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# Alkali Metal and Trimethylsilyl Carbamoselenothioates − Synthesis, Structure, and some Reactions

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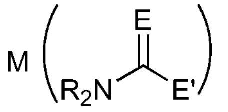
**Abstract.** This paper describes the synthesis and some reactions of potassium, rubidium , cesium and trimethylsilyl carbamoselenothioates. The potassium salts were synthesized in 70−80 % yields by reacting the corresponding thiocarbamoyl chlorides with potassium selenide in acetonitrile. Furthermore, the rubidium and cesium salts were obtained in good yields by treating the trimethylsilyl esters with the corresponding metal fluorides. The crystal structure of acetonitrile-solvated potassium *N*,*N*-dimethylcarbamoselenothioate consisted of dimeric units, featuring μ-carbamoselenothioate anions associated with potassium cations that are located on the upper and lower sides of a plane involving two opposing carbamoselenothioate groups. These heavier alkali metal salts readily reacted with alkyl halides to give both *S*- and *Se*-alkyl esters. The reaction of the potassium salts with trimethylsilyl chlorides forms *S*- and *Se*-trimethylsilyl carbamoselenothioates which are in equilibrium. The reaction of the salts and silyl esters with organo Group-14 and -15 elements halides gave exclusively the corresponding *Se*-substituted products in good yields.

**Keywords:** Potassium carbamoselenothioate; Silyl selenothioester; Germanium; Tin; Lead

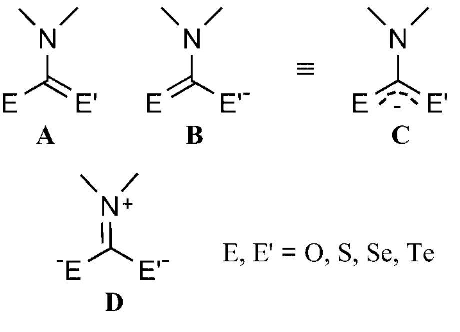
## Introduction

There are formally 6 groups of alkali metal carbamodichalcogenoates for each alkali metal, in which two oxygen atoms of carbamate group are replaced by sulfur, selenium or tellurium (Scheme 1). However, except for alkali metal carbamodithioates [1], little is known about their chemistry [2], although they are considered to be an important class of compounds both synthetically and theoretically because of *heteroallylic anion systems* (**A**, **B**, **C** or **D**) (Scheme 2). To the best of our knowledge, there has been no report on the synthesis of alkali metal carbamoselenothioates. Soon starting this study in the end of 1986, we found *Henriksen*'s report [3], in which the synthesis of two sodium carbamoselenothioates was described from the reaction of thiocarbamoyl chloride with sodium selenide. This method was almost same with our method by using potassium selenide. After then, we have developed the synthetic methods a series of alkali metal carbochalcogenoates [4, 5], and sodium and potassium carbamoselenoates [6] and carbamotelluroates [7]. Moreover, *O*-trimethylsilyl carboselenoate [8] and carbamoselenoates [9] have been found to readily react with rubidium and cesium fluorides to give the corresponding heavy alkali metal carbamoselenoates in good yields. As a part of our studies on the synthesis of new carbochalcogenoic and carbamochalcogenoic acid derivatives, we report



M = Li, Na, K, Rb, Cs
E, E' = S, Se, Te

**Scheme 1**



E, E' = O, S, Se, Te

**Scheme 2**

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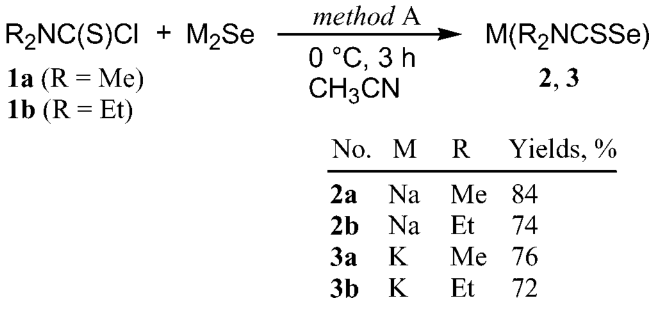
here the synthesis and characterization of potassium, rubidium, cesium, and triorganosilyl carbamoselenothioates and some of their reactions with organo Group-14 and -15 element halides.

## Results and Discussion

### *Synthesis of Salts*

First, the conditions for the reaction of *N,N*-dimethylthiocarbamoyl chloride (**1a**) with potassium selenide to give potassium *N,N*-dimethylcarbamoselenothioate (**3a**) were examined. The reaction conditions shown in Scheme 3 appeared to be preferred. Thus, an acetonitrile solution of **1a** was added dropwise to a suspension of excess freshly prepared potassium selenide in the same solvent and the mixture was stirred at room temperature 0 °C for 3 hours. Filtration of the insoluble part (KCl and excess $K_2Se$) and removal of the solvent under reduced pressure gave **3a** in a yield of 76 % as yellow crystals. (Scheme 3) Under the same conditions, the reaction with diethylthiocarbamoyl chloride (**1b**) led to potassium *N,N*-diethylcarbamoselenothioates (**3b**) in 72 % yield as an oil. In contrast to the use of potassium selenide, the reactions with sodium selenide gave the corresponding sodium carbamoselenothioates **2a** and **2b** in 84 and 74 % yields, respectively. On the other hand, rubidium **4** and cesium carbamoselenothioates **5** were obtained by reacting trimethylsilyl *N,N*-dimethylcarbamoselenothioates (**9**) with rubidium and cesium fluorides in respective yields of 77 and 79 %. (Scheme 4) However, the reaction of **9** with potassium fluoride resulted in the yield of below 65 % under the same coditions. The reactions with NaF, $MgF_2$, $CaF_2$, $SrF_2$, and $BaF_2$ led to the recovery of the starting salts.

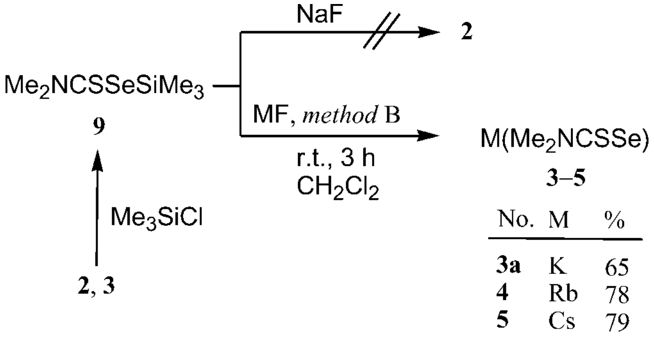


$$R_2NC(S)Cl + M_2Se \xrightarrow[0\,°C,\ 3\,h,\ CH_3CN]{method\ A} M(R_2NCSSe)$$

| No. | M | R | Yields, % |
|---|---|---|---|
| **2a** | Na | Me | 84 |
| **2b** | Na | Et | 74 |
| **3a** | K | Me | 76 |
| **3b** | K | Et | 72 |

**Scheme 3**

The obtained salts **2**−**5** are pale yellow to yellow oil or crystals and relatively stable towards oxygen and moisture. They can be stored in a refrigerator below 0 °C for one month. The structures of **2**−**5** were characterized by their $^1H$, $^{13}C$, and $^{77}Se$ -NMR spectra and by conversion into methyl **6**, phenacyl **7** or 2-acetophenoneoxime esters **8**. Moreover, the structure of **3a** was confirmed by single-crystal X-ray analyses. Their spectral data are shown in Table 1. In the $^1H$-NMR spectra of *N,N*-dimethyl derivatives **2a**, **3a**, **4**, and **5**, two characteristic signals due to the non-equivalent N-$CH_3$ groups are observed in the region of δ 3.20−3.70. In the $^{13}C$ NMR spectra, two signals due to the non-equivalent N-$CH_3$ groups and a signal due to -*C*SSe carbon appear near δ 44.2 and in the region of δ 204−207, respectively. The $^{77}Se$- NMR spectra show a signal due to the carbamoselenothioate selenium atom in the range of δ 499−584. The influence of alkali metal cations on the -*C*SSe carbon and $^{77}Se$ signals appeared to be little.



| No. | M | % |
|---|---|---|
| **3a** | K | 65 |
| **4** | Rb | 78 |
| **5** | Cs | 79 |

**Scheme 4**

**Table 1** Typical spectral data of compounds **2**−**19**

| Compd | $^{13}C$ NMR[a] / δ<br>*C*SSe | *C*=S | *C*=Se | $^{77}Se$ NMR[b]<br>δ |
|---|---|---|---|---|
| **2a** | 207.0 | | | 499.9 |
| **2b** | 204.4 | | | 582.4 |
| **3a** | 206.5 | | | 505.7 |
| **3b** | 204.7 | | | 583.8 |
| **4** | 206.8 | | | 575.7 |
| **5** | 207.0 | | | 529.2 |
| **6a** | | 195.2 | | 486.4 |
| **6b** | | | 200.5 | 539.7 |
| **7** | | 194.7 | | – |
| **8** | | 193.9 | | – |
| **9a** | | 190.8 | | -*c* |
| **9b** | | | 192.9 | -*c* |
| **10** | | 188.5 | | 529.0 |
| 11 | | 189.6 | | 590.5 |
| **12** | | 191.1 | | 592? |
| **13** | | 191.3 | | 633.9 |
| **14** | | 191.5 | | 655.7 |
| **15** | | 191.5 | | 670.4 |
| **16** | | 193.1 | | 624.8 |
| **17** | | 195.7 | | – |
| **18** | | 191.1 | | 624.8 |
| **19** | | 196.1 | | – |

[a] $CD_3OD$, standard: TMS. [b] $CD_3OD$, standard: $(CH_3)_2Se$. [c] No $^{77}Se$ signals were observed.

### *Crystal structure and Packing*

In general, it is difficult to obtain alkali metal carbamochalcogenoates as single crystals. To the best of our knowledge, X-ray structure analyses have only been reported for lithium [1c], sodium [1b], potassium [1b, 1d], and cesium *N,N*-dialkylcarbamodithioates [1a]. After we made several attempts to obtain single crystals of **2**−**5**, the acetonitrile-solvated salt K[$Me_2NCSSe$](MeCN) of **3a** allowed us to characterize it crystallographically. The structure of the solvated salt is shown in Figure 1, where the atoms E(11), E(12), E(21) and E(22) represent either sulfur or selenium atoms, which can not be defined due to disorder [10]. Similar large disorders have been observed for the sulfur and selenium atoms in ammonium [11] and alkali metal carboselenothioates [12]. The final atomic positional parameters are listed in Table 2. Selected bond distances and angles are shown in Table 3. The unit cell and coordination around the potassium metals are shown in Figure 2. The salt consists of discrete dimeric units, where the potassium metals are located on the upper and lower sides of the planes which include two facing carbamoselenothioate groups, and deviates somewhat from the center of a square that consists of two sulfur and two selenium atoms of the two carbamoselenothioate groups. The C−E(11) and C−E(12) (C−S or C−Se) bond distances (1.806−1.864 Å) in the carbamoselenothioate groups are significantly longer than common C=S (1.61−1.63 Å) in dithioesters [13] and the C=Se double bonds (1.785(4)−1.792(7) Å) in *S*-organyl selenothioesters [14]. On the other hand, the C−E(21) and C−E(22) bond lengths are longer than the $C_{(sp2)}$-S single bond (1.72−1.74 Å) in dithioesters [13] or comparable with those of *S*-organyl selenothioesters [14] and the $C_{(sp2)}$−Se single bonds [1.868(5) Å] in *Se*-organyl selenoesters [15]. The C−E(11) and C−E(12) (C−S or C−Se) bond distances (1.806−1.864 Å) are longer than those [1.757(9), 1.787(4) Å] in ammonium carboselenothioate [11], indicating the contribution of a lone-pair electron on the nitrogen atom, resulting in a partial C−N double bond character. In fact, the C(11)−N(11) and C(21)−N(21) distances of 1.291(2) and 1.305(2) Å, respectively, are substantially shorter than those [1.34 −1.36 (8) Å] of alkali metal carbamodithioates [1] and close to the sum (1.29 Å) of the C=N double bond radii [16]. These findings allowed us to conclude that among the canonical structures **I**−**III** in Scheme 5, **III** may be preferable due to electronic delocalization on the N-CSSe group. The K(11)-E(11), K(11)-E(12), K(21)-E(11) and K(21)-E(12) bond distances fall in the range of 3.29−3.45 Å which is comparable to that (3.25−3.45 Å) of the corresponding K−S distances in $K_2(4\text{-}CH_3C_6H_4CSS)_2$ [17]. The number of contacts between K and surrounding atoms is 7 (one nitrogen from $CH_3CN$ and three sulfur and selenium atoms, respectively, two sulfur and two selenium atoms of which are in the same plane as the two facing CSSe groups). The number of contacts for S and Se atoms

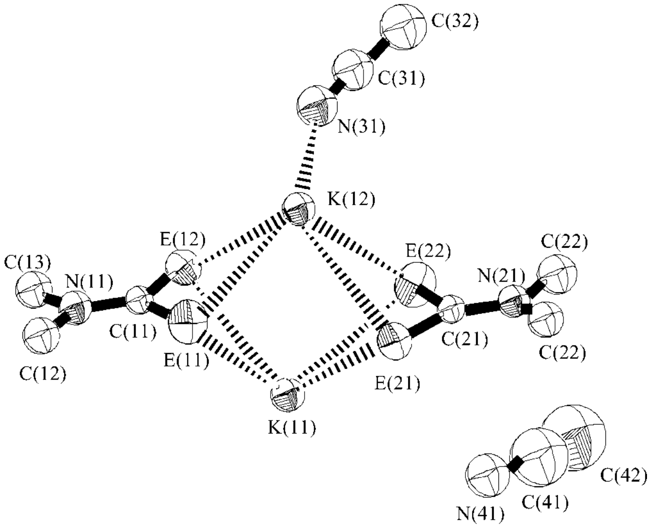


**Fig. 1** The ORTEP drawing of dimeric **3a**·MeCN [E(11), E(12), E(21), E(22) = S or Se]. Hydrogen atoms are omitted for clarification. Thermal ellipsoids are 20 % propability level.

**Table 2** Crystallographic data for dimeric of **3a**·MeCN

| | |
|---|---|
| empirical formula | $C_8H_{15}K_2N_3S_2Se_2$ |
| formula weight | 454.46 |
| color | yellow, prismatic |
| crystal system | orthorhombic |
| unit-cell dimentions | $a$ = 13.041(3) Å |
| | $b$ = 24.597(2) Å |
| | $c$ = 12.795(2) Å |
| volume of unit cell /Å$^3$ | 4104(2) |
| space group | *P*bca (#61) |
| *Z* value | 32 |
| $D_{calc}$/(g/cm$^3$) | 6.553 |
| crystal size/mm | 7.14x4.85x3.42 |
| $\mu$(Mo-$K_\alpha$/cm$^{-1}$ | 301.48 |
| temp/°C | 23.1(±1) |
| $\lambda_{MoK\alpha}$/Å | 0.71069 |
| $2\theta_{max}$/deg | 55.0° |
| no. of measured reflections | 5261 |
| no. of observations (I > 3σ(I)) | 2010 |
| no. of variables | 81 |
| residuals: $R^a$, $R_w^b$ | 0.0689; 0.0684 |
| goodness of fit indicator | 5.33 |

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

**Table 3** Selected bond distances and angles of dimeric **3a**·MeCN

Bond distances/Å

| | | | |
|---|---|---|---|
| E(11)−K(11) | 3.38(1) | E4′−K(12) | 3.40(1) |
| E(12)−K(11) | 3.44(1) | E(11)−C(11) | 1.864(5) |
| E(11)−K(12) | 3.45(1) | E(12)−C(11) | 1.826(5) |
| E(12)−K(12) | 3.32(2) | E(21)−C(21) | 1.858(5) |
| E(21)−K(11) | 3.32(2) | E(22)−C(22) | 1.806(4) |
| E(22)−K(11) | 3.31(2) | K(11)−N(31) | 2.944(4) |
| E(21)−K(12) | 3.41(1) | K(12)−N(41) | 3.055(4) |
| E(22)−K(12) | 3.29(1) | N(11)−C(11) | 1.291(2) |
| E1′−K(11) | 3.32(1) | N(21)−C(21) | 1.305(2) |
| E2′−K(11) | 3.50(1) | K(11)−K(21) | 3.967(5) |
| E3′−K(21) | 3.37(1) | | |

Angles/°

| | |
|---|---|
| E(11)−C(11)−E(12) | 117.6(1) |
| E(21)−C(21)−E(22) | 118.0(1) |
| E(11)−K(11)−E(12) | 56.0(1) |
| E(12)−K(12)−E(21) | 55.4(1) |
| E(21)−K(11)−E(22) | 56.4(1) |
| E(21)−K(12)−E(22) | 55.7(1) |

Torsion angles/°

| | |
|---|---|
| N(11)−C(11)−E(11)−K(11) | 155.2(1) |
| N(11)−C(11)−E(12)−K(11) | 156.2(1) |
| N(11)−C(11)−E(21)−K(12) | 155.2(1) |
| N(11)−C(11)−E(22)−K(12) | 156.2(1) |
| E(11)−C(11)−N(11)−C(12) | 14.0(7) |
| E(12)−C(11)−N(11)−C(13) | 6.0(4) |

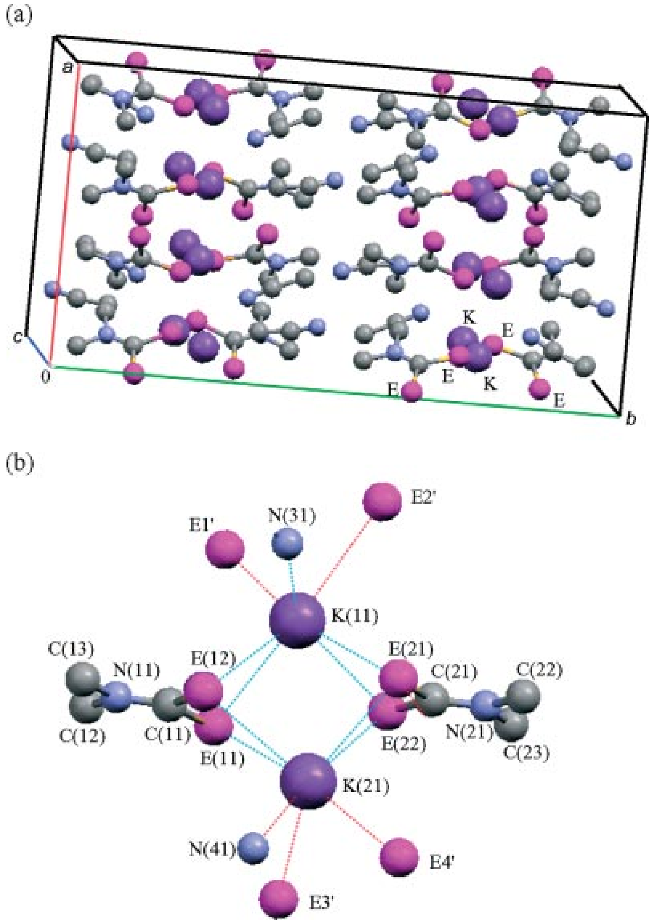
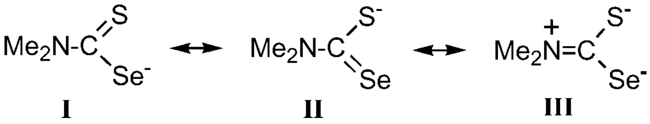


**Fig. 2** (a) Unit cell of **3a**·MeCN viewed down *c*-axis and (b) coordination at potassium, and sulfur or selenium atoms [(E(11), E(12), E(21), E(21), El′, E2′, E3′, E4′ = S or Se)]. Hydrogen atoms are omitted for clarify. Purple balls are potassium atom. Pink balls are sulfur or selenium atom. Gray balls are carbon atom. Blue balls are nitrogen atom.



**Scheme 5**

is two and three, respectively. The E(11)−C(11)−E(12) and E(21)−C(21)−E(22) angles are normal, 117.6 and 117.9°, respectively. In contrast, the E(11)−K(11)−E(12) and E(21)−K(11)−E(22) angles are relatively narrow 56.0 and 56.4°, respectively. In Figure 3, the arrangement of the potassium atoms in the crystals of **3a** is shown. It is noted that the metal atoms are arranged tessellately where each four metal cations form an irregular quadrilateral with angles of 85−102° ($4^4$ tessellated 2D) [18] (Fig. 3a). Alkali metal carbochalcogenoate and carbamochalcogenoate-arrangements containing such cations have yet to be reported.

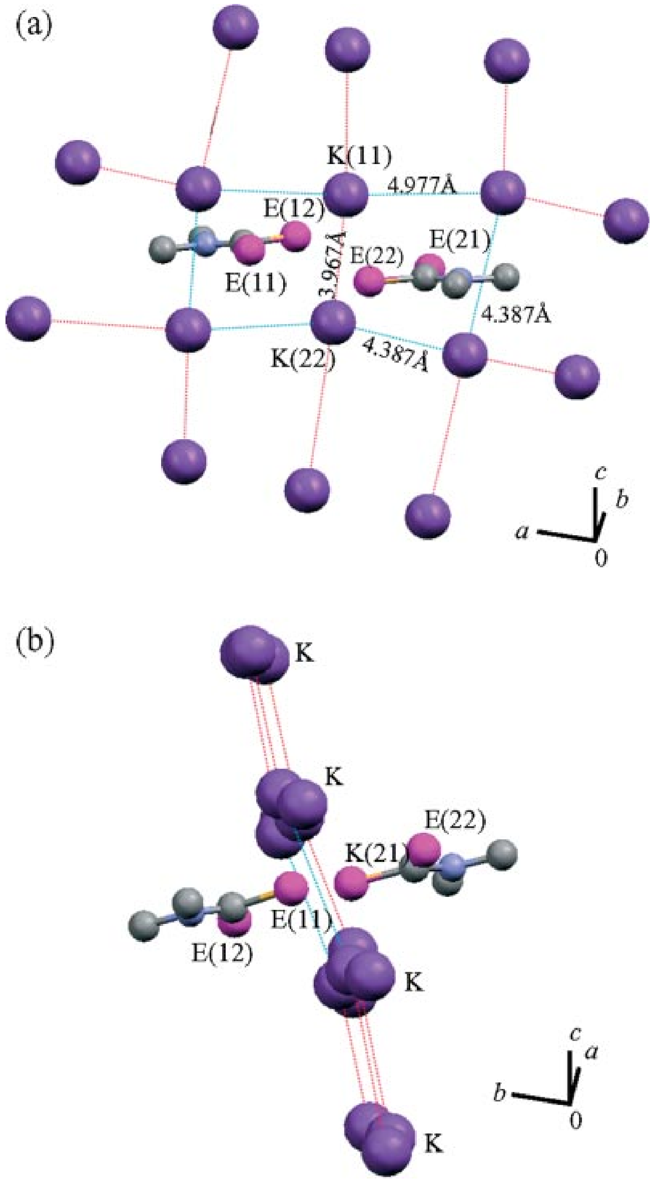
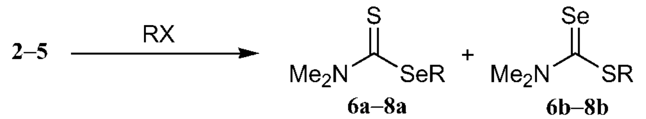


**Fig. 3** Arrangement of the potassium, ions in the crystals of **3a**·MeCN. The solvated MeCN molecules and hydrogen atoms are omitted for the clarification. (a) viewed down *b*-axis. (b) view down *a*-axis.

## *Reactions*

*With alkyl halides:* We previously reported that the methylation of tetraalkylammonium carboselenothioates with iodomethane occurred at both of their sulfur and selenium atoms to give *S*- and *Se*-methyl carboselenothioates [11]. Compound **3a** reacted with iodomethane at 0 °C to give the expected *S*- **6a** and *Se*-alkyl carbamoselenothioates **6b** in good yields (**6a**/**6b** = 1 : 9) (Scheme 6).

Similarly, the sodium **2**, rubidium **4** and cesium salts **5** gave the corresponding alkylated products at both the sulfur and selenium atoms in 70−90 % yields. The equimolar reactions of **3a** with phenacyl bromide or 2-chloroacetophenone oxime exclusively gave the corresponding *Se*-sub-

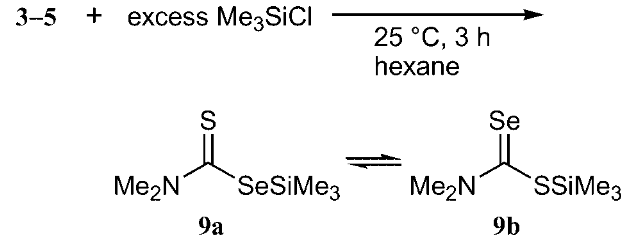


| salts 2–5 | RX | solv. | temp (°C) | time (h) | products **6**–**8**, % |
|---|---|---|---|---|---|
| **2a** | MeI | MeI | 0 | 3 | 92 (**6a**/**6b** = 83 : 17) |
| **3a** | MeI | MeI | 0 | 3 | 86 (**6a**/**6b** = 87 : 13) |
| **4** | MeI | MeI | 0 | 3 | 75 (**6a**/**6b** = 80 : 20) |
| **5** | MeI | MeI | 0 | 3 | 90 (**6a**/**6b** = 96 : 4) |
| **3a** | $PhCOCH_2Br$ | $CH_2Cl_2$ | rt | 3 | 96 (**7a**/**7b** = 100 : 0) |
| **3a** | $\overset{NOH}{\overset{\|}{PhCCH_2Cl}}$ | $CH_2Cl_2$ | rt | 3 | 91 (**8a**/**8b** = 100 : 0) |

**Scheme 6**

stituted esters **7** or **8** in quantitative yields, respectively. These alkylations may occur at both atoms because heating of a mixture of **6a** and **6b** (8 : 2) at 80 °C showed no change in the ratio of these compounds [19]. More *S*-methylated products are produced (10−30 %) than in the methylation of tetraalkylammonium carboselenothioate (< 2 %) [11].

*With trimethylsilyl chloride:* In contrast to carbochalcogenoic acids, carbamochalcogenoic acids can not be isolated because they are in rapid equilibrium with the starting compounds such as amines, carbonylchalcogenide or carbon dichalcogenides. Previously, we found that *O*-triorganosilyl carbochalcogenoates ($RCEOSiR'_3$, E = S, Se, Te), which are readily obtained by reacting the corresponding alkali metal carbochalcogenoates with triorganosilyl halides, act as carbochalcogenoic acids [20]. In these reactions, *O*-triorganosilyl carbochalcogenoates are formed *via* chalcogen-substituted products ($RCOESiMe_3$, E = S, Se, Te) [21]. Similarly, alkali metal carbamo-thioates and -selenoates reacted with *O*-trimethylsilyl chloride to give the corresponding *O*-silylated carbamochalcogenoates in good yields [9]. It would be interesting to determine whether sodium **2** and potassium carbamoselenothioates **3** react with trimethylsilyl chloride to give both *S*- **9a** and *Se*-trimethylsilyl carbamoselenoates **9b** or only one of them. When **3a** and excess trimethylsilyl chloride were stirred in hexane at 0 °C, the solution gradually changed from colorless to yellow. Filtration of the resulting precipitates (KCl) and removal of the solvent and excess trimethylsilyl chloride under reduced pressure gave pale yellow crystals with a melting point of 124−126 °C. The $^1$H-NMR spectrum of these crystals showed broad signals near δ 0.5 and 2.8−3.1 (proton ratio = 9 : 12), which are attributable to $SiCH_3$ and N-$CH_3$ protons, respectively. (Scheme 7) In the $^{13}$C-NMR spectrum at room temperature, two broad signals are observed in the region of δ 180−195, where thio- or seleno-carbonyl carbon signals appear. When these spectra were measured at a lower temperature of −15 °C, the broad signals near δ 0.5 became markedly sharp at δ 0.54 and 0.94, which is attributable to $SSiCH_3$ and $SeSiCH_3$ protons. (Fig. 4a) In the $^{13}$C-NMR spectrum, the two broad signals at δ 180−195 became sharp signals at δ 190.8 and 192.9, which can be attributed to the *C*=S and *C*=Se carbons, respectively [22]. (Fig. 4b) When the temperature was allowed to rise to 65 °C, the two sharp signals at δ 0.54 and 0.94 due to $SeSiCH_3$ and $SSiCH_3$ protons and the two sharp signals at δ 190.8 and 192.9 due to the C=S and C=Se carbons coalesced, respectively. These results clearly indicate that tautomeric equilibrium exists between the thioxo- **9a** and selenoxo-forms **9b** over −15 °C. This is the first example of tautomeric equilibrium of organosilyl group between differ-



**Scheme 7**

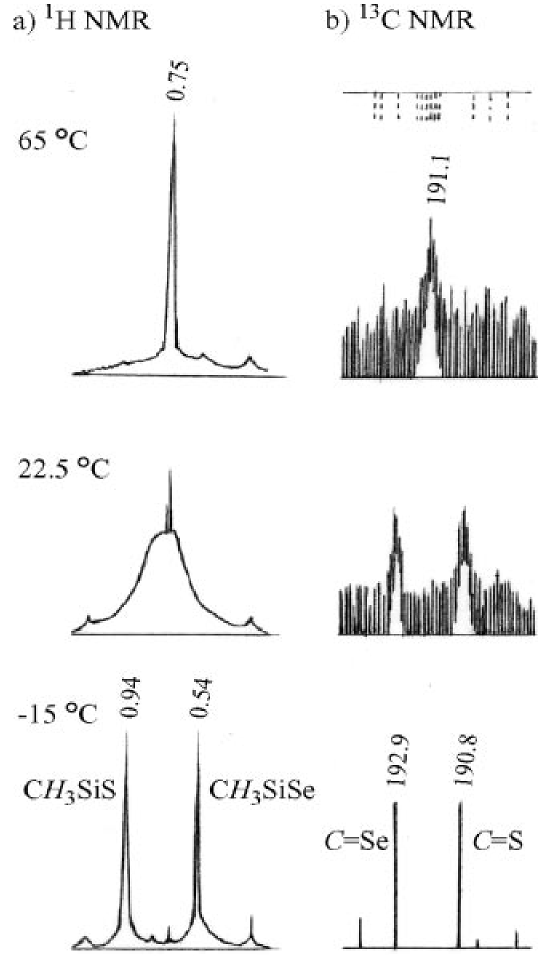
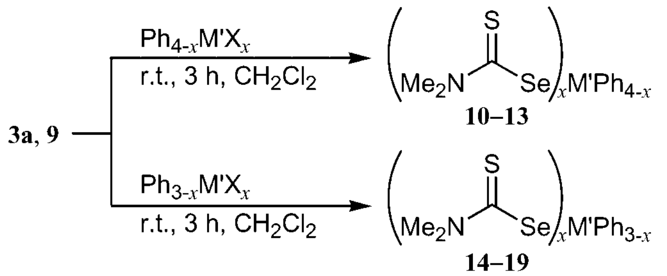


**Fig. 4** $^1$H and $^{13}$C Variable temperature NMR spectra in $CDCl_3$ for trimethylsilyl *N,N*-dimethylcarbamoselenothioate **9**



| starting compounds | products No. | M' | X | $x$ | Yield, % |
|---|---|---|---|---|---|
| **3a** | **10** | Ge | Br | 1 | 81 |
| **3a** | **11** | Sn | Cl | 1 | 90 |
| **9** | **12** | Sn | Cl | 2 | 47[a] |
| **3a** | **13** | Pb | Cl | 1 | 93 |
| **3a** | **14** | P | Cl | 2 | 65 |
| **3a** | **15** | As | Cl | 1 | 86 |
| **3a** | **16** | As | Cl | 2 | 90 |
| **3a** | **17** | As | Cl | 3 | 95 |
| **3a** | **18** | Sb | Cl | 1 | 70 |
| **3a** | **19** | Sb | Cl | 3 | 93 |

[a] The low yields are due to the loss by recrystallization. The reaction proceeded quantitatively.

**Scheme 8**

ent chalcogen atoms [23] and in sharp contrast to the results with the corresponding *O*-triorganosilyl carbamo-thioates [9] and -selenoates [9] and carbochalcogenoates [20−22], which show no tautomeric equilibrium between *O*- and *E*-silylated esters (E = chalcogen atoms).

*With organo Group-14 and -15 element halides:* The first carbamoselenothioic acid main group derivatives were reported in 1970 by *Kametani* and *Tanaka*, who isolated $Me_2NCSSeSnClMe$ and $Me_2NCSSeSnMe_2$ from the reaction of **1a** with trimeric dimethyltin selenide [24]. To the best of our knowledge, no other main group element derivatives have been reported, most likely due to the difficulty of their synthesis. Previously, we found that *O*-trimethylsilyl carboselenoates react with organo Group-14 and -15 metal halides to give exclusively the corresponding *Se*-substituted carboselenoates [22b]. A series of selenocarbamic acid *Se*-substituted organo Group-14 element esters were obtained by using sodium [6], potassium [6] and *O*-trimethylsilyl carbamoselenoates [9]. As expected, the reactions of the potassium salt **3a** or the silylester **9** with triphenyl-germanium, -tin, and -lead halides and with aryl-phosphoric, -arsenic and -antimony halides proceeded readily at room temperature to give the expected *Se*-substituted derivatives **10−19** in good yields, Scheme 8. Compounds **10−19** were identified by elemental analyses and by the similarity of their IR and $^{1}$H-, $^{13}$C- and $^{77}$Se-NMR spectra to those of of the authentic samples prepared from **2** with the corresponding organo Group 14 element halides. Their typical spectral data are shown in Table 1. The $^{77}$Se-NMR signals (629−670 ppm) of the Group-15 element-substitured carbamoselenothioates **14−19** were observed at upfield region of 9−127 ppm than those of the corresponding Group-14 element-substituted derivatives **10−13**.

## Experimental Section

**General.** The melting point was determined by a Yanagimoto micromelting point apparatus and uncollected. The IR spectra were measured on PERKIN-ELMER FT-IR 1640. The $^{1}$H-NMR spectra were recorded on JEOL JNM-GX-270 (270 MHz) and JEOL $\alpha$-400 (100 MHz) with tetramethylsilane as an internal standard. The $^{13}$C-NMR spectra were obtained from JEOL JNM-GX-270 (68 MHz) and JEOL $\alpha-400$ (100 MHz). The $^{31}$P NMR spectra were recorded on JEOL $\alpha$-400 (162 MHz) with phosphoric acid as external standard. The $^{77}$Se-NMR spectra were obtained from JEOL $\alpha$-400 (76 MHz) with dimethylselenide as an external standard. The $^{119}$Sn-NMR spectra were obtained from JEOL $\alpha$-400 (149 MHz) with tetramethylstannane as an external standard. The mass spectra were taken on Shimadzu Qp1000 (A) (EI/CI model) and 9020DF (EI/CI model) high resolution mass spectrometer. The high resolution mass spectroscopy (HRMS) was taken on a Shimadzu GCM 9020DF high resolution mass spectrometer. The High Performance Liquid Chromatography (HPLC) was carried out by Japan Analytical Industry Co. (column: JAIGEL 1H, 2H; eluent: $CHCl_3$). Elemental analyses were performed by the Elemental Center of Kyoto University.

**Materials.** Methanol, diethyl ether and hexane were refluxed with sodium metal using benzophenone as indicator and distilled before use. Acetonitrile and dichloromethene were distilled over phosphorus pentoxide. The following reagents were commercial grade and used without further purification: selenium (powder), sodium and potassium metals, methyl and ethyl iodides, phenacyl bromide, and trichloroantimony (from Nacalai tesque Co. Kyoto), triphenyltin chloride, dichlorophenylphosphine, triphenyllead bromide, *N,N*-dimethylthiocarbamoyl and *N,N*-diethylthiocarbamoyl chlorides (from Aldrich), and trichloro-arsenic and antimony (from Wako Pure Chemical Industries Ltd. Osaka). Trimethylsilyl chloride is obtained from Shin-etsu Chemical Industry Ltd. and was distilled before use. Diphenylarsenic chloride [25], phenylarsenic dichloride [26], diphenylantimony chloride and bromide [27, 28], and *2*-Chloroacetophenone oxime [29] were prepared according to the literatures.

## *X-Ray crystallography*

All measurements were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å). The structure was solved and refined using the teXan® crystallographic software package on an IRIS Indigo computer. X-Ray quality crystals of **3a** were obtained by slow diffusion of hexane into methanol solution containing a small amount of acetonitrile. Used crystals were cut from the grown needles. In order to avoid the decomposition of the sample, a crystal mounted on a glass fiber was coated with an epoxy resin. The cell dimensions were determined by least-squares refinement of diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections and no decay was detected. Lorentz and polarization corrections were applied to the data and empirical absorption corrections (DIFABS) [30] were also applied. The structure was solved by direct methods SIR88 [31] and expanded using DIRDIF 92 [32]. Scattering factors for neutral atoms were from *Cromer* and *Waber* [33]. Anomalous dispersion effects were included in Fcalc [34]; the values for $\Delta f'$ and $\Delta F''$ were those of *Creagh* and *McAuley* [35]. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$, and the weighting scheme employed was $w = [\sigma^2(F_o) + \sigma^2(F_o)^2/4]^{-1}$. Full-matrix least-squares refinement was executed with non-hydrogen atoms 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.

**Preparation of single crystals.** Microcrystals of compound **3a** (0.1 g) were dissolved in degassed MeOH (4 ml) and hexane (1 ml) was added slowly and allowed to stand in refrigerator (−17 °C) for two weeks.

## *Syntheses of alkali metal carbamoselenothioates (2−5)*

All manipulations of air-sensitive materials were performed under a dry nitrogen atmosphere or an argon atmosphere. The preparation of **2a**, **3a**, **3b**, and **4a** are described in detail as typical procedures for potassium **3**, rubidium **4** and cesium salts **5**, respectively. The compounds **2a**, **3a**, **3b**, **4** and **5** were determined by conversion into their methyl esters.

**Sodium *N,N*-dimethylcarbamoselenothioate (2a).** A solution of *N,N*-dimethylthiocarbamoyl chloride (**1a**) (3.948 g, 31.94 mmol) in acetonitrile (20 mL) was added to a suspension of sodium selenide (7.98 g, 65.87 mmol) in the same solvent (20 mL) at 0 °C under argon atmosphere. The mixture was stirred at 0 °C for 3 h (the color of the solution changed from yellow to orange). Filtration of the insoluble part (sodium chloride and excess of sodium selenide) and removal of the solvent from the filtrate under reduced pressure gave **2a** as pale yellow crystals. Yield: 5.103 g (84 %).

**IR** (KBr) /cm$^{-1}$: 2919, 1630, 1493, 1364, 1244 1120, 1038, 971, 961, 937, 632, 521. − $^1$H-NMR ($CD_3OD$): $\delta$ = 3.24 (s, $\mathrm{C}H_3$), 3.28 (s, $\mathrm{C}H_3$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 44.3 ($C\mathrm{H}_3$), 45.1 ($C\mathrm{H}_3$), 207.0 (*C*SSe). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 99.9.

**Sodium *N,N*-diethylcarbamoselenothioate (2b).** Similarly to **2a**, the reaction of *N,N*-diethylthiocarbamoyl chloride (**1b**) (4.909 g, 32.37 mmol) in acetonitrile (20 ml) with sodium selenide (7.98 g, 65.87 mmol) in the same solvent (20 ml) at 0 °C gave **2b** as pale yellow oil. Yield: 5.225 g (74 %).

**IR** (neat) /cm$^{-1}$: 3358, 2935, 1460, 1417, 1377, 1353, 1266, 1196, 1136, 1093, 960, 894, 772, 538. − **$^1$H-NMR** ($CD_3OD$): $\delta$ = 1.31 (b, $\mathrm{C}H_3$), 3.77 (b, $\mathrm{C}H_3$), 4.02 (b, $\mathrm{C}H_2$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 11.0, 12.0 ($C\mathrm{H}_3$), 48.2, 49.1 ($C\mathrm{H}_2$), 204.4 (*C*SSe). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 582.4.

**Potassium *N,N*-dimethylcarbamoselenothioate (3a) (*Method* A).** A solution of *N,N*-dimethylthiocarbamoyl chloride (**1a**) (3.027 g, 24.46 mmol) in acetonitrile (20 ml) was added to a suspension of potassium selenide (5.517 g, 35.10 mmol) in the same solvent (20 ml) at 0 °C under argon atmosphere. The mixture was stirred at 0 °C for 3 h. Filtration of the insoluble part (potassium chloride and excess of potassium selenide) and removal of the solvent from the filtrate under reduced pressure gave 1.784 g of crude **3a** as orange crystals. Recrystallization from a mixed solvent (2.8 ml) of metanol/ether (1.2 : 1) at −25 °C gave **3a** as pale yellow crystals. Yield: 3.858 g (76 %). Mp 155−168 °C (dec).

**IR** (KBr) /cm$^{-1}$: 3447, 2920, 1654, 1604, 1480, 1437, 1397, 1359, 1246, 1124, 1043, 970, 943, 865, 552. − **$^1$H-NMR** ($CD_3OD$): $\delta$ = 3.53 (s, $\mathrm{C}H_3$), 3.68 (s, $\mathrm{C}H_3$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 44.1, 44.3 ($C\mathrm{H}_3$), 206.5 (*C*=SSe). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 505.7.

**Potassium *N,N*-diethylcarbamoselenothioate (3b) (*Method* A).** A solution of *N,N*-diethylthiocarbamoyl chloride (**1b**) (3.713 g, 24.48 mmol) in acetonitrile (20 ml) was added to a suspension of potassium selenide (6.412 g, 40.80 mmol) in the same solvent (20 ml) at 0 °C under argon atmosphere. The mixture was stirred at 0 °C for 3 h (The color of the solution changed from yellow to red). Filtration of the insoluble part (potassium chloride and excess of potassium selenide) and removal of the solvent from the filtrate under reduced pressure gave **3b** as pale yellow oil. Yield: 4.129 g (72 %).

**IR** (neat) /cm$^{-1}$: 2974, 2932, 2872, 2251, 2189, 1679, 1488, 1418, 1380, 1353, 1297, 1270, 1197, 1144, 1094, 1075, 1006, 959, 915, 880, 825, 778, 652, 564, 542. − **$^1$H-NMR** ($CD_3OD$): $\delta$ = 1.32 (b, $\mathrm{C}H_3$), 3.77 (b, $\mathrm{C}H_3$), 4.02 (b, $\mathrm{C}H_2$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 204.7 (*C*SSe). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 583.8.

***Method* B (from $Me_2NCSSeSiMe_3$ and KF)**. Potassium fluoride (0.162 g, 2.79 mmol) was added to a solution of freshly prepared trimethylsilyl *N,N*-dimethylcarbamoselenothioate (**9**) (0.840 g, 3.51 mmol) in dichloromethane (20 ml) at 25 °C under argon atmosphere. The mixture was stirred at 25 °C for 3 h. Filtration of the resulting precipitates, followed by recrystallization from a mixed solvent (6.5 ml) of acetonitrile/ether (3 : 1) at −25 °C, gave **3a** as pale yellow crystals. Yield: 0.375 g (65 %).

**Rubidium *N,N*-dimethylcarbamoselenothioate (4).** Rubidium fluoride (0.408 g, 3.90 mmol) was added to a solution of freshly prepared trimethylsilyl *N,N*-dimethylcarbamoselenothioate (**9**) (1.560 g, 6.48 mmol) in dichloromethane (20 ml) at 25 °C under argon atmosphere. The mixture was stirred at 25 °C for 3 h. Filtration of the resulting precipitates, follwed by recrystallization from a mixed solvent (6.5 ml) of acetonitrile/ether (3 : 1) at −25 °C, gave **4** as pale yellow crystals. Yield: 0.765 g (77 %). Mp 124−134 °C (dec).

**IR** (KBr) /cm$^{-1}$: 1655, 1492, 1373, 1245, 1188, 1124, 1944, 943, 920, 851, 754. − **$^1$H-NMR** ($CD_3OD$): $\delta$ = 3.54 (s, $\mathrm{C}H_3$), 3.68 (s, $\mathrm{C}H_3$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 44.4 ($C\mathrm{H}_3$), 206.8 (*C*=S). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 575.7.

**Cesium *N,N*-dimethylcarbamoselenothioate (5).** Similarly to **4**, the reaction of **9** (0.600 g, 2.52 mmol) with cesium fluoride (0.339 g, 2.23 mmol), followed by recrystallization from a mixed solvent (6.5 ml) of acetonitrile/ether (3 : 1) at −25 °C, gave **5** as pale yellow crystals.Yield: 0.531 g (79 %). Mp: 151−153 °C (dec.).

**IR** (KBr) /cm$^{-1}$: 2919, 2367, 1483, 1353, 1240, 1110, 935, 865. − **$^1$H-NMR** ($CD_3OD$): $\delta$ = 3.53 (s, $\mathrm{C}H_3$), 3.67 (s, $\mathrm{C}H_3$). − **$^{13}$C-NMR** ($CD_3OD$): $\delta$ = 44.3, 207.0 (C=S). − **$^{77}$Se-NMR** ($CD_3OD$): $\delta$ = 529.2.

## Reactions of compound 3a to leading to Group-14 and -15 elements derivatives

**Methyl *N,N*-dimethylcarbamoselenothioate (6).** Iodomethane (5 ml, 78.0 mmol) was added to potassium *N,N*-dimethylcarbamoselenothioate (**3a**) (0.618 g, 3.00 mmol) at 0 °C under argon atmosphere. The mixture was stirred at 0 °C for 3 h. Filtration of the insoluble part (potassium iodide) and removal of excess of iodomethane from the filtrate under reduced pressure gave a mixture of *Se*-methyl (**6a**) and *S*-methyl *N,N*-dimethyl carbamoselenothioate **6b** (**6a**/**6b** = 7 : 1) as yellow solid; 0.468 g (86 %).

**6a: IR** (KBr) /cm$^{-1}$: 2908, 1508, 1378, 1241, 1148, 1053, 968, 908, 862, 726. − **$^{13}$H-NMR** ($CDCl_3$): $\delta$ = 2.75 (s, 3H, $\mathrm{C}H_3$Se); 3.40 ? (s, 3H, $\mathrm{C}H_3$N), 3.56 (s, 3H, $\mathrm{C}H_3$N). − **$^{13}$C-NMR** ($CDCl_3$): $\delta$ = 24.2 (s, $C\mathrm{H}_3$Se), 42.6, 49.4 ($C\mathrm{H}_3$N), 195.2 [C(=S)Se, $J_{\text{C-Se}}$ = 136.5 Hz]. − **$^{77}$Se-NMR** ($CDCl_3$): 486.4.

− **HRMS** *m/z* (EI, 20 eV) for $C_4H_9SSe$: 182.96187 (calcd. 182.96209); **MS** (CIDI, 70 eV) *m/z* (%): 184 [M+1] (2), 137 [$(CH_3)_2NCSe$], 89 [$(CH_3)_2NCS$].

**6b: IR** (KBr) /cm$^{-1}$: 2919, 1500, 1449, 1371, 1244, 1144, 1049, 962, 904, 852. − **$^1$H-NMR** ($CDCl_3$): δ = 2.75 (s, 3H, $CH_3S$); 3.37 (s, 3H, $CH_3N$), 3.40 ? (s, 3H, $CH_3N$). - **$^{13}$C-NMR** ($CDCl_3$): δ = 15.2 ($CH_3S$), 42.8, 45.4 ($CH_3N$), 200.5 [($C$=Se), $J_{\mathrm{C\text{-}Se}}$ = 230.1 Hz]. − **$^{77}$Se-NMR** ($CDCl_3$): δ = 539.7 (C=*Se*). − **HRMS** *m/z* (EI, 20 eV) for $C_4H_9SSe$: 182.96187 (calcd. 182.96209); − MS (CIDI, 70 eV) *m/z* (%): 184 [M+1] (3), 137 [$(CH_3)_2NCSe$], 89 [$(CH_3)_2NCS$].

***Se*-Phenacyl *N,N*-dimethylcarbamoselenothioate (7).** A solution of phenacyl bromide (0.412 g, 2.07 mmol) in dichloromethane (10 ml) was added to a suspension of potassium *N,N*-dimethylselenothiocarbamate (**3a**) (0.412 g, 2.00 mmol) in the same solvent (20 ml) at 0 °C under argon atmosphere. The mixture was stirred at 25 °C for 3 h. Filtration of the insoluble part (potassium bromide) and removal of the solvent from the filtrate under reduced pressure, followed by recrystallization from a mixed solvent (5.0 ml) of hexane/dichoromethane (1 : 4) at −25 °C gave **7a** as pale yellow crystals. Yield: 0.547 g (96 %). Mp 103−105 °C.

**IR** (KBr) /cm$^{-1}$: 2966, 2919, 2837, 1684, 1593, 1507, 1448, 1375, 1268, 1197, 1149, 957, 850, 746, 686, 627, 534. − **$^1$H-NMR** ($CDCl_3$): δ = 3.30 (s, 3H, $CH_3$), 3.49 (s, 3H, $CH_3$), 4.77 (s, $J_{\mathrm{C\text{-}Se}}$ = 13.4 Hz, 2H, $CH_2$), 7.36−8.00 (m, 5H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 42.7, 42.8 ($CH_3$), 45.8 ($CH_2$) 128.5, 128.6, 133.4, 133.8, 135.6 (Ph), 192.5 ($C$=O), 194.7 ($C$=S).

***Se*-(*N,N*-Dimethylcarbamoselenothioate)acetophenone oxime (8).** Similarly to **7**, the reaction of 2-chloroacetophenone oxime (0.445 g, 2.95 mmol) with **3a** (0.515 g, 2.50 mmol), followed by recrystallization from a mixed solvent (6.0 ml) of hexane/dichloromethane (1 : 2) at −25 °C, gave **8a** as colorless crystals. Yield: 0.685 g (91 %). Mp 136−139 °C. $C_{11}H_{14}N_2OSSe$ (301.26): C, 43.65 (calcd. 43.86), H, 4.78 (calcld. 4.68) %.

**IR** (KBr) /cm$^{-1}$: 3217, 3060, 2915, 2859, 1450, 1450, 1376, 1319, 1243, 1148, 1051, 960, 941, 850, 754, 701, 688, 658, 646, 550, 476. − **$^1$H-NMR** ($CDCl_3$): δ = 3.32 (s, 3H, $CH_3$), 3.54 (s, 3H, $CH_3$), 4.71 (s, $J_{\mathrm{H\text{-}Se}}$ = 13.2 Hz), 7.36−7.78 (m, 5H, Ph), 9.76 (s, 1H, OH). − **$^{13}$C-NMR** ($CDCl_3$): δ = 42.7, 46.0 ($CH_3$), 28.4 ($CH_2$, $J_{\mathrm{C\text{-}Se}}$ = 66 Hz), 128.1, 128.5, 128.9, 129.1, 136.4, 136.7, 137.1, 141.1 (Ph), 156.4 ($C$N), 193.9 ($C$=S).

**Trimethylsilyl *N,N*-dimethylcarbamoselenothioate (9).** Trimethylsilyl chloride (3.0 ml, 4.50 mmol) was added to a suspension of potassium *N,N*-dimethylcarbamoselenothioate **3a** (1.274 g, 6.18 mmol) in hexane (20 ml) at 0 °C under argon atmosphere. The mixture was stirred at 25 °C for 3 h (the color of the solution changed from colorless to pale yellow). Filtration of the insoluble part (potassium chloride) and removal of the solvent and excess of trimethylsilyl chloride from the filtrate under reduced pressure gave a mixture of **9a, 9b** as pale yellow crystals. Yield: 1.420 g (96 %). Mp 124−126 °C.

**IR** (KBr) /cm$^{-1}$: 2964, 2369, 2345, 1522, 1508, 1458, 1389, 1361, 1262, 1094, 1020. 905, 867, 803, 905, 474. − **$^1$H-NMR** ($CDCl_3$, at −15 °C): δ = 0.54 (s, $CH_3SiS$), 0.94 (s, $CH_3SiSe$), 2.78 [s, $CH_3NC(S)$], 2.85 [s, $CH_3NC(Se)$], 2.97 [s, $CH_3NC(S)$], 3.09 [s, $CH_3NC(Se)$]. − **$^{13}$C-NMR** ($CDCl_3$, at −15 °C): δ = 2.3 ($CH_3SiS$), 2.7 ($CH_3SiSe$), 44.7, 46.2 [$CH_3NC(S)$], 43.9, 48.3 [$CH_3NC(Se)$], 190.8 ($C$=S, $J_{\mathrm{C\text{-}Se}}$ = 131.2 Hz), 192.9 ($C$=Se, $J_{\mathrm{C\text{-}Se}}$ = 226.1 Hz). − **HRMS** *m/z* (EI, 20 eV) calcd. for $C_6H_{15}SSeSi$: 240.98391 (calcd. 240.98589).

***Se*-Triphenylgermanium *N,N*-dimethylcarbamoselenothioate (10).** Similarly to **11**, the reaction of triphenylgermyl bromide (0.500 g, 1.30 mmol) with **3a** (0.309 g, 1.50 mmol), followed by recrystallization from a mixed solvent (3.0 ml) of hexane/dichloromethane (2 : 1) at −25 °C, gave **10** as colorless crystals. Yiled: 0.497 g (81 %). Mp 137−145 °C. The IR and $^1$H-and $^{13}$C-NMR spectra of **10** were exactly consistent with those of the authentic sample prepared by the reaction of trimethylsilyl *N,N*-dimethylcarbamoselenothioate (**9**) with triphenylgermanium chloride.

**IR** (KBr) /cm$^{-1}$: 3049, 3013, 1507, 1484, 1431, 1375, 1242, 1146, 1088, 998, 965, 854, 758, 695, 550, 475, 462. − **$^1$H-NMR** ($CDCl_3$): δ = 3.32 (s, 3H, $CH_3$), 3.45 (s, 3H, $CH_3$), 7.37−7.74 (m, 15H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.0, 46.4 ($CH_3$), 128.2, 128.5, 129.5, 130.1, 134.1, 135.5, 135.7 (Ph), 188.5 ($C$=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 529.0.

***Se*-Triphenyltin *N,N*-dimethylcarbamoselenothioate (11).** A solution of triphenyltin chloride (0.309 g, 0.8 mmol) in dichloromethane (15 ml) was added to a suspension of potassium *N,N*-dimethylcarbamoselenothioate (**3a**) (0.520 g, 2.5 mmol) in the same solvent (15 ml) at 0 °C under argon atmosphere. The mixture was stirred at 25 °C for 3 h. Filtration of the insoluble part (potassium chloride and excess of **3a**) and removal of the solvent from the filtrate under reduced pressure gave crude *Se*-triphenyltin *N,N*-dimethylcarbamoselenothioate (**11**) (Yield: 0.410 g (99 %)). Recrystallization from a mixed solvent (6.5 ml) of hexane/dichloromethane (3 : 1) at −25 °C gave **11** as colorless crystals. Yield: 0.373 g (90 %). Mp 151−153 °C. The IR and $^1$H- and $^{13}$C-NMR spectra of **11** were exactly consistent with those of the authentic samples by the reaction of **2a** or trimethylsilyl ester **9** with triphenyltin chloride. $C_{21}H_{21}NSSeSn$ (517.11): C, 48.38 (calcd. 48.78), H, 4.04 (calcd. 4.09) %.

**IR** (KBr) /cm$^{-1}$: 3059, 2367, 1577, 1518, 1480, 1429, 1406, 1382, 1331, 1242, 1151, 1071, 1020, 997, 959, 862, 732, 696, 548, 458. − **$^1$H-NMR** ($CDCl_3$): δ = 3.28 (s, 3H, $CH_3$), 3.45 (s, 3H, $CH_3$), 7.31−7.84 (m, 15H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.0, 48.4 ($CH_3$), 128.2, 128.5, 128.9, 129.1, 136.4, 136.7, 137.1, 141.1 (Ph), 189.6 ($C$=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 590.5; **$^{119}$Sn-NMR** ($CDCl_3$): δ = −337.0 ($J_{\mathrm{Sn\text{-}Se}}$= 779 Hz).

***Se*-Diphenyltin bis(*N,N*-dimethylcarbamoselenothioate) (12).** Similarly to **11**, the reaction of diphenyltin dichloride (0.688 g, 2.00 mmol) with **3a** (0.825 g, 4.00 mmol), followed by recrystallization the resulting from dichloromethane/hexane (1.1 : 1) at −17 °C, gave **12** as slight yellow needles. Yield: 0.576 g (47 %). − Mp 205−208 °C. $C_{22}H_{22}N_2S_2Se_2Sn$ (607.11): C, 35.33 (calcd. 35.61), H, 3.63 (3.65) %.

**IR** (KBr) /cm$^{-1}$: 3064, 3038, 2365, 1542, 1475, 1428, 1395, 1331, 1302, 1260, 1237, 1153, 1060, 1020, 996, 944, 873, 855, 802, 729, 695, 536. − **$^1$H-NMR** ($CDCl_3$): δ = 33.28 (s, 3H, $CH_3$), 3.31 (s, 3H, $CH_3$), 7.40−8.14 (m, 15H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 344.6 ($CH_3$), 48.9 ($CH_3$), 128.1−141.3 (Ph), 191.1 ($C$=S).

***Se*-Triphenyllead *N,N*-dimethylcarbamoselenothioate (13).** Similarly to **11**, the reaction of triphenyllead chloride (0.474 g, 1.00 mmol) with **3a** (0.247 g, 1.20 mmol), followed by recrystallization from hexane/dichloromethane (4 : 1) at −25 °C, gave **13** as pale yellow crystals. Yield: 0.563 g (93 %). The IR and $^1$H-and $^{13}$C-NMR spectra of **13** were exactly consistent with those of the authentic sample prepared by the reaction of **9** with triphenyllead chloride. Mp 195−198 °C.

**IR** (KBr) /cm$^{-1}$: 3059, 3042, 1568, 1507, 1474, 1430, 1403, 1375, 1327, 1242, 1187, 1147, 1059, 1014, 995, 954, 860, 722, 691, 549. − **$^1$H-NMR** ($CDCl_3$): δ = 3.33 (s, 3H, $CH_3$), 3.42 (s, 3H, $CH_3$), 7.30−7.99 (m, 15H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 45.0, 48.4 ($C_{H3}$), 128.8, 129.0, 129.7, 137.0, 156.1 (Ph), 191.3 ($C$=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 633.9.

***Se*-Diphenylphosphonic *N,N*-dimethylcarbamoselenothioate (14).** Similarly to **11**, the reaction of diphenylphosphonic chloride (0.352 g, 1.59 mmol) with **3a** (0.329 g, 1.60 mmol) in the same solvent (10 ml), followed by recrystallization from a mixed solvent (4.0 ml) of hexane/dichloromethane (1 : 1) at −25 °C, gave **14** as pale yellow needles. Yield: 0.364 g (65 %). Mp 125−127 °C. The IR and $^1$H and $^{13}$C NMR spectra of **14** were exactly consistent with those of the authentic samples by the reaction of trimethylsilyl ester **9** with diphenylphosphonic chloride. $C_{15}H_{16}NPSSe$ (352.29): C, 51.24 (calcd. 51.14), H, 4.53 (4.58) %.

**IR** (KBr) /cm$^{-1}$: 2966, 2925, 2362, 1560, 1499, 1428, 1397, 1367, 1262, 1238, 1139, 1091, 1066, 1024, 964, 852, 801, 741, 696, 508, 485. − **$^1$H-NMR**

($CDCl_3$): δ = 3.40 (s, 3H, $C\mathit{H}_3$), 3.48 (s, 3H, $C\mathit{H}_3$), 7.31−7.64 (m, 10H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.7, 44.8 ($\mathit{C}H_3$), 128.3, 128.4, 129.2, 133.4, 133.7 (Ph), 191.5 (*C*=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 655.7.

***Se*-Diphenylarsenic *N,N*-dimethylcarbamoselenothioate (15).** Similarly to **11**, the reaction of diphenylarsenic chloride (0.264 g, 1.00 mmol) with **3a** (0.229 g, 1.11 mmol), followed by recrystallization from a mixed solvent (1.0 ml) of hexane/dichloromethane (4 : 1) at −25 °C, gave **15** as pale yellow crystals. Yield: 0.339 g (86 %). Mp 125−127 °C. $C_{15}H_{16}AsNSSe$ (396.24): C, 45.26 (calcd. 45.47), H, 4.07 (4.07) %.

**IR** (KBr) /cm$^{-1}$: 3064, 3044, 2368, 1479, 1577, 1505, 1478, 1429, 1366, 1268, 1236, 1137, 1064, 1021, 998, 962, 477, 457. − **$^{1}$H-NMR** ($CDCl_3$): δ = 3.43 (s, 3H, $C\mathit{H}_3$), 3.48 (s, 3H, $C\mathit{H}_3$), 7.34−7.61 (m, 10H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.8, 45.2 ($\mathit{C}H_3$), 128.6, 133.6, 137.8 (Ph), 191.5 (*C*=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 670.4.

***Se*-Phenylarsenic bis(*N,N*-dimethylcarbamoselenothioate) (16).** Similarly to **11**, the reaction of phenylarsenic dichloride (0.334 g, 1.50 mmol) with **3a** (0.722 g, 3.50 mmol), followed by recrystallization from a mixed solvent (23 ml) of hexane/dichloromethane (9 : 14) at −25 °C gave **16** as pale yellow crystals. Yield: 0.657 g (90 %). Mp 125−127 °C. $C_6H_{17}AsNS_2Se_2$ (486.24): C, 29.36 (calcd. 29.64), H, 3.72 (3.72) %.

**IR** (KBr) /cm$^{-1}$: 3057, 2920, 1517, 1474, 1427, 1381, 1296, 1235, 1147, 1069, 1020, 990, 946, 854, 952, 687, 546, 459. − **$^{1}$H-NMR** ($CDCl_3$): δ = 3.43 (s, 6H, $C\mathit{H}_3$), 3.46 (s, 6H, $C\mathit{H}_3$), 7.34−7.61 (m, 5H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.8, 44.9 ($\mathit{C}H_3$), 128.1, 128.8, 134.3 (Ph), 193.1 (*C*=S). **Se-NMR** ($CDCl_3$): δ = 624.8.

***Se*-Arsenic tris(*N,N*-dimethylcarbamoselenothioate) (17).** Similarly to **11**, the reaction of trichloroarsenic (0.112 g, 0.62 mmol) with **3a** (0.425 g, 2.06 mmol), followed by recrystallization from a mixed solvent (5.5 ml) of hexane/dichloromethane (3 : 8) at −25 °C gave **17** as pale yellow crystals. Yield: 0.337 g (95 %). Mp 224−228 °C. $C_{18}H_{18}AsNS_2Se_2$ (576.24): C, 18.79 (calcd. 18.80), H, 3.23 (3.15) %.

**IR** (KBr) /cm$^{-1}$: 2955, 2922, 2849, 1508, 1379, 1263, 1240, 1144, 1102, 1044, 951, 858, 801, 730, 695, 546). − **$^{1}$H-NMR** ($CDCl_3$): δ = 3.45 (s, $C\mathit{H}_3$), 3.50 (s, $C\mathit{H}_3$). − **$^{13}$C-NMR** ($CDCl_3$): δ = 44.0 ($\mathit{C}H_3$), 195.7 (*C*=S).

***Se*-Diphenylantimony *N,N*-dimethylcarbamoselenothioate (18).** Similarly to **11**, the reaction of diphenylantimony chloride (0.538 g, 1.73 mmol) with **3a** (0.428 g, 2.08 mmol), followed by recrystallization from a mixed solvent (1.1 ml) of hexane/dichloromethane (8 : 3) at −25 °C, gave **18** as colorless crystals.Yiled: 0.538 g (70 %). The IR and $^{1}$H- and $^{13}$C-NMR spectra of **18** were exactly consistent with those of the authentic samples by the reaction of **2a** or trimethylsilyl ester **9** with diphenylantimony chloride. Mp 115−117 °C. $C_{15}H_{16}NSSbSe$ (443.07): C, 0.55 (calcd. 40.66); H, 3.64 (3.67) %.

**IR** (KBr) /cm$^{-1}$: 2371, 2346, 1508, 1428, 1370, 1232, 1136, 1059, 957, 728, 694, 458. − **$^{1}$H-NMR** ($CDCl_3$): δ = 43.43 (s, 6H, $C\mathit{H}_3$), 7.30−7.67 (m, 10H, Ph). − **$^{13}$C-NMR** ($CDCl_3$): δ = 45.0, 45.9 ($\mathit{C}H_3$), 128.8, 136.1, 140.0 (Ph), 191.1 (C=S). − **$^{77}$Se-NMR** ($CDCl_3$): δ = 4624.8.

***Se*-Antimony tris(*N,N*-dimethylselenothiocarbamate) (19).** Similarly to **11**, the reaction of trichloroantimony (0.228 g, 1.00 mmol) with **3a** (0.722 g, 3.50 mmol), followed by recrystallization from a mixed solvent (23 ml) of hexane/dichoromethane (14 : 9) at −25 °C, gave **19** as yellow crystals. Yield: 0.580 g (93 %). Mp 205−207 °C. $C_{18}H_{18}NSSb_2Se_2$ (623.07): C, 17.43 (calcd. 17.3), H, 3.09 (2.91) %.

**IR** (KBr) /cm$^{-1}$: 2919, 2366, 1508, 1400, 1374, 1242, 1144, 945, 863, 732, 547. − **$^{1}$H-NMR** ($CDCl_3$): δ = 43.47 (s, $C\mathit{H}_3$). − **$^{13}$C-NMR** ($CDCl_3$): δ = 4 44.0, 45.9 ($\mathit{C}H_3$), 196.1 (*C*=S).

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