Preparation and Characterization of *N*-Alkyl-*Se*-alkylselenocarbamates

Mamoru Koketsu,* Masaru Ishida, Naotaka Takakura, and Hideharu Ishihara*

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

koketsu@cc.gifu-u.ac.jp

Received July 27, 2001

Several *N*-alkyl-*Se*-alkylselenocarbamates were prepared. The structure was confirmed by X-ray diffraction. *N*-Alkyl-*Se*-alkylselenocarbamates showed interesting NMR spectral features in ^{13}C and ^{77}Se NMR. They could be explained by the equilibrium between the major s-trans and the minor s-cis forms. This assumption was confirmed by the theoretical calculations.

Introduction

Reports of *N*-alkyl-*Se*-alkylselenocarbamates are scarce; only a few preparation methods have appeared.[1] Antiviral effects of the selenocarbamates have been investigated, and they are important compounds.[2] Recently, we developed a method for the preparation of LiAlHSeH, a novel selenating reagent. The LiAlHSeH can be readily prepared by the reaction of $LiAlH_4$ with elemental selenium in THF. The use of LiAlHSeH can afford a wide range of selenium-containing compounds.[3] The alkali metal salts of hydrogen selenide, which can be readily prepared in situ by the reactions of elemental selenium and a reducing reagent such as Li, $LiBEt_3H$, Na, $NaBH_4$, $NaBEt_3H$, and i-Bu_2AlH, have often been utilized as selenating reagents for the introduction of selenium into organic molecules.[4] However, the utilization of these salts as selenating reagents has been limited. For instance, alcohol or water must be used as solvent for the reaction of NaHSe because of the solubility. The reaction of NaHSe with *N*,*N*-dimethyl selenocarbamoyl chloride in alcohol gave only selenocarbamate bearing the *O*-alkyl group derived from alcohol by the nucleophilic attack of alcohol to the selenocarbonyl carbon.[3,4a] On the other hand, because the nucleophilic attack by solvent does not take place in the similar reaction using LiAlHSeH under aprotic conditions, the various carbamate derivatives bearing various kinds of alkyl groups are readily prepared by the reactions with various kinds of nucleophiles, i.e., lithium alkylselenolate, lithium alkylthiolate, and amines.[3]

Herein, we report the facile preparation of *N*-alkyl-*Se*-alkylselenocarbamates from the reaction of aromatic isocyanates with LiAlHSeH and haloalkanes. The crystal structure of the *Se*-methyl-*N*-phenylselenocarbamate was determined by X-ray diffraction. Their interesting NMR spectra were observed, and they were rationalized by theoretical calculations using B3LYP/6-31G*.

Scheme 1

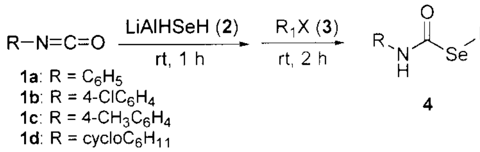


Table 1. Synthesis of *N*-Alkyl-*Se*-alkylselenocarbamates

entry	isocyanate (**1**)	haloalkane (**3**)	yield[a] (%) (**4**)
1	**1a**	CH_3I	70 (**4a**)
2	**1a**	C_2H_5I	59 (**4b**)
3	**1a**	C_4H_9I	39 (**4c**)
4	**1a**	$C_6H_5CH_2Br$	52 (**4d**)
5	**1a**	$C_6H_5(CH_2)_2Br$	29 (**4e**)
6	**1b**	CH_3I	73 (**4f**)
7	**1b**	$C_6H_5CH_2Br$	63 (**4g**)
8	**1c**	CH_3I	66 (**4h**)
9	**1c**	$C_6H_5CH_2Br$	44 (**4i**)
10	**1d**	CH_3I	72 (**4j**)
11	**1d**	$C_6H_5CH_2Br$	57 (**4k**)

[a] Isolated yield.

Results and Discussion

The reaction leading to *N*-alkyl-*Se*-alkylselenocarbamate **4** is shown in Scheme 1. Phenyl isocyanate **1a** was added to an anhydrous THF solution of LiAlHSeH **2**.[3] The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere. Methyl iodide **3a** in THF was added to the reaction mixture at room temperature. The reaction mixture was furthermore stirred for 2 h. After workup, *Se*-methyl-*N*-phenylselenocarbamate **4a** was obtained in a 70% yield. Reactions of four isocyanates **1** with several haloalkanes **3** also gave the corresponding *N*-alkyl-*Se*-alkylselenocarbamates **4** (Table 1). The haloalkanes bearing longer carbon chains tended to decrease the yield because they are less electrophilic. When similar reactions were attempted using NaHSe generated in ethanol, the observed products resulted from ethanolysis of the isocyanates, leading to the isolation of *O*-ethyl-*N*-alkylcarbamate. The use of LiAlHSeH **2** could

---

(1) (a) Henriksen, L. H. C. *Int. J. Sulfur Chem.* **1973**, *8*, 389. (b) Kondo, K.; Takarada, M.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 597. (c) Barrett, A. G. M.; Kwon, H.; Wallace, E. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1760. (d) Ferraz de Souza., W.; Kambe, N.; Sonoda, N. *J. Phys. Org. Chem.* **1996**, *9*, 179. (e) Reinerth, W. A.; Tour, J. M. *J. Org. Chem.* **1998**, *63*, 2397. (f) Ribby, J. H.; Danca, D. M.; Horner, J. H. *Tetrahedron Lett.* **1998**, *39*, 8413.

(2) Klimochkin, Y. N.; Moiseev, I. K.; Abramov, O. V.; Vladyko, G. V.; Korobchenko, L. V.; Boreko, E. I. *Khim. Farm. Zh.* **1991**, *25*, 49.

(3) Ishihara, H.; Koketsu, M.; Fukuta, Y.; Nada, F. *J. Am. Chem. Soc.* **2001**, *123*, 8408.

(4) (a) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197. (b) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204. (c) Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109. (d) Copeland, C. M.; Ghosh, J.; McAdam, D. P.; Skelton, B. W.; Stick, R. V.; White, A. H. *Aust. J. Chem.* **1998**, *41*, 549. (e) Li, G. M.; Zingaro, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 647.

10.1021/jo010763k CCC: $22.00

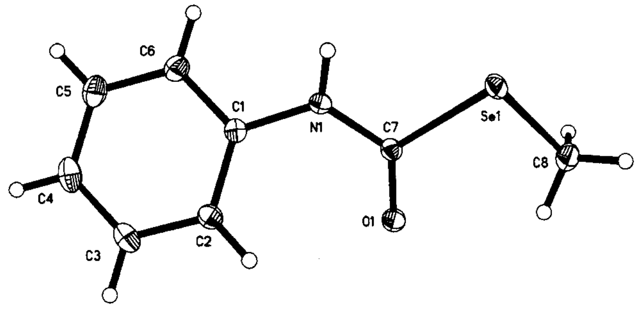


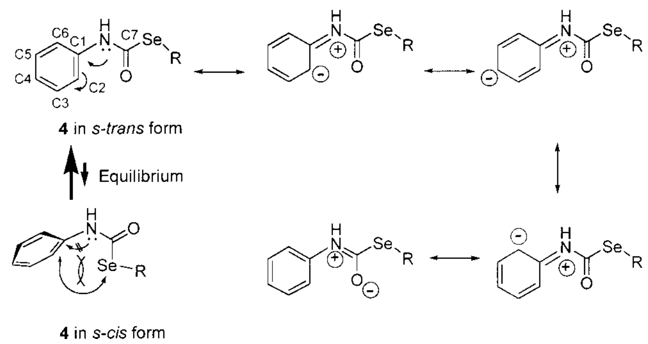
Figure 1. ORTEP diagram (50% thermal ellipsoids) of compound **4a**.

supply various *N*-alkyl-*Se*-alkylselenocarbamates **4** as shown in Table 1.

An X-ray diffraction analysis was carried out to characterize the structure of *Se*-methyl-*N*-phenylselenocarbamate **4a** (Figure 1). The bond length of C7−Se1 (1.934(4) Å) in **4a** is shorter than that of the normal selenium−carbon single bond (1.98 Å).[5] The two bond lengths of both N1−C7 (1.348(5) Å) and C1−N1 (1.422(5) Å) in **4a** also are shorter than the usual value of 1.47 Å.[6] The sum of the three angles around the C7 is 360.0°. The arrangement of O1, C7, N1, Se1, and C1 atoms is almost planar owing to the result of the double bond character of the C7−N1 bond. Additionally, the C2−C1−N1 bond angle (122.4(4)°) is 5.1° larger than the corresponding bond angle for the N1−C1−C6 fragment (117.3(4)°). Similar bond angles (117.9 and 121.9°) have been reported for the *N*-phenyl compound.[7] These results can be attributed to the delocalization of the lone-pair electrons on N1 to the C7(−O1)−N1−C1. The bond length and the double-bond character of the carbonyl group adjacent to nitrogen are most affected by the nitrogen, but are hardly influenced by the oxygen, sulfur, and selenium atoms adjacent to the selenocarbonyl group.[8] This viewpoint also applies to the case of **4a**. The bond angle of C−Se−C was reported to be 100.32(16)° in *Se*-phenyl-*N,N*-dimethyldiselenocarbamate owing to the steric repulsion between the bulky selenium atom and hydrogen of the aromatic.[9] When the *Se*-phenyl-*N,N*-dimethyldiselenocarbamate was compared with *Se*-methyl-*N*-phenylselenocarbamate **4a**, it was thought that the relaxation of steric repulsion by the replacement selenium into an oxygen atom at the carbonyl group decreased the bond angle of C−Se−C to 96.28(18)° in **4a**.

In the ^{13}C and ^{77}Se NMR spectra of **4a** in $CDCl_3$, an interesting spectral feature was observed. This was the significant line broadening of the peaks of C1, C2, C4, C6, C7, and selenium, while those of C3 and C5 were observed as sharp peaks as usual (see the Supporting Information).[10] This feature was highly dependent on the conditions of NMR measurement. For example, the broad signals of **4a** became slightly sharper when the spectrum was measured in DMSO-d_6 or measured in $CDCl_3$ at lower temperatures, such as 0 and −20 °C. The ^{13}C and ^{77}Se NMR spectra measured in $CDCl_3$ at −40 °C showed sharp peaks such as ordinary spectra along with new small satelite peaks (Figure 2, see the Supporting Information).

Scheme 2



These interesting observations in the NMR spectra can be rationalized by considering the equilibrium of **4** between the major s-trans and the minor s-cis forms. The planar structure of **4** in the s-trans form allows full conjugation of the lone pair electrons on the nitrogen atom to the entire π-system, while, in the s-cis form, the repulsive interaction between the selenium atom and the phenyl ring destroys the planarity to diminish the conjugation. The change of the conjugation resulted in the changes of the chemical shifts of the atoms in the π-system, especially, C2, C4, and C6. When the equilibration takes place with an appropriate rate, the resulting changes of the chemical shifts should be observed as the broadening of the corresponding signals.

This assumption was confirmed by theoretical calculations (Scheme 2). The molecular geometries of **4a** in the s-trans and s-cis forms, and the transition state of the equilibrium, were fully optimized at the DFT (B3LYP) level of theory using the 6-31G* basis set (see the Supporting Information).[11] The calculations of **4a** gave the optimized geometries of *s-trans*-**4a** and *s-cis*-**4a**, respectively, as the local minima (Figure 3).[11] The energy of *s-cis*-**4a** is 1.70 kcal/mol less favorable than *s-trans*-**4a**. The phenyl ring of *s-cis*-4a is considerably twisted with dihedral angles $D_{C7-N-C1-C2}$ of −56.0°. The geometry of the transition state of the conversion from trans-**4a** to *cis*-**4a** was optimized to be *ts*-**4a** with the dihedral angles $D_{C7-N-C1-C2}$ and $D_{Se-C7-N-C1}$ of 45.9 and −121.2°, respectively. The activation enthalpy $\Delta H^{\ddagger}$ for the conversion is 13.34 kcal/mol.[12]

---

(5) Fernández-Bolaños Guzmán, J.; Skrydstrup, T.; López-Castro, A.; Millán, M. J. D.; Oya, M. D. E. *Carbohydr. Res.* **1992**, *237*, 303.

(6) Barba, V.; Hernández, C.; Rojas-Lima, S.; Farfán, N.; Santillan, R. *Can. J. Chem.* **1999**, *77*, 2025.

(7) Giumanini, A. G.; Toniutti, N.; Verardo, G.; Merli, M. *Eur. J. Org. Chem.* **1999**, 141.

(8) Murai, T.; Kato, S. In *Organoselenium Chemistry. Modern Developments in Organic Synthesis*; Springer-Verlag: New York, 2000; p 177.

(9) Koketsu, M.; Fukuta, Ishihara, H. *J. Org. Chem.*, in press.

(10) The ^{1}H and ^{13}C NMR spectra of **4a** were completely assigned by using DQF-COSY, HMBC, and HMQC.

(11) To characterize stationary points as minima (equilibrium structures, no imaginary frequencies) or first-order saddle points (transition structures, one imaginary frequency) and to include the effects of zero-point vibrational energies in estimating the relative energies of the structures, harmonic vibrational frequencies were calculated at the same level. Gaussian 98, Revision A.9: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(12) Other minima: see the Supporting Information.

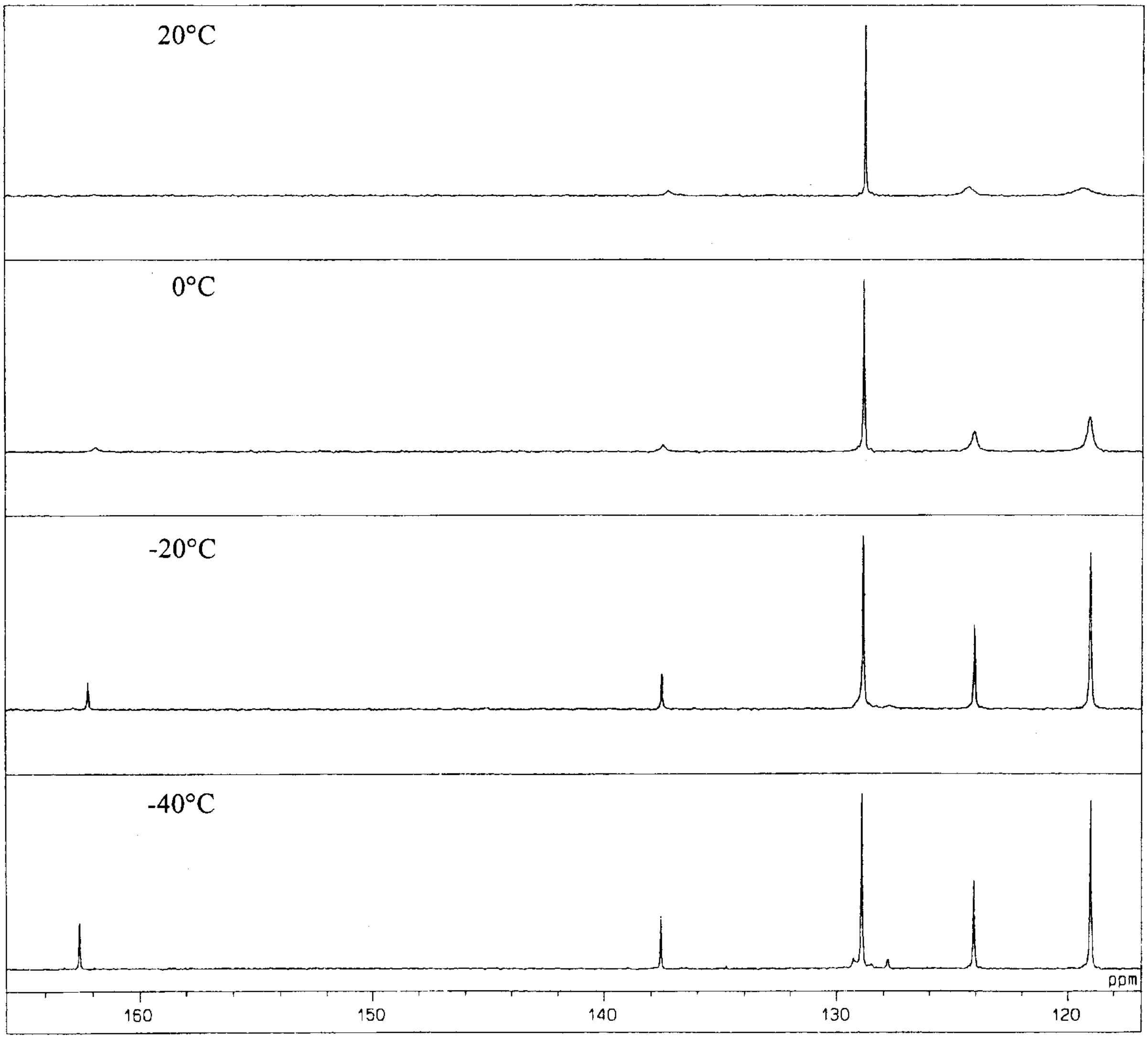


Figure 2. ^{13}C NMR spectra of compound **4a** at various temperatures.

The NMR chemical shifts of *s-trans*-**4a** and *s-cis*-**4a** were calculated on those structures using the gauge-independent atomic orbital method (GIAO[10,13]) as found in the Gaussian 98 program by RHF level of theory using 6-31* basis set. Calculated chemical shifts, relative chemical shifts ($\Delta\delta$), and the observed chemical shifts are summarized in Table 2.

The chemical shifts of C1, C2, C4, C6, and C7 of *s-cis*-**4a** were found to be significantly lowered from those of *s-trans*-**4a**, while those of C3, C5, and C8 tended to sustain unchanged shifts. The lower field shifts of C2, C4, and C6 in the *s-cis* forms were well consistent with not only the prediction of the less effective conjugation in nonplaner π-systems[14] but also the spectral feature observed in the ^{13}C NMR spectra, since the larger $\Delta\delta$ resulted in the broader signal in NMR. The theoretical calculations were supported by the observation of the small satellite peaks appearing in the ^{13}C and ^{77}Se NMR spectra of **4a** at −40 °C. The peaks could be reasonably assigned to those of the less favorable conformer, *s-cis*-**4a**, by considering the calculated chemical shifts (see the Supporting Information).

Table 2. Calculated Chemical Shifts of *s-trans*- and *s-cis*-4a (δ, ppm, Relative to TMS), Relative Chemical Shifts $\Delta\delta = \delta_{s\text{-}cis\text{-}4a} - \delta_{s\text{-}trans\text{-}4a}$, Using the GIAO Method and the 6-31* Basis Set

	calcd chemical shifts (RHF-GIAO/6-31G*)			obsd peaks ($CDCl_3$)[a,b]
atoms	*s-trans*-**4a**	*s-cis*-**4a**	$\Delta\delta$[d]	δ and appearance
C1	139.1	135.6	−3.5	137.2 (broad)
C2	116.9	125.9	9.0	119.8 (very broad)
C3	130.8	128.5	−2.3	128.9 (sharp)
C4	121.0	125.6	4.6	124.6 (broad)
C5	128.8	129.0	0.2	128.9 (sharp)
C6	113.3	123.7	10.4	119.8 (very broad)
C7	172.8	177.4	4.6	162.2 (broad)
C8	11.2	10.4	−0.8	6.2 (sharp)
Se[c]	273.4	264.7	−8.7	334.5 (broad)[b,d]

[a] At 20 °C. [b] See the Supporting Information. [c] Relative to the selenium in dimethyl selenide. [d] Very small satellite peak (δ = 319.7) also appeared in the ^{77}Se NMR spectrum at −40 °C.

---

(13) (a) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028. (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (c) Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419. (d) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (e) Cheeseman, J. R., Trucks, G. W., Keith, T. A. Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(14) The calculation showed that the C2, C4, and C6 carbons of *s-trans*-**4a** were more negatively charged than those of *s-cis*-**4a** (see the Supporting Information).

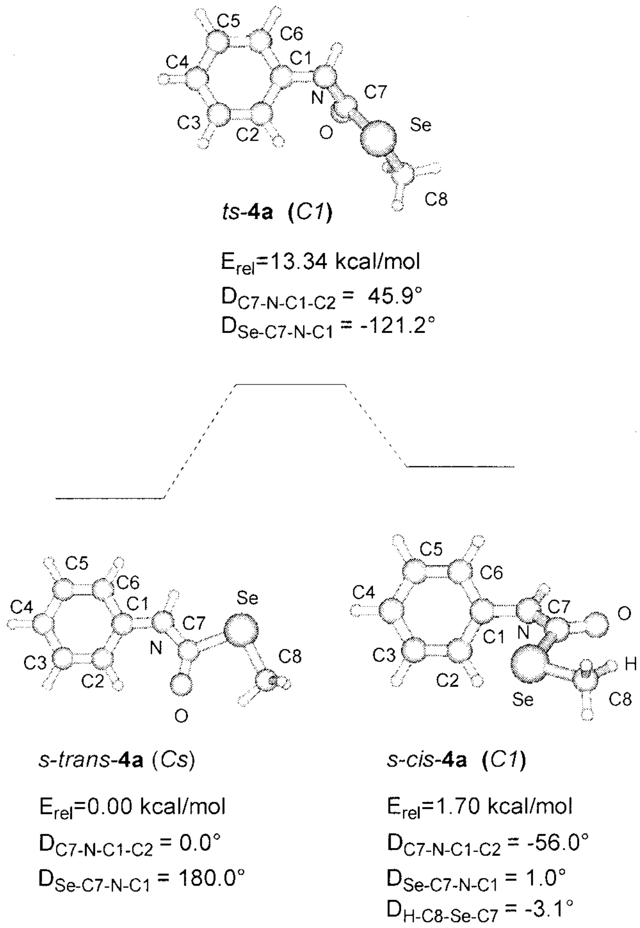


Figure 3. Computed structures, relative energy (E_{rel}), and selected dihedral angles (deg) of *s-trans*-**4a**, *ts*-**4a**, and *s-cis*-**4a** (B3LYP/6-31G*).

Experimental Section

General Methods. Tetrahydrofuran was distilled from sodium benzophenone immediately prior to use. The ^{77}Se chemical shifts were expressed in ppm deshielded with respect to neat Me_2Se in $CDCl_3$. LiAlHSeH **2** were prepared according to a previously reported method.[3] Briefly, the preparation of LiAlHSeH **2** is as follows: to a solution of selenium powder (0.80 g, 10.0 mmol) in dry THF (100 mL) was added lithium aluminum hydride (0.38 g, 10.0 mmol) at 0 °C under an argon atmosphere. The mixture was stirred for 30 min. The black selenium powder was consumed in less than 10 min. The reaction mixture became a heterogeneous grayish suspension. The reagent was formed in situ and was then ready for further reaction.

***Se*-Methyl-*N*-phenylselenocarbamate 4a.** Phenyl isocyanate **1a** (0.11 mL, 1.0 mmol) was added to the THF solution (10 mL) of LiAlHSeH **2** (1.0 mmol). The reaction mixture was stirred at room temperature for 1 h. Methyl iodide **3a** (0.06 mL, 1.0 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 2 h. The mixture was extracted with diethyl ether and washed with water. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane/*n*-hexane (4:1) to give **4a** 0.15 g (70%) as yellow crystals: mp 90.8−93.0 °C; IR (KBr) 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.31 (3H, s, CH_3), 7.08−7.42 (5H, m, Ar), 7.79 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 6.5, 119.0, 124.1, 128.9, 137.6, (Ar), 162.6; ^{77}Se NMR ($CDCl_3$) δ 334.1; MS (EI) *m/z* = 215 [M$^+$]. Anal. Calcd for C_8H_9NOSe: C, 44.87; H, 4.24; N, 6.54. Found: C, 45.13; H, 4.09; N, 6.56.

***Se*-Ethyl-*N*-phenylselenocarbamate 4b:** yield 59% as white crystals; mp 65.2−65.8 °C; IR (KBr) 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (3H, t, *J* = 7.6 Hz, CH_3), 3.00 (2H, q, *J* = 7.6 Hz, CH_2), 7.08−7.42 (5H, m, Ar), 7.55 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 16.4, 21.0, 119.7−137.6 (Ar), 162.2; ^{77}Se NMR ($CDCl_3$) δ 452.3; MS (CI) *m/z* = 230 [M$^+$ + 1]. Anal. Calcd for $C_9H_{11}NOSe$: C, 47.38; H, 4.86; N, 6.14. Found: C, 47.36; H, 4.85; N, 6.35.

***Se*-Butyl-*N*-phenylselenocarbamate 4c:** yield 39% as yellow crystals; mp 57.2−58.4 °C; IR (KBr) 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, *J* = 7.6 Hz, CH_3), 1.40 (2H, m, *J* = 7.6 Hz, CH_2), 1.73 (2H, quint, *J* = 7.6 Hz, CH_2), 3.00 (2H, t, *J* = 7.6 Hz, CH_2), 7.08−7.42 (5H, m, Ar), 7.50 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 13.5, 22.9, 27.1, 33.0, 119.7−137.6 (Ar), 161.9; ^{77}Se NMR ($CDCl_3$) δ 418.6; MS (CI) *m/z* = 258 [M$^+$ + 1]. Anal. Calcd for $C_{11}H_{15}NOSe$: C, 51.57; H, 5.90; N, 5.47. Found: C, 51.55; H, 5.87; N, 5.47.

***Se*-Benzyl-*N*-phenylselenocarbamate 4d:** yield 52% as white powder; mp 95.0−97.6 °C; IR (KBr) 1654 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 4.23 (2H, s, CH_2), 7.06−7.36 (10H, m, Ar), 7.55 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 16.4, 21.0, 119.7−137.6 (Ar), 162.2; ^{77}Se NMR ($CDCl_3$) δ 498.3; MS (CI) *m/z* = 292 [M$^+$ + 1]. Anal. Calcd for $C_{14}H_{13}NOSe$: C, 57.94; H, 4.51; N, 4.83. Found: C, 57.96; H, 4.57; N, 4.84.

***Se*-Phenethyl-*N*-phenylselenocarbamate 4e:** yield 29% as yellow crystals; mp 95.4−96.8 °C; IR (KBr) 1654 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 3.08 (2H, t, *J* = 7.7 Hz, CH_2), 3.25 (2H, t, *J* = 7.7 Hz, CH_2), 7.10−7.42 (10H, m, Ar), 7.43 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 28.2, 37.3, 119.7−140.9 (Ar), 160.9; ^{77}Se NMR ($CDCl_3$) δ 424.6; MS (CI) *m/z* = 306 [M$^+$ + 1]. Anal. Calcd for $C_{15}H_{15}NOSe$: C, 59.22; H, 4.97; N, 4.60. Found: C, 59.26; H, 5.01; N, 4.61.

***N*-(4-Chlorophenyl)-*Se*-methylselenocarbamate 4f:** yield 73% as white powder; mp 111.6−114.0 °C; IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s, CH_3), 7.22−7.36 (4H, m, Ar), 7.67 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 6.4, 121.1−136.0 (Ar), 162.6; ^{77}Se NMR ($CDCl_3$) δ 337.7; MS (CI) *m/z* = 250 [M$^+$ + 1]. Anal. Calcd for $C_8H_8ClNOSe$: C, 38.66; H, 3.24; N, 5.63. Found: C, 38.75; H, 3.42; N, 5.36.

***Se*-Benzyl-*N*-(4-chlorophenyl)selenocarbamate 4g:** yield 63% as white powder; mp 124.0−127.2 °C; IR (KBr) 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.25 (2H, s, CH_2), 7.21−7.37 (9H, m, Ar), 7.35(1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 30.7, 121.1−138.8 (Ar), 162.1; ^{77}Se NMR ($CDCl_3$) δ 500.5; MS (CI) *m/z* = 326 [M$^+$ + 1]. Anal. Calcd for $C_{14}H_{12}ClNOSe$: C, 51.79; H, 3.73; N, 4.31. Found: C, 51.70; H, 3.65; N, 4.36.

***Se*-Methyl-*N*-(4-methylphenyl)selenocarbamate 4h:** yield 66% as white powder; mp 101.8−103.0 °C; IR (KBr) 1657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (6H, s, CH_3), 7.09−7.29 (4H, m, Ar), 7.37 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 6.3, 20.8, 119.5−135.0 (Ar), 161.4; ^{77}Se NMR ($CDCl_3$) δ 330.9; MS (CI) *m/z* = 230 [M$^+$ + 1]. Anal. Calcd for $C_9H_{11}NOSe$: C, 47.38; H, 4.86; N, 6.14. Found: C, 47.20; H, 4.62; N, 6.34.

***Se*-Benzyl-*N*-(4-methylphenyl)selenocarbamate 4i:** yield 44% as white powder; mp 110.6−114.2 °C; IR (KBr) 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.27 (3H, s, CH_3), 4.21 (2H, s, CH_2), 7.05−7.32 (9H, m, Ar), 7.39 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 20.8, 30.4, 119.6−139.1 (Ar), 161.0; ^{77}Se NMR ($CDCl_3$) δ 496.5; MS (CI) *m/z* = 306 [M$^+$ + 1]. Anal. Calcd for $C_{15}H_{15}NOSe$: C, 59.22; H, 4.97; N, 4.60. Found: C, 59.11; H, 4.68; N, 4.61.

***N*-Cyclohexyl-*Se*-methylselenocarbamate 4j:** yield 72% as white powder; mp 94.6−96.2 °C; IR (KBr) 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10−1.26 (3H, m), 1.28−1.42 (2H, m), 1.56−1.65 (1H, m), 1.66−1.78 (2H, m), 1.90−2.02 (2H, m), 2.26 (3H, s, CH_3), 3.68−3.88 (1H, m), 5.41 (1H, br s, NH); ^{13}C NMR ($CDCl_3$) δ 5.8, 24.7, 25.4, 33.0, 51.0, 161.4; ^{77}Se NMR ($CDCl_3$) δ 307.4; MS (CI) *m/z* = 222 [M$^+$ + 1]. Anal. Calcd for $C_8H_{15}NOSe$: C, 43.64; H, 6.36; N, 6.87. Found: C, 43.58; H, 6.66; N, 6.68.

***Se*-Benzyl-*N*-cyclohexylselenocarbamate 4k:** yield 57% as white powder; mp 94.0−94.6 °C; IR (KBr) 1647 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08−1.22 (3H, m), 1.26−1.42 (2H, m), 1.54−1.64 (1H, m), 1.65−1.76 (2H, m), 1.90−2.02 (2H, m), 3.71−3.84 (1H, m), 4.19 (2H, s, CH_2), 5.29 (1H, br s, NH), 7.20 (1H, t, *J* = 7.3 Hz, Ar), 7.27 (2H, t, *J* = 7.3 Hz, Ar), 7.33 (2H, d, *J* = 7.3 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.3, 29.9, 33.0, 51.2, 126.9, 128.5, 128.8, 139.7, 161.3; ^{77}Se NMR ($CDCl_3$) δ 477.2;

MS (CI) $m/z = 298$ [$M^+ + 1$]. Anal. Calcd for $C_{14}H_{19}NOSe$: C, 56.76; H, 6.46; N, 4.73. Found: C, 56.76; H, 6.38; N, 4.52.

Acknowledgment. We thank Prof. Satoshi Inagaki for critical and helpful discussions and Dr. Dale Swenson, University of Iowa Chemistry Department X-ray Diffraction Facility, for his assistance in acquiring X-ray crystallographic data.

Supporting Information Available: Complete tables of crystallographic data, structure-refinement parameters, final atomic coordinates, equivalent isotropic thermal parameters, bond distances, bond angles, torsion angles, and an ORTEP figure of **4a**, NMR spectra at various temperatures, and results. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010763K