Heteroatom Chemistry
Volume 6, Number 3, 1995

Synthesis and Reaction of Selenocarbamic Acid Sodium and Potassium Salts and Organo-Germanium, -Tin, and -Lead Esters

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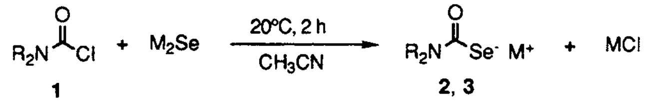
Received 27 September 1994

ABSTRACT

Sodium **2** *and potassium selenocarbamates* **3** *were found to be synthesized in moderate to good yields by the reaction of carbamoyl chlorides with sodium and potassium selenides. The salts* **2** *and* **3** *reacted with alkyl halides and organo-germanium, -tin, and -lead chlorides to give the corresponding esters* **7–9** *in good yields.*



No.	R	M
2a	CH_3	Na
2b	C_2H_5	Na
2c	C_6H_5	Na
3a	CH_3	K

SCHEME 1

INTRODUCTION

The chemistry of chalcogenocarbamates and related compounds has been the subject of considerable research for over 100 years [1]. Most of these studies have focused on thio- and dithiocarbamic acid derivatives, not only on their synthetic utility, but also on their many applications as fungicides, pesticides, vulcanization accelerators, antioxidants of rubber, etc. In contrast, selenocarbamates and related compounds have received relatively little attention [2,3]. Except for potassium *N,N*-pentamethylenecarbamoselenoate [4], prepared by treatment of the corresponding bis(carbamoyl) diselenide with a KOH/methanol solution, syntheses and spectral data of alkali metal selenocarbamates have not been described in the literature, even though they are the most important starting compounds for the synthesis of selenocarbamic acid derivatives. We have recently reported the preparation of lithium [5], sodium [6], and potassium selenocarboxylates [7,8]. These results prompted us also to prepare alkali metal selenocarbamates. We report here the preparation of sodium and potassium selenocarbamates and *Se*-organo-germanium, -tin, and -lead selenocarbamates.

RESULTS AND DISCUSSION

Preliminarily, the synthetic conditions for the preparation of alkali metal selenocarbamates, using *N,N*-diethylcarbamoyl chlorides with sodium selenides, have been examined. The reaction conditions shown in Scheme 1 appeared to be pre-

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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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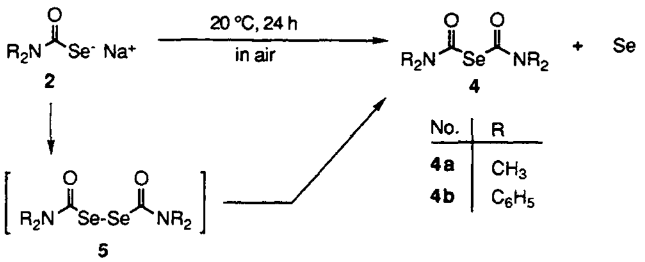
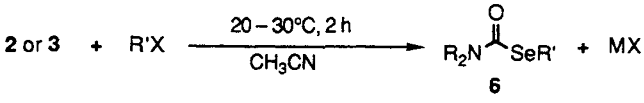
1042-7163/95/$5.00 + .25



No.	R
4a	CH_3
4b	C_6H_5

SCHEME 2



No.	R	R'
6a	CH_3	CH_3
6b	CH_3	4-$BrC_6H_4COCH_2$
6c	C_2H_5	CH_3
6d	C_2H_5	4-$BrC_6H_4COCH_2$
6e	C_6H_5	CH_3
6f	C_6H_5	4-$BrC_6H_4COCH_2$

SCHEME 3

ferred. Thus, an acetonitrile solution of a carbamoyl chloride was added dropwise to a suspension of 5 molar amounts of freshly prepared sodium or potassium selenide, and the mixture was stirred at room temperature for 2 hours. Removal of the solid (MCl and the excess of M_2Se (M = Na, K) by filtration and removal of the solvent in vacuo, afforded the sodium **2** or potassium selenocarbamate **3** in moderate to good yields. In these reactions, an excess of the metal selenides and carefully controlled oxygen-free conditions are required in order to prevent the formation of byproducts, such as dicarbamoyl selenides and diselenides. The use of other solvents, such as ether, tetrahydrofuran, methanol and ethanol, led to oily substances consisting of the salts containing the solvents. The structures of **2** and **3** were confirmed by IR and ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy and by conversion into *Se*-methyl or 4-bromophenacyl esters **6** [9].

The sodium **2** and potassium salts **3** are colorless to pale yellow microfine crystalline solids [10] or oils and, upon exposure to the air at room temperature, decompose with liberation of red selenium to give the corresponding dicarbamoyl selenides **4** which appeared to be formed by deselenation of dicarbamoyl diselenides **5** [11]. Under an inert atmosphere at −20°C, however, the aromatic derivatives are relatively stable, and no appreciable change is observed at least for a week.

In their ^{13}C NMR spectra, the C=O signals of **2** and **3** were observed in the region of δ 170–180, regardless of the substituents attached to the C=O group. The ^{77}Se NMR resonances can be observed at about δ 115–230.

As mentioned previously, **2** reacted with alkyl halides, such as methyl iodide and phenacyl bromide, to give the corresponding *Se*-alkyl esters **6** in good yields.

Only five organotin selenocarbamates are known, and they were prepared by the reaction of organotin chlorides with ammonium selenocarbamates generated in a mixture of secondary amines, CO and Se [12]. We carried out the reactions of **2** with organo-germanium, -tin, and -lead chlorides. The reactions proceeded at 20°C to give the corresponding esters **7–9** in 60–90% yields (Table 1). The structures of **7–9** were established by mass, IR, and ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy and elemental analyses.

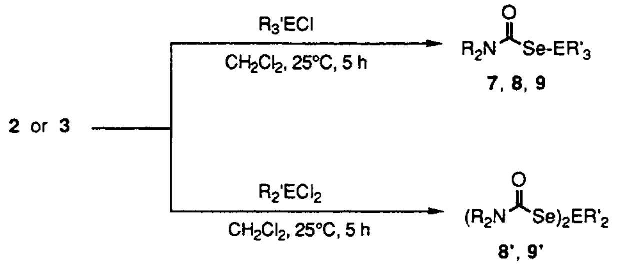
The carbonyl stretching frequencies and ^{13}C and ^{77}Se NMR spectra are collected in Table 2. The νC=O bands, which occur in the range of 1625–1650 cm^{-1}, shift to lower frequency in going from the Ge to the Pb compound. This may be due in part to the delocalization of an electron pair on selenium to form a diene type of conjugated system involving the C=O and *Se*-heteroatom bonds [13]. A downfield shift in the signals of the ^{77}Se NMR spectra was observed by substitution of the germanium atom with tin or lead. In contrast, the ^{13}C=O signals were almost independent of the heteroatom attached to Se.

In general, unsymmetrical diacyl sulfides [14] and selenides [13] are difficult to obtain from the corresponding chalcogenocarboxylate anions by reaction with acyl halides having different acyl groups. In order to prepare unsymmetrical dicar-

TABLE 1 Yields of *Se*-Organo Group 14 Element Selenocarbamates **7–9**

	$(R_2NCOSe)_xER'_{4-x}$					
Number	*R*	*E*	*R'*	**x**	*Yield* (%)	*Mp* (°C)^a *Bp* (°C/Torr)
7a	CH_3	Ge	CH_3	1	92	103–104/12
7b	CH_3	Ge	C_6H_5	1	64	129–131
7c	C_2H_5	Ge	C_6H_5	1	83	124–126
7d	C_6H_5	Ge	CH_3	1	81	222–224
8a	CH_3	Sn	C_6H_5	1	80	112–114
8b	C_2H_5	Sn	C_6H_5	1	84	90–91
8c	C_6H_5	Sn	CH_3	1	80	93–95
8'a	CH_3	Sn	C_6H_5	2	67	201–203
8'b	C_2H_5	Sn	C_6H_5	2	75	136–137
8'c	C_6H_5	Sn	CH_3	2	69	192–194
9a	CH_3	Pb	C_6H_5	1	63	109–112
9b	C_2H_5	Pb	C_6H_5	1	62	129–132
9c	C_6H_5	Pb	C_6H_5	1	75	198–201
9'a	CH_3	Pb	C_6H_5	2	71	132–136
9'b	C_2H_5	Pb	C_6H_5	2	61	135–137

^{a}Decomposition.



No.	E	R	R'
7a	Ge	CH_3	CH_3
7b	Ge	CH_3	C_6H_5
7c	Ge	C_2H_5	C_6H_5
8a, 8'a	Sn	CH_3	C_6H_5
8b, 8'b	Sn	C_2H_5	C_6H_5
8c, 8'c	Sn	C_6H_5	CH_3
9a, 9'a	Pb	CH_3	C_6H_5
9b, 9'b	Pb	C_2H_5	C_6H_5
9c	Pb	C_6H_5	C_6H_5

SCHEME 4

bamoyl selenides **10**, the reactions of **1a** with *N,N*-diethylcarbamoyl chloride were carried out under various conditions. However, a number of attempts to isolate **10a** (R = CH_3, R' = C_2H_5) were unsuccessful.

EXPERIMENTAL

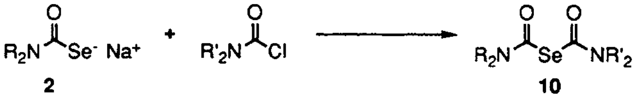
General

The melting points were obtained using a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrometer IR-G and a Perkin-Elmer FT-IR 1640 spectrometer. The ^1H NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) instrument with tetramethylsilane as an internal standard. The ^{13}C NMR spectra were obtained by use of a JEOL JNM-GX-270 (67.8 MHz) instrument. The ^{77}Se NMR spectra were recorded on a JEOL JNM-GX-270 (51.5 MHz) instrument with dimethyl selenide as an external standard. The mass spectra were taken on a Shimadzu GCMS QP1000 (A) (EI/CI, model, at 70 eV) mass spectrometer. The high resolution mass spectroscopy (HRMS) was taken on a Shimadzu GCMS 9020 DF high resolution mass spectrometer. Elemental analyses were carried out at the Elemental Analyses Center of Kyoto University.

TABLE 2 *Se*-Triphenyl Group 14 Element *N*, *N*, Dimethylselenocarbamates **7b**, **8b**, and **9a**

Number	*Me₂NCOSeEPh₃* *E*	*IR (KBr)* *νC=O (cm⁻¹)*	*¹³C NMR*[a] *(δ)*	*⁷⁷Se NMR*[b] *(δ)*
7b	Ge	1647	161.8	248.3
8a	Sn	1628	163.6	262.4
9a	Pb	1625	163.0	294.5

[a] $CDCl_3$.
[b] $CDCl_3$, standard: Me_2Se.



SCHEME 5

Materials

Carbamoyl chlorides, methyl iodide, 4-bromophenacyl bromide, and triphenyl-germanium, -tin and -lead chlorides were purchased and used without further purification. Diphenyl-tin [15] and -lead dichlorides [16] and sodium [6] and potassium selenides [8] were prepared according to the literature. Dichloromethane and acetonitrile, methanol and ethanol, and ether and tetrahydrofuran were distilled from phosphorus pentoxide, magnesium powder, and sodium benzophenone ketyl, respectively, and were degassed prior to use. All manipulations were carried out under argon.

Typical Procedure for the Preparation of Alkali Metal Selenocarbamates **2**, **3** *and for Their Conversion into Se-Alkyl Selenocarbamates* **6**

Sodium N,N-Dimethylselenocarbamate **2a**. A solution of *N,N*-dimethylcarbamoyl chloride **1a** (0.89 g, 8.30 mmol) in acetonitrile (10 mL) was added dropwise to a suspension of sodium selenide (1.35 g, 10.8 mmol) in the same solvent (10 mL), and the mixture was stirred at 20°C for 2 hours. Removal of solid (NaCl and the excess of Na_2Se) by filtration and evaporation of the solvent in vacuo afforded 1.24 g (86%) of sodium *N,N*-dimethylselenocarbamate **2a** as a white microcrystalline solid containing a trace amount of acetonitrile: Mp 88–94°C (dec); IR (KBr) 2926, 2187, 1654, 1534 (C=O), 1421, 1399, 1357, 1257, 1100, 904, 678 cm^{-1}; ^{13}C NMR (CD_3OD) δ 35.7 (CH_3), 43.9 (CH_3), 179.8 (C=O); ^{77}Se NMR (CD_3OD) δ 121.1.

Sodium N,N-Diethylselenocarbamate **2b**. 62%, A slightly yellow oil. IR (neat) 2970, 2930, 2160, 1652, 1577, 1560 (C=O), 1420, 1390, 1358, 1250, 1100, 905, 680 cm^{-1}; ^{13}C NMR (CD_3OD) δ 13.9 (CH_3), 14.6 (CH_3), 43.6 (CH_2), 45.7 (CH_2), 177.8 (C=O); ^{77}Se NMR (CD_3OD) δ 119.2.

Sodium N,N-Diphenylselenocarbamate **2c**. 72%, Pale yellow microcrystalline solid. ^{13}C NMR (CD_3OD, the signals of the aromatic ring carbons are considered to accumulate.) δ 126.7, 129.5, 147.5 (Ar), 180.5 (C=O); ^{77}Se NMR (CD_3OD) δ 225.2.

Potassium N,N-Dimethylselenocarbamate **3a.** 84%, Pale yellow microcrystalline solids. mp 91–98°C (dec); IR (KBr) 2926, 2187, 1654, 1534 (C=O), 1421, 1399, 1357, 1257, 1100, 904, 678 cm^{-1}; ^{1}H NMR (CD_3OD) δ 2.92 (s, CH_3), 3.29 (s, CH_3); ^{13}C NMR (CD_3OD) δ 38.3 (CH_3), 43.8 (CH_3), 179.6 (C=O); ^{77}Se NMR (CD_3OD) δ 120.7.

Se-Methyl N,N-Dimethylselenocarbamate **6a.** The salt **2a** (0.76 g, 4.4 mmol) was stirred in methyl iodide (5 mL) at 25°C for 2 hours. Removal of the precipitates by filtration and vacuum distillation of the filtrate yielded 0.67 g (91%) of *Se*-methyl *N,N*-dimethylselenocarbamate **6a**: colorless liquid. IR (neat) 2950, 1665 (C=O), 1410, 1370, 1260, 1100, 900, 680, 630, 460, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H, CH_3Se), 2.99 (s, 3H, CH_3N), 3.02 (s, 3H, CH_3N); ^{13}C NMR ($CDCl_3$) δ 6.3 (CH_3Se), 36.6 (CH_3N), 37.1 (CH_3N), 165.2 (C=O); ^{77}Se NMR ($CDCl_3$) δ 304.9; EIMS (*m/z*) (*rel* intensity, %) 167 [M^+] (100), 95 [CH_3Se] (95); HRMS (20 eV) calcd for C_4H_9NOSe: *m/z* 166.98489; found: 166.98486.

Se-4-Bromophenacyl N,N-Dimethylselenocarbamate **6b**. To a solution of **2a** (0.654 g, 3.8 mmol) in acetonitrile (20 mL) was added 4-bromophenacyl bromide (0.935 g, 3.5 mmol), and the mixture was stirred at 30°C for 2 hours. The solvent was removed under reduced pressure, and ether (10 mL) was added. The insoluble solids (NaBr and the excess of **2a**) were filtered off. Evaporation of the ether in vacuo and recrystallization of the residue from a mixed solvent of dichloromethane and hexane (1:2) afforded 0.682 g (58%) of pure **6b** as slightly yellow crystals: mp 94–96°C; IR (KBr) 3050, 2946, 2917, 1678 (C=O), 1590, 1415, 1375, 1280, 1070, 1000, 900, 855, 770, 680, 620, 460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.89 (s, 3H, CH_3), 2.96 (s, 3H, CH_3), 4.26 (s, 2H, CH_2, $^2J_{Se-H}$ = 12.9 Hz), 7.5–7.9 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 32.2 (CH_2), 37.0 (CH_3), 37.1 (CH_3), 128.6, 130.3, 131.9, 134.1, (Ar), 163.2 (NC=O), 194.9 (C=O); ^{77}Se NMR ($CDCl_3$) δ 409.1; EIMS (*m/z*) (*rel* intensity, %) 349 [M^+] (14), 72 [$(CH_3)_2NCO^+$] (100); anal. calcd for $C_{11}H_{12}NO_2SeBr$: C, 37.85, H, 3.47; found: C, 37.70, H, 3.44.

Se-Methyl N,N-Diethylselenocarbamate **6c**. 80%, Colorless liquid. IR (neat) 2960, 1660 (C=O), 1450, 1240, 1220, 1110, 845, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3H, CH_3), 1.04 (t, 3H, CH_3), 2.15 (s, 3H, CH_3Se), 3.23 (q, 2H, CH_2), 3.36 (q, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 5.7 (CH_3Se), 13.0 ($\underline{C}H_3C$), 13.7 ($\underline{C}H_3C$), 41.8 (CH_2), 42.9 (CH_2), 163.5 ($\underline{C}$=O); ^{77}Se NMR ($CDCl_3$) δ 308.2; EIMS (*m/z*) (*rel* intensity, %) 195 [M^+] (27), 100 [$(C_2H_5)_2NCO^+$] (100); HRMS (20 eV) calcd for $C_6H_{13}NOSe$: *m/z* 195.01617; found: 195.01723.

Se-4-Bromophenacyl N,N-Diethylselenocarbamate **6d**. 62%, A slightly yellow oil. IR (KBr) 3020, 2950, 1640 (C=O), 1580, 1395, 1290, 1290, 1235, 1210, 1175, 1055, 990, 840, 810, 625, 550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, 3H, CH_3), 1.20 (t, 3H, CH_3), 3.28 (q, 2H, CH_2), 3.45 (q, 2H, CH_2), 4.34 (s, 2H, CH_2Se, $^2J_{Se-H}$ = 10.9 Hz), 7.5–8.0 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.1 (CH_3), 13.9 (CH_3), 31.7 (CH_2Se), 42.5 (CH_2), 43.3 (CH_2), 128.5, 130.3, 131.8, 134.2, (Ar), 161.8 (NC=O), 195. 1 (C=O); ^{77}Se NMR ($CDCl_3$) δ 414.0; EIMS (*m/z*) (*rel* intensity, %) 377 [M^+] (4), 100 [$(C_2H_5)_2NCO^+$] (100); HRMS (20 eV) calcd for $C_{13}H_{16}NO_2SeBr$: *m/z* 376.95287; found: 376.95456.

Se-Methyl N,N-diphenylselenocarbamate **6e**. 72%, Colorless crystals. Mp 91–93°C; IR (KBr) 3050, 1670 (C=O), 1590, 1490, 1285, 1250, 1140, 1070, 760, 700, 600 cm^{1}; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3H, CH_3Se), 7.3–7.5 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 7.7 (CH_3), 127.5–129.2 (Ar), 166.3 (C=O); ^{77}Se NMR ($CDCl_3$) δ 347.8; CIMS (*m/z*) (*rel* intensity, %) 292 [M^+ + 1] (100), 196 [$(C_6H_5)_2NCO^+$] (41); anal. calcd for $C_{14}H_{13}NOSeBr$: C, 57.94, H, 4.51; found: C, 57.69; H, 4.36.

Se-4-Bromophenacyl N,N-diphenylselenocarbamate **6f**. 71%, Pale yellow crystals. Mp 169–170°C [recryst solvent = dichloromethane/hexane (1:1)]; IR (KBr) 3050, 3000, 1675 (C=O), 1500, 1280, 1190, 1150, 990, 810, 760, 700, 600, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.29 (s, 2H, CH_2), 7.34 (m, 10H, Ar), 7.5–8.0 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) 33.5 (CH_2), 128.7, 129.4, 130.4, 132.0, 134.3, (Ar), 164.7 (NC=O), 196.0 (C=O); ^{77}Se NMR ($CDCl_3$) δ 444.3; EIMS (*m/z*) (*rel* intensity, %) 473 [M^+] (2), 196 [$(C_6H_5)_2NCO^+$] (100); anal. calcd for $C_{21}H_{16}NO_2SeBr$: C, 53.30, H, 3.41; found: C, 53.02; H, 3.12.

General Procedures for Decomposition of Sodium Selenocarbamates **2**

A solution of each compound **2** (3.6 mmol) in acetonitrile (20 mL) was stirred at 20°C for 24 hours. The solution changed from colorless to a pale yellow, with formation of a slightly red precipitate. Removal of the precipitate by filtration and removal of the solvent in vacuo gave the appropriate dicarbamoyl selenide **4**. The IR spectra of **4** were consistent with those of the authentic samples prepared by the reaction of each corresponding **2** with carbamoyl chlorides.

4a: 32%, A pale yellow oil. IR (neat) 2950, 1660 (C=O), 1400, 1350, 1250, 1080, 900, 800, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3H, CH_3), 3.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 36.5 (CH_3), 39.4 (CH_3), 159.5 (C=O); ^{77}Se NMR ($CDCl_3$) 607.7; CIMS (*rel* intensity, %) 225 [M^+ + 1] (100); HRMS (20 eV) calcd for $C_6H_{12}N_2O_2Se$: *m/z* 224.00634; found: 224.00595.

4b: 42%, Pink crystals (containing a trace of red selenium). Mp 219–221°C (dec); IR (neat) 3050, 1680

(C=O), 1585, 1490, 1250, 1180, 945, 760, 685 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.3 (s, Ar), 7.4 (s, Ar); ^{13}C NMR (CDCl$_3$) δ 117.7, 120.8, 129.4, 141.3 (Ar), 160.5 (C=O); ^{77}Se NMR (CDCl$_3$) 580.6; EIMS (*rel* intensity, %) 472 [M$^+$] (1), 196 [(C$_6$H$_5$)$_2$NCO$^+$]; HRMS (20 eV) calcd for $C_{26}H_{20}N_2O_2Se$: *m/z* 472.06890; found 472.06686.

General Procedure for the Preparation of Group 14 Organometalloids N,N-Diorganoselenocarbamates 7, 8, 8′, 9, and 9′

Each triorgano-germanium, -tin, or -lead chloride (2.0 mmol) or diorgano-germanium, -tin, or -lead dichloride (2 mmol) was added to a suspension of alkali metal *N,N*-diorganoselenocarbamate **2** or **3** (2.5 mmol for R$_3$ECl or 5 mmol for R$_2$ECl$_2$, E = Ge, Sn, Pb) in dichloromethane (20 mL) and the mixture was stirred at 30°C for 5 hours. Removal of the insoluble part by filtration (NaCl and the excess of **2**), removal of the solvent in vacuo, and subsequent recrystallization afforded each of the group 14 organometalloids *N,N*-diorganoselenocarbamates **7**, **8**, **8′**, **9**, and **9′**, respectively, as liquid or crystals.

Se-Trimethylgermanium N,N-Dimethylselenocarbamate **7a**. A pale yellow liquid. Bp 103–104°C/12 Torr; IR (neat) 2908, 1647 (C=O), 1438, 1403, 1359, 1257, 1093, 897, 832, 760, 673, 609, 568 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.70 (s, 9H, CH$_3$Ge), 2.96 (s, 3H, CH$_3$N), 3.10 (s, 3H, CH$_3$N); ^{13}C NMR (CDCl$_3$) δ 2.5 (CH$_3$Ge), 35.6 (CH$_3$), 39.8 (CH$_3$), 163.4 (C=O); ^{77}Se NMR (CDCl$_3$) δ 239.4; EIMS (*m/z*) (*rel* intensity, %) 271 [M$^+$] (5.2), 256 [M$^+$ − CH$_3$] (21.4), 241 [M$^+$ − 2CH$_3$] (48.2), 119 [(CH$_3$)$_3$Ge$^+$] (82.4), 72 [(CH$_3$)$_2$NCO$^+$] (100); HRMS (20 eV) calcd $C_6H_{15}NOGeSe$: 270.95296; found: 270.95360.

Se-Triphenylgermanium N,N-Dimethylselenocarbamate **7b**. Colorless plates. Mp 129–131°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3100, 3050, 2980, 1647 (C=O), 1492, 1430, 1252, 1089, 894, 737, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.82 (s, 3H, CH$_3$N), 3.07 (s, 3H, CH$_3$N), 7.3–7.7 (m, 15H, Ar); ^{13}C NMR (CDCl$_3$) δ 36.2 (CH$_3$), 40.4 (CH$_3$), 128.3, 128.5, 129.5, 134.9, (Ar), 161.8 (C=O); ^{77}Se NMR (CDCl$_3$) δ 248.3; EIMS (*m/z*) (*rel* intensity, %) 457 [M$^+$] (18.5), 380 [M$^+$ − C$_6$H$_5$] (73.4), 305 [Ge(C$_6$H$_5$)$_3$$^+$] (57.9), 72 [(CH$_3$)$_2NCO^+$] (100); anal. calcd for $C_{21}H_{21}NOGeSe$: C, 55.68; H, 4.65; found: C, 55.83; H, 4.37.

Se-Triphenylgermanium N,N-Diethylselenocarbamate **7c**. Pale yellow crystals. Mp 124–126°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3071, 3051, 2978, 1656 (C=O), 1484, 1242, 1094, 1025, 998, 736, 695, cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.1–1.3 (m, 6H, CH$_3$), 3.3–3.4 (m, 4H, CH$_2$), 7.2–7.5 (m, 15H, Ar); ^{13}C NMR (CDCl$_3$) δ 13.4, 14.2 ($\underline{C}H_3C$), 40.2, 40.4 (CH$_2$N), 128.4, 128.6, 132.4, 153.8 (Ar), 162.8 (C=O); ^{7}Se NMR (CDCl$_3$) δ 160.8; EIMS (*m/z*) (*rel* intensity, %) 485 [M$^+$] (5.2), 408 [M$^+$ − C$_6$H$_5$] (24.3), 331 [M$^+$ − 2C$_6$H$_5$] (67), 305 [(C$_6$H$_5$)$_3$Ge+] 100 [(C$_2$H$_5$)$_2$NCO$^+$] (100); anal. calcd for $C_{23}H_{25}NOGeSe$: C, 57.19; H, 5.22; found C, 57.35; H, 5.32.

Se-Trimethylgermanium N,N-Diphenylselenocarbamate **7d**. Pale yellow crystals. Mp 222–224°C (dec) [recryst solvent = dichloromethane/hexane (2:1)]; IR (KBr) 3060, 3027, 2924, 2910, 1657 (C=O), 1590, 1488, 1452, 1406, 1263, 1141, 1072, 956, 841, 754, 693, 604, 571 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.60 (s, 9H, CH$_3$Ge), 7.1–7.2 (m, 10H, Ar); ^{13}C NMR (CDCl$_3$) δ 2.5 (CH$_3$Ge), 126.9, 127.1, 129.0, 142.7 (Ar), 164.4 (C=O); ^{77}Se (CDCl$_3$) δ 239.4; EIMS (*m/z*) (*rel* intensity, %) 395 [M$^+$] (51.1), 380 [M$^+$ − CH$_3$] (21.3), 365 [M$^+$ − 2CH$_3$] (90.2), 196 [(C$_6$H$_5$)$_2$NCO$^+$] (93.8), 168 [(C$_6$H$_5$)$_2$N$^+$] (100), 119 [(CH$_3$)$_3$Ge$^+$] (67), 196 [(C$_6$H$_5$)$_2$NCO$^+$] (93.8); anal. calcd for $C_{16}H_{19}NOGeSe$: C, 48.91; H, 4.87; found C, 49.21; H, 4.92.

Se-Triphenyltin N,N-Dimethylselenocarbamate **8a**. Colorless plates. Mp 112–114°C (dec) [recryst solvent = ether/hexane (1:2)]; IR (KBr) 3080, 1628 (C=O), 1480, 1425, 1360, 1250, 1100, 1075, 990, 730, 695, 450 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.79 (s, 3H, CH$_3$), 3.02 (s, 3H, CH$_3$), 7.3–7.7 (m, 15H, Ar); ^{13}C NMR (CDCl$_3$) δ 36.0 (CH$_3$), 42.0 (CH$_3$), 128.6, 129.2, 136.7, 139.1 (Ar), 163.6 (C=O); ^{77}Se NMR (CDCl$_3$) δ 262.4; EIMS (*m/z*) (*rel* intensity, %) 426 [M − $C_6H_5^+$] (100); anal. calcd for $C_{21}H_{21}NOSeSn$: C, 50.34; H, 4.22; found: C, 50.43; H, 4.37.

Se-Triphenyltin N,N-Diethylselenocarbamate **8b**. Colorless crystals: mp 90–91°C (dec) [recryst solvent = ether/hexane (1:2)]; IR (KBr) 3050, 2890, 1610 (C=O), 1425, 1400, 1250, 1210, 1180, 1070, 890, 740, 730, 700, 440 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.99 (t, 3H, CH$_3$), 1.17 (t, 3H, CH$_3$), 3.23 (q, 2H, CH$_2$), 3.40 (q, 2H, CH$_2$), 7.3–7.7 (m, 15H, Ar); ^{13}C NMR (CDCl$_3$) δ 13.1 (CH$_3$), 14.0 (CH$_3$), 41.4 (CH$_2$), 47.7 (CH$_2$), 128.5, 129.2, 136.7, 139.4 (Ar), 162.4 (C=O); ^{77}Se NMR (CDCl$_3$) δ 239.6; EIMS (*m/z*) (*rel* intensity, %) 454 [M − C$_6$H$_5$]$^+$ (100); anal. calcd for $C_{23}H_{25}NOSeSn$: C, 52.21; H, 4.76; found: C, 52.28; H, 4.76.

Se-Trimethyltin N,N-Diphenylselenocarbamate **8c**. Colorless crystals. Mp 93–95°C (dec) (recryst solvent = hexane); IR (KBr) 3050, 2890, 1640 (C=O), 1590, 1490, 1260, 1140, 1065, 955, 780, 750, 695, 600, 525 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.45 (s, 9H, CH$_3$, $J_{Sn^{119}-CH_3}$ 56 Hz), 7.33 (s, 10H, Ar); ^{13}C NMR (CDCl$_3$) δ −4.1 (CH$_3$), 129.1 ~ 139.0 (Ar), 165.4 (C=O); ^{77}Se NMR (CDCl$_3$) δ 236.9; CIMS (*m/z*) (*rel* intensity, %) 442 [M$^+$ + 1] (90) 426 [M − CH_3^+] (91); anal. calcd for $C_{16}H_{19}NOSeSn$: C, 43.78; H, 4.36; found: C, 43.89; H, 4.25.

Se-Diphenyltin Bis(N,N-dimethylselenocarbamate) **8′a**. Colorless crystals. Mp 201–203°C (dec) [recryst solvent = dichloromethane/hexane (3:1)]; IR (KBr) 3050, 2980, 1600 (C=O), 1560, 1470, 1430, 1360, 1250, 1100, 990, 890, 740, 695, 625, 440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.84 (s, 6H, CH_3), 3.08 (s, 6H, CH_3), 7.3–7.9 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 36.0 (CH_3), 42.2 (CH_3), 128.5, 129.4, 135.7, 140.6 (Ar), 166.1 (C=O); ^{77}Se ($CDCl_3$) δ 281.1; CIMS (*m/z*) (*rel* intensity, %) 501 [M^+ − C_6H_5] (100), 426 [$Et_2NCOSeSnPh_2^+$] (42).

Se-Diphenyltin Bis(N,N-diethylselenocarbamate) **8′b**. Colorless needles. Mp 136–137°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3040, 3000, 2970, 2933, 1586 (C=O), 1450, 1400, 1360, 1250, 1205, 1120, 1165, 990, 845, 735, 690, 440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 6H, CH_3), 1.20 (t, 6H, CH_3), 3.24 (q, 4H, CH_2), 3.41 (q, 4H, CH_2), 7.3–7.9 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.1 (CH_3), 14.0 (CH_3), 41.4, 47.8 (CH_2), 128.3, 129.2, 135.7, 140.9 (Ar), 164.9 (C=O); ^{77}Se ($CDCl_3$) δ 239.6; CIMS (*m/z*) (*rel* intensity, %) 557 [M^+ − C_6H_5] (100), 454 [$Et_2NCOSeSn(C_6H_5)_2^+$] (50), 100 [$(C_2H_5)_2NCO^+$] (59.7); anal. calcd for $C_{22}H_{30}N_2O_2Se_2Sn$: C, 41.87; H, 4.79; found C, 41.77; H, 4.89.

Se-Dimethyltin Bis(N,N-diphenylselenocarbamate) **8′c**. Colorless crystals. Mp 190–194°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3050, 2970, 2933, 1590 (C=O), 1490, 1402, 1352, 1270, 1130, 945, 848, 750, 690, 600, 500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 6H, CH_3, $J_{Sn^{119}-CH_3}$ 70 Hz), 7.3 (s, 20H, Ar); ^{13}C NMR ($CDCl_3$) δ 4.1 (CH_3), 129.5, 137.6, 156.2 (Ar), 168.0 (C=O); ^{77}Se NMR ($CDCl_3$) δ 326.6; CIMS (*m/z*) (*rel* intensity, %) 426 [$(C_6H_5)_2NCOSeSn(CH_3)_2^+$] (63); anal. calcd for $C_{28}H_{26}N_2O_2Se_2Sn$: C, 48.10; H, 3.75; found: C, 48.29; H, 3.74.

Se-Triphenyllead N,N-Dimethylselenocarbamate **9a**. Pale yellow crystals. Mp 109–112°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3057, 2957, 1625 (C=O), 1471, 1430, 1354, 1253, 1093, 993, 797, 728, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.87 (s, 3H, CH_3), 3.07 (s, 3H, CH_3), 7.2–7.7 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$) δ 36.3 (CH_3), 42.3 (CH_3), 128.6, 129.8, 137.6, 153.8 (Ar), 163.0 (C=O); ^{77}Se NMR ($CDCl_3$) δ 294.5 CIMS (*m/z*) 592 [M^+ + 1], 439 [$(C_6H_5)_3Pb^+$] (7).

Se-Triphenyllead N,N-Diethylselenocarbamate **9b**. Pale yellow crystals. Mp 129–132°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3050, 2948, 1621 (C=O), 1468, 1402, 1348, 1220, 1106, 992, 843, 721, 602 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–1.3 (t, 6H, CH_3), 3.1–3.5 (q, 4H, CH_2), 7.1–7.7 (m, 15H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.1 (CH_3), 14.4 (CH_3), 42.6 (CH_2) 45.0 (CH_2), 128.6, 129.3, 138.2, 153.9 (Ar), 164.2 (C=O); ^{77}Se NMR ($CDCl_3$) δ 284.9; CIMS (*m/z*) (*rel* intensity, %) 542 [M^+ − C_6H_5] (4.6), 439 [$(C_6H_5)_3Pb^+$] (80).

Se-Triphenyllead N,N-Diphenylselenocarbamate **9c**. Pale yellow crystals. Mp 198–201°C (dec) [recryst solvent = dichloromethane/hexane (2:1)]; IR (KBr) 3056, 1637 (C=O), 1588, 1489, 1429, 1275, 1014, 995, 752, 724, 692, 604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.2–7.4 (m, 25H, Ar); ^{13}C NMR ($CDCl_3$) δ 128.6, 129.0, 129.1, 129.7, 137.2, 137.6, 150.1, 153.6 (Ar), 165.0 (C=O); ^{77}Se NMR ($CDCl_3$) δ 412.8; CIMS (*m/z*) (*rel* intensity, %) 638 [M^+ − C_6H_5] (4.1), 439 [$(C_6H_5)_3Pb^+$] (100).

Se-Diphenyllead Bis(N,N-dimethylselenocarbamate) **9′a**. Pale yellow crystals. Mp 132–136°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3048, 2980, 1602 (C=O), 1561, 1473, 1433, 1365, 1096, 985, 891, 720, 673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.80 (s, 6H, CH_3), 2.97 (s, 6H, CH_3), 7.2–7.9 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 36.1 (CH_3), 41.4 (CH_3), 129.4, 129.7, 135.4, 156.0 (Ar), 166.6 (C=O); ^{77}Se NMR ($CDCl_3$) δ 362.8; EIMS (*m/z*) (*rel* intensity, %) 514 [$(CH_3)_2NCOSePbPh_2^+$] (3.6), 285 [$C_6H_5Pb^+$] (72.4).

Se-Diphenyllead Bis(N,N-diethylselenocarbamate) **9′b**. Pale yellow needles. Mp 135–137°C (dec) [recryst solvent = dichloromethane/hexane (1:2)]; IR (KBr) 3046, 2970, 2933, 1586 (C=O)), 1434, 1402, 1352, 1245, 1207, 1121, 987, 848, 728, 686, 640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (t, 6H, CH_3), 1.23 (t, 6H, CH_3), 3.28 (q, 4H, CH_2), 3.45 (q, 4H, CH_2), 7.3–8.0 (m, 10H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.3 (CH_3), 14.1 (CH_3), 41.4, 48.2 (CH_2), 128.5, 129.5, 137.6, 156.2 (Ar), 165.4 (C=O); ^{77}Se ($CDCl_3$) δ 350.9; CIMS (*m/z*) (*rel* intensity, %) 723 [M^+ + 1] (2.4), 442 [Ph_2PbSe^+] (5), 100 [$(C_2H_5)_2NCO^+$] (60); anal. calcd for $C_{22}H_{30}N_2O_2PbSe_2$: C, 36.72; H, 4.18; found: C, 36.72, H, 4.18.

ACKNOWLEDGMENTS

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 and Grant-in-Aid for Scientific Research (B) No. 06453127 from the Ministry of Education, Science and Culture, Japan.

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