid  $O$ -methyl esters. Secondary, the reaction of these esters with tetramethylammonium fluoride gave the diselenocarboxylic acid tetramethylammonium salts. Various spectroscopic data and X-ray crystallography suggest the double bond structure of the diselenocarboxyl group in the salts.

In chapter 7, the synthesis and structure of carbamic selenocarboxylic mixed acid anhydrides was described. The X-ray crystallography showed a planar intramolecular six-membered ring formed by a hydrogen bond between the carbonyl oxygen and NH hydrogen atoms in solid state. On the other hand, the tautomers existed at a rate of 10:1 — 20:1 from NMR spectroscopic data in  $\text{CDCl}_3$  solution.

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