

# O-Triorganosilyl Carbamoselenoates – Synthesis and Reactions

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**Abstract.** A series of *O*-triorganosilyl carbamoselenoates were isolated in good yields from the reaction of sodium or potassium carbamoselenoates with triorganosilyl chlorides. The *O*-silyl carbamoselenoates readily reacted with RbF and CsF and with organogermanium, -tin, and -lead halides and gave the corresponding

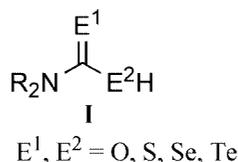
heavy alkali metal and *Se*-substituted Group 14 organometal and carbamoselenoates in moderate to good yields.

**Keywords:** Silyl carbamoselenoate; Rubidium carbamoselenoate; Cesium carbamoselenoate; Tin selenoate; Lead carbamotelluroate

## Introduction

There are 15 possible carbamochalcogenoic acids in which one or two oxygen atoms of the R<sub>2</sub>NCOO group in carbamic acid are replaced by S, Se or Te atom (**I**, Scheme 1).

Similar to carbamic acids, these carbamochalcogenoic acids can not be isolated due to



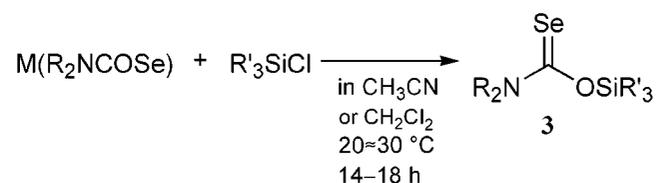
Scheme 1

an equilibrium between the acid and the starting the starting compounds: amines and carbon chalcogenides. Therefore, their alkali metal and ammonium salts have been used for the synthesis of carbamochalcogenoic acid derivatives such as thio- and dithiocarbamate transition metal complexes [1]. Although these alkali metal and ammonium salts are useful carbamochalcogenoating agents, most of them are insoluble in common aprotic solvents such as ether and benzene. Aprotic solvent-soluble carbamochalcogenoating agents are needed. Previously, we have found that *O*-triorganosilyl carbamoselenoates and carbomtelluroates act as the corresponding carbomochalcogenoating agents in aprotic solvents [2]. Moreover, we have established a method for the preparation of a series of sodium and potassium carbamoselenoates [3]. We report here the synthesis of *O*-triorganosilyl carbamoselenoates and some reactions leading to the

synthesis of organo Group 14 metal and rubidium and cesium carbamoselenoates.

## Results and Discussion

Treatment of freshly prepared sodium or potassium carbamoselenoates with an excess of trimethylsilyl chloride gave the expected *O*-trimethylsilyl carbamoselenoates **3** in good yields (Scheme 2). For example, when sodium **1a** or potassium



No.	R	M	No.	R	R' <sub>3</sub> Si	Yield, %
<b>1a</b>	Me	Na	<b>3a</b>	Me	Me <sub>3</sub> Si	78
<b>1b</b>	Et	Na	<b>3b</b>	Me	( <i>t</i> -Bu)Me <sub>2</sub> Si	60
<b>1c</b>	Ph	Na	<b>3c</b>	Et	Me <sub>3</sub> Si	73
<b>2a</b>	Me	K	<b>3d</b>	Et	( <i>t</i> -Bu)Me <sub>2</sub> Si	80
<b>2b</b>	Ph	K	<b>3e</b>	Ph	Me <sub>3</sub> Si	53
			<b>3f</b>	Ph	( <i>t</i> -Bu)Me <sub>2</sub> Si	24

Scheme 2

*N,N*-dimethylcarbamoselenoates **2a** and excess trimethylsilyl chloride (5 ml) were stirred at room temperature for 5 h, the reaction solution gradually changed from colorless to pale yellow. Removal of the precipitates, solvent and excess Me<sub>3</sub>SiCl, and distillation of the resulting residue under reduced pressure afforded *O*-trimethylsilyl *N,N*-dimethylcarbamoselenoate **3a** in 78 % yield. Similarly the reactions of sodium or potassium *N,N*-diethyl- **1b** or *N,N*-diphenylcarbamoselenoates **1c** with trimethylsilyl and (*t*-butyl)dimeth-

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ylsilyl halides led to the corresponding *O*-triorganosilyl carbamoselenoates **3b–3f** in moderate to good yields.

The obtained *O*-silyl esters **3** are pale yellow liquid or crystals and readily dissolve in hexane, ether and dichloromethane. They are thermally stable, but sensitive toward oxygen and moisture. Upon exposure to air, they gradually decomposed with the liberation of red selenium. Under oxygen-free and dry conditions, however, they can be stored in a refrigerator ( $-17\text{ }^{\circ}\text{C}$ ) for at least one month.

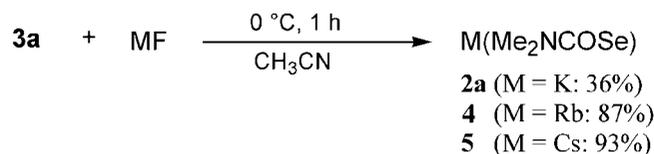
Table 1 shows the  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectra of **3**. The  $^{13}\text{C}$  and  $^{77}\text{Se}$  signals of the  $\text{R}_2\text{NC}(\text{Se})\text{O}$ - group are observed within relatively narrow ranges of 184–190 ppm and 741–886 ppm, respectively. (Table 1)

**Table 1** The  $^{13}\text{C}$  and  $^{77}\text{Se}$  chemical shifts of the  $\text{NC}(\text{=Se})\text{O}$  group in compounds **3**

compd	$\delta$ , $\text{CDCl}_3$	
	$^{13}\text{C}=\text{Se}$	$^{77}\text{Se}^b$
No.		
<b>3a</b>	185.3	758.6
<b>3b</b>	186.0	762.9
<b>3c</b>	184.6	741.6
<b>3d</b>	184.3	751.2
<b>3e</b>	189.5	876.4
<b>3f</b>	190.1	885.4

<sup>a</sup> Standard:  $\text{Me}_2\text{Se}$ ; shifts were determined relative to diphenyl diselenide and related to  $\text{Me}_2\text{Se}$  with  $\delta(\text{Ph}_2\text{Se}_2) = 464.1$  ppm.

To the best of our knowledge, the synthesis of rubidium and cesium carbamoselenoates has not yet been reported, most likely due to the difficulty of preparing rubidium and cesium amides. Previously, we found that *O*-trimethylsilyl carbamoselenoates react with  $\text{RbF}$  and  $\text{CsF}$  at room temperature to afford the corresponding heavy alkali metal carbamoselenoates in good yields [4]. Under similar conditions, treatment of *O*-trimethylsilyl *N,N*-dimethylcarbamoselenoate **3a** with  $\text{RbF}$  and  $\text{CsF}$  gave the expected rubidium **4** and cesium carbamoselenoates **5** in yields of 87% and 93%, respectively. (Scheme 3) In the case of  $\text{KF}$ , potassium carbamoselenoate **2a** resulted in a low yield of 36%. In addition, the reactions with  $\text{LiF}$  and  $\text{NaF}$  did not occur even with a prolonged reaction time.



**Scheme 3**

The  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectra of the carbamoselenoate group in alkali metal *N,N*-dimethylcarbamoselenoates are shown in Table 2. The values are observed within narrow ranges of  $\delta$  179–181 ppm and 584–590 ppm, respectively. Metal cations appeared to have very little effect on the carbonyl carbon chemical shifts of alkali metal carbamoselenoates, while the  $^{77}\text{Se}$  NMR signal shows a tendency for

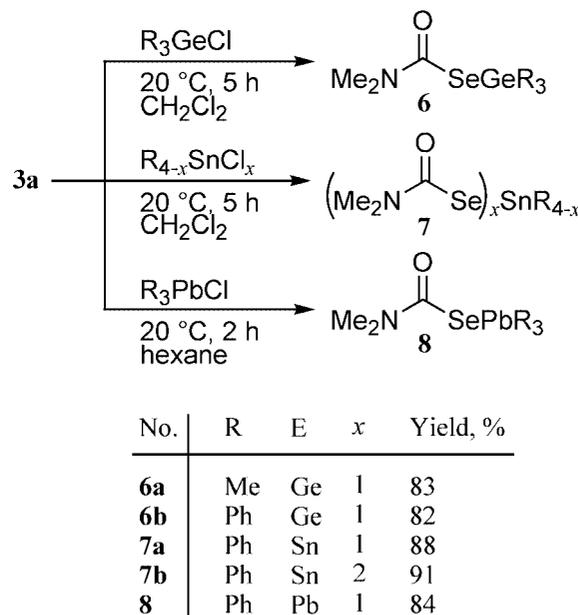
**Table 2** The  $^{13}\text{C}=\text{O}$  and  $^{77}\text{Se}$  Chemical shifts of alkali metal *N,N*-dimethylcarbamoselenoates

$\text{M}(\text{Me}_2\text{COSe})$		$\delta$ , (in $\text{CD}_3\text{OD}$ )		Ref.
No.	M	$^{13}\text{C}=\text{O}$	$^{77}\text{Se}^a$	
<b>1a</b>	Na	179.8	585.2	[3]
<b>2a</b>	K	179.7	584.6	[3]
		179.6	584.8	
<b>4</b>	Rb	180.1	587.6	
<b>5</b>	Cs	180.3	589.8	

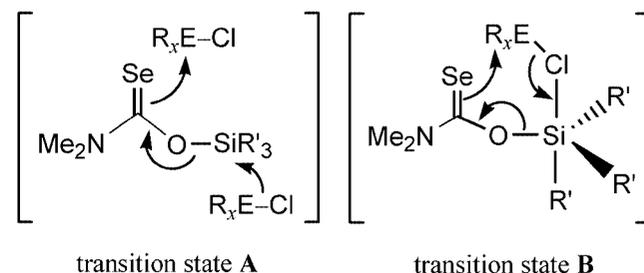
<sup>a</sup> Standard:  $\text{Me}_2\text{Se}$ ; shifts were determined relative to diphenyl diselenide and related to  $\text{Me}_2\text{Se}$  with  $\delta(\text{Ph}_2\text{Se}_2) = 464.1$  ppm.

a downfield shift in the order of potassium, rubidium and cesium salts.

The *O*-silyl esters **3** also reacted with organo-germanium, -tin, and -lead halides at room temperature to afford the corresponding *Se*-substituted Group 14 metal carbamoselenoates **6–8** in good yields. (Scheme 4) Compounds **6–8** would be formed *via* transition state **A** or **B** in Figure 1, although no spectroscopic data to support this conjecture are currently available.



**Scheme 4**



**Fig. 1** Plausible transition states for the formation of *Se*-substituted Group 14 metal carbamoselenoates **6–8**.

## Experimental Section

The melting points were measured by a Yanagido micromelting point apparatus and uncorrected. The IR spectra were measured on a PERKIN ELMER FT-IR 1640. The  $^1\text{H}$  NMR spectra were recorded on a JEOL JMN-GX 270 (270 MHz) with tetramethylsilane as an internal standard. The  $^{13}\text{C}$  NMR spectra were obtained from a JEOL JMN-GX 270 (67.9 MHz). The  $^{77}\text{Se}$  NMR spectra were obtained from a JEOL JMN-GX 270 (51.5 MHz) with dimethyl selenide as an external standard. The  $^{119}\text{Sn}$  NMR spectra were obtained from a JEOL a-400 (149 MHz) with tetramethyltin as an external standard. The mass spectra were recorded on Shimadzu GCMS QP1000 (A) (EI/CI, model). The high resolution mass spectroscopy (HRMS) was taken on Shimadzu GCMS 9020DF high resolution mass spectrometer. Elemental analyses were done at the Elemental Analyses Center of Kyoto University.

**Materials:** Sodium and potassium carbamoselenoates were prepared according to the method described previously [3]. Carbamoyl chlorides, potassium, rubidium and cesium fluorides, and trimethylsilyl and (*t*-butyl)dimethylsilyl chlorides are purchased from Nacarai tesque (Kyoto, Japan). Triphenylgermanium, triphenyltin and triphenyllead chlorides were obtained from Alfa Products and used without further purification. Diphenyltin dichloride was prepared according to literature [5]. Dichloromethane and acetonitrile were distilled from phosphorus pentoxide and degassed prior to use. Ether and hexane were distilled from sodium metal prior use and degassed. All manipulations were carried out under argon.

### O-Triorganosilyl carbamoselenoates (3)

The preparation of *O*-trimethylsilyl *N,N*-dimethylcarbamosenoate **3a** is described in detail as typical procedures:

**O-Trimethylsilyl *N,N*-dimethylcarbamosenoate (3a).** Trimethylsilyl chloride (1.19 ml, 9.40 mmol) was added to a solution of sodium *N,N*-dimethylcarbamosenoate **1a** (1.363 g, 7.84 mmol) in acetonitrile (10 ml) and the mixture was stirred at 20 °C for 14 h. Sodium chloride was filtered out and the solvent and excess of trimethylsilyl chloride were removed under reduced pressure (0.3 torr). Vacuum distillation of the resulting residue gave **3a** as pale yellow liquid. Yield: 2.740 g (78 %). B.p. 78–81 °C/0.7 torr.

**IR** (KBr) [neat /  $\text{cm}^{-1}$ ]: 2972, 2881, 2840, 1574, 1044, 1018, 933, 773, 659, 613, 500. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.40 (s, 9H,  $\text{CH}_3\text{Si}$ ), 3.03 (s, 3H,  $\text{CH}_3\text{N}$ ), 3.37 (s, 3H,  $\text{CH}_3\text{N}$ ). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.62 ( $\text{CH}_3\text{Si}$ ), 37.7, 44.2 ( $\text{CH}_3\text{N}$ ),  $\delta$  185.3 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 758.6. – **MS** (CID, 70 eV), *m/z* (rel. intensity, %): 225 [ $\text{M}^+$  + 1] (100), 136 [ $\text{Me}_2\text{NCSe}$ ] (9.8). – **HRMS** (20 eV) calcd for  $\text{C}_6\text{H}_{15}\text{NOSeSi}$ : *m/z* 225.00702 (calcd. 225.00874).

**O-Dimethyl-*t*-butylsilyl *N,N*-dimethylcarbamosenoate (3b).** Similarly to **3a**, the reaction of dimethyl-*t*-butylsilyl chloride (0.806 g, 5.36 mmol) with sodium *N,N*-dimethylcarbamosenoate **1a** (0.741 g, 3.66 mmol) gave **3b** as pale yellow liquid. Yield: 0.580 (60 %). B.p. 130–131 °C/0.35 torr.

**IR** (KBr) [neat /  $\text{cm}^{-1}$ ]: 2940, 2870, 1255, 1089, 867, 835, 773, 668, 496. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.50 (s, 6H,  $\text{CH}_3\text{Si}$ ), 0.91 [t, 9H, ( $\text{CH}_3$ ) $_3\text{CSi}$ ], 3.07 (s, 3H,  $\text{CH}_3\text{N}$ ), 3.40 (s, 3H,  $\text{CH}_3\text{N}$ ). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = –3.73 ( $\text{CH}_3\text{Si}$ ), 18.1 [ $\text{C}(\text{CH}_3)_3$ ], 25.6 [ $\text{C}(\text{CH}_3)_3$ ], 38.2 ( $\text{CH}_3\text{N}$ ),  $\delta$  186.0 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 762.9. – **MS** (EI, 20 eV): *m/z* (rel. intensity, %): 267 [ $\text{M}^+$ ] (18.2), 210 [ $\text{M}^+$  - *t*-Bu] (100). – **HRMS** (20 eV) calcd for  $\text{C}_9\text{H}_{21}\text{NOSeSi}$ : *m/z* 267.05707 (267.05566).

**O-Trimethylsilyl *N,N*-diethylcarbamosenoate (3c).** Similarly to **3a**, the reaction of trimethylsilyl chloride (1.57 ml, 13.2 mmol) with so-

dium *N,N*-diethylcarbamosenoate **1b** (1.777 g, 8.80 mmol) gave **3c** as yellow liquid. Yield: 1.621 (73 %). B.p. 48–50 °C/0.35 torr.

**IR** (KBr) [neat /  $\text{cm}^{-1}$ ]: 2969, 2935, 1509, 1459, 1399, 1304, 1243, 1210, 1105, 900, 834, 645, 496. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.46 (s, 9H,  $\text{CH}_3\text{Si}$ ), 1.10 (t,  $J$  = 7.3 Hz, 3H,  $\text{CH}_3\text{C}$ ), 1.20 (t,  $J$  = 7.3 Hz, 3H,  $\text{CH}_3\text{C}$ ), 3.39 (q, 3H,  $\text{CH}_2\text{N}$ ), 3.84 (q, 3H,  $\text{CH}_2\text{N}$ ). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.88 ( $\text{CH}_3\text{Si}$ ), 11.8, 12.7 ( $\text{CH}_3\text{C}$ ), 43.4, 49.3 ( $\text{CH}_2\text{N}$ ), 184.4 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 741.6. – **MS** (CID, 70 eV), *m/z* (rel. intensity, %) 267 [ $\text{M}^+$  + 1] (2.0), 164 [ $\text{Et}_2\text{NCSe}$ ] (39.2), 100 [ $\text{Et}_2\text{NCO}$ ] (100). – **HRMS** (20 eV) calcd for  $\text{C}_9\text{H}_{21}\text{NOSeSi}$ : *m/z* 253.36398 (calcd. 253.04002).

**O-(*t*-Butyl)dimethylsilyl *N,N*-diethylcarbamosenoate (3d).** The reaction of (*t*-butyl)dimethylsilyl chloride (0.920 g, 9.0 mmol) with sodium *N,N*-diethylcarbamosenoate **1b** (1.480 g, 7.33 mmol) in dichloromethane (20 ml) at 20 °C for 14 h gave **3d** as pale yellow liquid. Yield: 1.716 (80 %). B.p. 119–121 °C/0.22 torr.  $\text{C}_{11}\text{H}_{25}\text{NOSeSi}$  (295.09): C, 44.88 (calcd. 44.68), H, 8.56 (8.70 %).

**IR** (KBr) [neat /  $\text{cm}^{-1}$ ]: 975, 2931, 2872, 1485, 1399, 1306, 1240, 1209, 1096, 941, 834, 784, 647, 498. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.32 (s, 6H,  $\text{CH}_3\text{Si}$ ), 0.73 (t, 9H, [( $\text{CH}_3$ ) $_3\text{CSi}$ ]), 0.96 (t, 3H,  $\text{CH}_3\text{C}$ ), 1.04 (t, 3H,  $\text{CH}_3\text{C}$ ), 3.28 (q, 2H,  $\text{CH}_2\text{N}$ ), 3.40 (q, 2H,  $\text{CH}_2\text{N}$ ). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = –4.04 ( $\text{CH}_3\text{Si}$ ), 11.4, 12.5 ( $\text{CH}_3\text{CH}_2\text{N}$ ), 17.4 [ $\text{C}(\text{CH}_3)_3$ ], 25.2 [ $\text{C}(\text{CH}_3)_3$ ], 42.6, 48.8 ( $\text{CH}_3\text{CH}_2\text{N}$ ), 184.3 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 751.2. **MS** (EI, 20 eV): *m/z* (rel. intensity, %) 295 [ $\text{M}^+$ ] (52.1), 238 [ $\text{M}^+$  - (*t*-Bu)] (100), 100 [ $\text{Et}_2\text{NCO}$ ] $^+$  (88.7). – **HRMS** (20 eV) calcd for  $\text{C}_{11}\text{H}_{25}\text{NOSeSi}$ : *m/z* 295.08903 (calcd. 295.08694).

**O-Trimethylsilyl *N,N*-diphenylcarbamosenoate (3e).** Similarly to **3a**, the reaction of trimethylsilyl chloride (1.85 ml, 14.4 mmol) with sodium *N,N*-diphenylcarbamosenoate **1c** (0.860 g, 0.96 mmol), followed by dichloromethane/hexane (1:8), gave **3e** as pale yellow crystals. Yield: 1.763 (53 %). M.p. 45–48 °C (dec).

**IR** (KBr) / $\text{cm}^{-1}$ : 3050, 2980, 2881, 2840, 1591, 1516, 1493, 1314, 1250, 1135, 950, 870, 795, 690, 601, 506. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.37 (s, 9H,  $\text{CH}_3\text{Si}$ ), 7.2–7.4 (m, 10H, arom). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.67 ( $\text{CH}_3\text{Si}$ ), 126.2, 127.8, 129.3, 143.2 (arom),  $\delta$  189.5 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 876.4. – **MS** (CI, 70 eV): *m/z* (rel. intensity, %) 350 [ $\text{M}^+$  + 1] (67.0), 170 [ $\text{Ph}_2\text{NH}$ ] (100), 100 [ $\text{Ph}_2\text{N}$ ] (57). – **HRMS** (20 eV) calcd. for  $\text{C}_{10}\text{H}_{19}\text{NOSeSi}$ : *m/z* 391.08847 (calcd. 391.08694).

**O-Dimethyl-*t*-butylsilyl *N,N*-diphenylcarbamosenoate (3f).** Similarly to **3d**, the reaction of dimethyl-*t*-butylsilyl chloride (0.990 g, 6.58 mmol) with sodium *N,N*-diphenylcarbamosenoate **1c** (1.650 g, 5.54 mmol), followed by dichloromethane/hexane (1:8), gave **3f** as pale yellow crystals. Yield: 0.525 (24 %). M.p. 52–54 °C (dec).

**IR** (KBr) / $\text{cm}^{-1}$ : 3050, 2972, 2940, 1564, 1502, 1394, 1302, 1284, 1149, 998, 826, 689, 622, 503. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 0.22 (s, 6H,  $\text{CH}_3\text{Si}$ ), 0.72 [t, 9H, ( $\text{CH}_3$ ) $_3\text{CSi}$ ], 7.0–7.5 (m, 10H, arom). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = –3.89 ( $\text{CH}_3\text{Si}$ ), 18.1 [ $\text{Si}(\text{CH}_3)_3$ ], 25.1 [ $\text{C}(\text{CH}_3)_3$ ], 117.8, 126.8, 127.9, 129.4 (Ar), 190.1 ( $\text{C}=\text{Se}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 885.6. – **MS** (EI, 20 eV): *m/z* (rel. intensity, %) 390 [ $\text{M}^+$ ] (33.8), 334 [ $\text{M}^+$  - (*t*-Bu)] (100), 196 [ $\text{Ph}_2\text{NCO}$ ] $^+$  (99.2). – **HRMS** (20 eV) calcd for  $\text{C}_{10}\text{H}_{19}\text{NOSeSi}$ : *m/z* 349.03945 (calcd. 349.04002).

**Potassium *N,N*-dimethylcarbamosenoate (2a).** Similarly to **4**, the reaction of **3a** (1.386 g, 6.16 mmol) with potassium fluoride (0.965 g, 6.35 mmol) gave **2a** as white micro crystals. Yield: 1.62 g (36 % as **2a**). M.p. 90–96 °C (dec.).

**IR** (KBr) / $\text{cm}^{-1}$ : 2926, 2185, 1653, 1534, 1421, 1400, 1357, 1257, 1100, 904, 678. –  **$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  2.92 (s,  $\text{CH}_3$ ), 3.27 (s,  $\text{CH}_3$ ). –  **$^{13}\text{C-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 38.4 ( $\text{CH}_3$ ), 43.8 ( $\text{CH}_3$ ), 179.7 ( $\text{C}=\text{O}$ ). –  **$^{77}\text{Se-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 584.6.

**Rubidium *N,N*-dimethylcarbamosenoate (4).** Rubidium fluoride (0.599 g, 5.75 mmol) was added to a solution of freshly prepared *O*-trimethylsilyl *N,N*-dimethylcarbamosenoate **3a** (1.274 g, 5.66 mmol) in acetonitrile (15 ml) at 0 °C and the mixture was stirred at this temperature for 1 h (the color changed from orange

to yellow). The excess of RbF was filtered out and removed the solvent under reduced pressure. The resulting residue was washed with ether (2 x 5 ml) and then petro-ether (bp: <45 °C, 5 ml) gave **4** as white micro crystals. Yield: 1.16 g (87 % as **4**). M.p. 105–106 °C (dec.).

IR (KBr) /cm<sup>-1</sup>: 2926, 2187, 1655, 1535, 1420, 1400, 1358, 1257, 1100, 902, 678. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.94 (s, CH<sub>3</sub>), 3.30 (s, CH<sub>3</sub>). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 38.4 (CH<sub>3</sub>), 43.7 (CH<sub>3</sub>), 180.1 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 587.6.

**Cesium *N,N*-dimethylcarbamoseleenoate (5)**. Similarly to **4**, the reaction of **3a** (1.386 g, 6.16 mmol) with cesium fluoride (0.965 g, 6.35 mmol) gave **5** as white micro crystals. Yield: 1.62 g (93 % as **5**). M.p. 118–126 °C (dec.).

IR (KBr) /cm<sup>-1</sup>: 2928, 2185, 1653, 1533, 1420, 1400, 1355, 1247, 1100, 900, 675. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.92 (s, CH<sub>3</sub>), 3.27 (s, CH<sub>3</sub>). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 37.4 (CH<sub>3</sub>), 43.8 (CH<sub>3</sub>), 180.3 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 589.8.

The preparation of **6b**, **7a** and **8** are described in detail as typical procedures. The IR of **6–8** were exactly consistent with those of authentic samples, respectively [3].

**Se-Trimethylgermanium *N,N*-dimethylcarbamoseleenoate (6a)**. Similarly to **6b**, the reaction of **3a** (0.474 g, 2.12 mmol) with trimethylgermanium chloride (0.310 ml, 2.12 mmol) gave **6a** as colorless liquid. Yield: 0.469 g (83 %). B.p. 74–75 °C/0.65 torr.

IR (neat, KBr) /cm<sup>-1</sup>: 2908, 1647, 1438, 1403, 1359, 1257, 1093, 897, 832, 760, 673, 609, 568. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.71 (s, 9H, GeCH<sub>3</sub>), 2.97 (s, 3H, NCH<sub>3</sub>), 3.11 (s, 3H, NCH<sub>3</sub>). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 2.4 (GeCH<sub>3</sub>), 35.8 (CH<sub>3</sub>), 39.8 (CH<sub>3</sub>), 163.3 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 702.3 (703.5) [3].

**Se-Triphenylgermanium *N,N*-dimethylcarbamoseleenoate (6b)**. Triphenylgermanium chloride (0.673 ml, 2.00 mmol) was added to a yellow solution of *O*-trimethylsilyl *N,N*-dimethylcarbamoseleenoate **3a** (0.448 g, 2.0 mmol) in dichloromethane (10 ml). The mixture was stirred at 20 °C for 5 h. Filtration of black precipitates and evaporation of the filtrate under reduced pressure followed by recrystallization from a mixed solvent of dichloromethane/hexane (1:2) gave **6b** as colorless needles. Yield: 0.748 g (82 %). M.p. 128–131 °C.

IR (neat, KBr) /cm<sup>-1</sup>: 3100, 3050, 2980, 1647, 1492, 1430, 1252, 1089, 894, 737, 697. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.81 (s, 3H, NCH<sub>3</sub>), 3.08 (s, 3H, NCH<sub>3</sub>), 7.3–7.7 (m, 15H, arom). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 36.4 (GeCH<sub>3</sub>), 40.6 (CH<sub>3</sub>), 128.4, 128.6, 129.5, 134.9 (arom), 161.5 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 711.6 (712.4) [3].

**Se-Triphenyltin *N,N*-dimethylcarbamoseleenoate (7a)**. Triphenyltin chloride (1.193 ml, 3.09 mmol) was added to a solution of *O*-trimethylsilyl *N,N*-dimethylcarbamoseleenoate **3a** (0.693 g, 3.09 mmol) in dichloromethane (10 ml). The mixture was stirred at 20 °C for 5 h. Filtration of the resulting precipitates and recrystallization from a mixed solvent of ether and hexane (3: 1) yielded **7a** as colorless needles. Yield: 0.7960 g (88 %). M.p. 112–114 °C.

IR (KBr) /cm<sup>-1</sup>: 3082, 1628, 1480, 1425, 1360, 1250, 1100, 1075, 990, 730, 695, 450. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.79 (s, 3H, CH<sub>3</sub>), 3.03 (s, 3H, CH<sub>3</sub>), 7.3–7.7 (m, 15H, arom). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 36.2 (CH<sub>3</sub>), 42.2 (CH<sub>3</sub>), 128.6, 129.6, 136.5, 139.9 (arom), 163.5 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 725.8 (726.5) [3]. – <sup>119</sup>Sn-NMR (CDCl<sub>3</sub>): δ = –272 (*J*<sub>Sn-Se</sub> = 857 Hz).

**Se-Diphenyltin bis(*N,N*-dimethylcarbamoseleenoate) (7b)**. Similarly to **6a**, the reaction of *O*-trimethylsilyl *N,N*-dimethylcarbamoseleenoate **7a** (0.683 g, 3.05 mmol) and diphenyltin dichloride (0.518 g, 1.53 mmol) followed by recrystallization from dichloromethane/

hexane (3:1) gave **7b** as colorless needles. Yield: 0.796 g, (91 %). M.p. 143–145 °C. The IR and <sup>1</sup>H NMR spectra were consistent with those of the authentic sample prepared by the reaction of potassium *N,N*-dimethylcarbamoseleenoate with diphenyltin dichloride.

IR (KBr) /cm<sup>-1</sup>: 3050, 2980, 1600, 1560, 1470, 1430, 1360, 1250, 1100, 990, 980, 740, 695, 625, 440 cm<sup>-1</sup>. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.85 (s, 3H, CH<sub>3</sub>), 3.09 (s, 3H, CH<sub>3</sub>), 7.3–7.9 (m, 10H, arom). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 36.1 (CH<sub>3</sub>), 42.3 (CH<sub>3</sub>), 128.5, 129.5, 135.7, 140.9 (arom), 166.2 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 744.3 (745.2) [3].

**Se-Triphenyllead *N,N*-dimethylcarbamoseleenoate (8)**. Triphenyllead chloride (1.939 ml, 4.17 mmol) was added to a solution of *O*-trimethylsilyl *N,N*-dimethylcarbamoseleenoate **3a** (0.939 g, 4.17 mmol) in hexane (10 ml). The mixture was stirred at 20 °C for 2 h. Filtration of the resulting precipitates, followed by recrystallization from a mixed solvent of ether and hexane (3:1) gave **8**. Yield: 2.077 g (84 %). M.p. 110–112 °C.

IR (KBr) /cm<sup>-1</sup>: 3057, 2957, 1625, 1471, 1430, 1354, 1253, 1093, 993, 797, 728, 695. – <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 2.86 (s, 3H, CH<sub>3</sub>), 3.08 (s, 3H, CH<sub>3</sub>), 7.2–7.9 (m, 15H, arom). – <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 36.3 (CH<sub>3</sub>), 42.4 (CH<sub>3</sub>), 128.6, 129.7, 137.7, 153.9 (arom), 163.2 (C=O). – <sup>77</sup>Se-NMR (CDCl<sub>3</sub>): δ = 757.1 (758.6) [3].

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