

# New Stable Germylenes, Stannylenes, and Related Compounds. 3. Stable Monomers $XGeOCH_2CH_2NMe_2$ ( $X = Cl, OCOMe$ ) with Only One Intramolecular Coordination Metal–Nitrogen Bond: Synthesis and Structure

Nikolay N. Zemlyansky,<sup>\*,†</sup> Irina V. Borisova,<sup>†</sup> Victor N. Khrustalev,<sup>‡</sup> Mikhail Yu. Antipin,<sup>‡</sup> Yuri A. Ustynyuk,<sup>\*,§</sup> Mikhail S. Nechaev,<sup>§</sup> and Valery V. Lunin<sup>§</sup>

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), 29 Leninsky prosp., 119991-GSP-1, Moscow, Russia, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russia, and Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russia

Received July 25, 2003

New stable monomeric germanium(II) derivatives  $XGeOCH_2CH_2NMe_2$  (**1**,  $X = Cl$ ; **2**,  $X = OCOMe$ ) with ligands that are not sterically bulky at the Ge atom and only one intramolecular coordination  $Ge \leftarrow N_{sp^3}$  bond have been synthesized. The molecular and crystal structures of these compounds were studied by X-ray diffraction analysis. The electronic structures of **1** and **2** were studied by DFT. Compound **2** is the first structurally characterized acyloxy derivative of germanium(II).

## Introduction

The chemistry of stable organic derivatives of divalent germanium and tin has developed very rapidly in the last decades.<sup>1,2</sup> Steric protection of the metal atom by bulky substituents R and intramolecular coordination  $M \leftarrow Y$  ( $Y = N, O$ ) with donor groups of suitable geometry in the side chain are two main factors responsible for their kinetic and thermodynamic stabilization. Monomeric germanium(II) compounds with small ligands are so far practically unknown. In continuation of our study on germanium(II) compounds<sup>3</sup> we report here the synthesis and the results of experimental (X-ray, NMR) and DFT theoretical studies of two stable monomeric compounds,  $XGeOCH_2CH_2NMe_2$  (**1**,  $X = Cl$ ; **2**,  $X = OAc$ ), stabilized by only one intramolecular coordination  $Ge \leftarrow N_{sp^3}$  bond without any steric protection. Rare examples of such compounds, namely, dialkoxy derivative  $MeN(CH_2CH_2O)_2Ge$ ,<sup>4a</sup> oxyisobutyrate,<sup>4b</sup> oxysalicylate,<sup>4c,d</sup> and oxythiosalicylate<sup>4c,d</sup> germanium(II), have been reported previously without structural characterization.

## Results and Discussion

The chloro derivative  $ClGeOCH_2CH_2NMe_2$  (**1**) is formed easily in 74% yield by the exchange of one chelating  $OCH_2CH_2NMe_2$  ligand of  $Ge(OCH_2CH_2NMe_2)_2^3$  (**3**) in the 1:1 redistribution reaction with  $GeCl_2 \cdot D$  ( $D = dioxane$ ) (**4**) in THF at 20 °C (Scheme 1).

\* Address correspondence to these authors. N.N.Z.: E-mail zemlyan@mail.cnt.ru. Y.A.U.: E-mail yust@nmr.chem.msu.

<sup>†</sup> A. V. Topchiev Institute of Petrochemical Synthesis.

<sup>‡</sup> A. N. Nesmeyanov Institute of Organoelement Compounds.

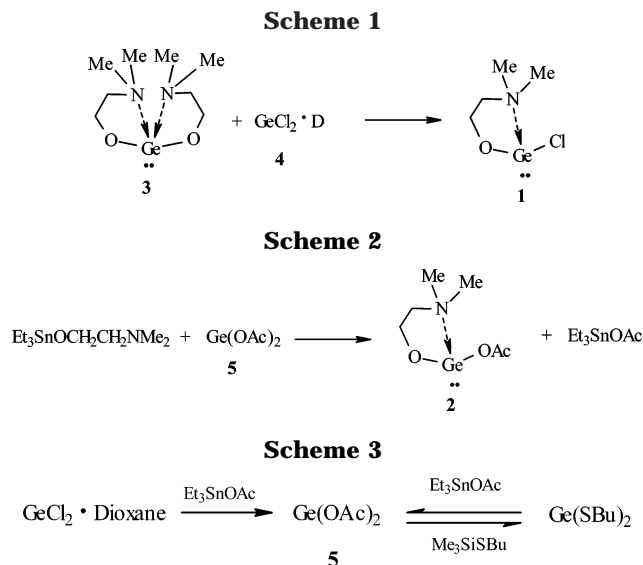
<sup>§</sup> Moscow State University.

(1) Recent reviews: (a) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251. (b) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178–180*, 593.

The compound  $AcOGeOCH_2CH_2NMe_2$  (**2**) has been prepared in 67% yield by the reaction of (*N,N*-dimethylaminoethoxy)triethyltin with germanium(II) acetate (**5**) at 1:1 reagent ratio in THF at room temperature (Scheme 2).

(2) Recent selected publications: (a) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammer, A.; Stammer, H.-G. *Organometallics* **2001**, *20*, 42. (b) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammer, H.-G. *Organometallics* **1999**, *18*, 4778. (c) Schmidt, H.; Keitemeyer, S.; Neumann, B.; Stammer, H.-F.; Schnoeller, W. W.; Jutzi, P. *Organometallics* **1998**, *17*, 2149. (d) Barrau, J.; Rima, G.; El Amraoui, T. *Organometallics* **1998**, *17*, 607. (e) Barrau, J.; Rima, G.; El Amraoui, T. *J. Organomet. Chem.* **1998**, *561*, 167. (f) Akkari, A.; Byrne, J. J.; Saur, I.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2001**, *622*, 190. (g) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Patel, D.; Smith, J. D.; Zhang, S. *Organometallics* **2000**, *19*, 49. (h) Borisova, I. V.; Eaborn, C.; Hill, M. S.; Khrustalev, V. N.; Kuznetsova, M. G.; Smith, J. D.; Ustynyuk, Yu. A.; Lunin, V. V.; Zemlyansky, N. N. *Organometallics* **2002**, *21*, 4005. (i) Chorley, R. W.; Hitchcock, P. B.; Jolly, B. S.; Lappert, M. F.; Lawless, G. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1302. (j) Leung, W.-P.; Kwok, W.-H.; Zhou, Z.-Y.; Mak, T. C. W. *Organometallics* **2003**, *22*, 1751. (k) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Zoutberg, M. C.; Heljdenrijk, D. *Organometallics* **1989**, *8*, 1373, and references therein. (l) Ayers, A. E.; Klapötke, T. M.; Dias, H. V. R. *Inorg. Chem.* **2001**, *40*, 1000. (m) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190. (n) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (o) Ding, Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Usón, I.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2002**, *21*, 5216. (p) Kitamura, C.; Maeda, N.; Kamada, N.; Ouchi, M.; Yoneda, A. *J. Chem. Soc., Perkin Trans.* **2000**, *1*, 781. (q) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 662. (r) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785. (s) Francis, M. D.; Hitchcock, P. B. *Organometallics* **2003**, *22*, 2891. (t) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204. (u) Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. *Organometallics* **2001**, *20*, 4460. (v) Karsch, H. H.; Schlüter, P. A.; Reisky, M. *Eur. J. Inorg. Chem.* **1998**, 433. (w) Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. (x) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650.

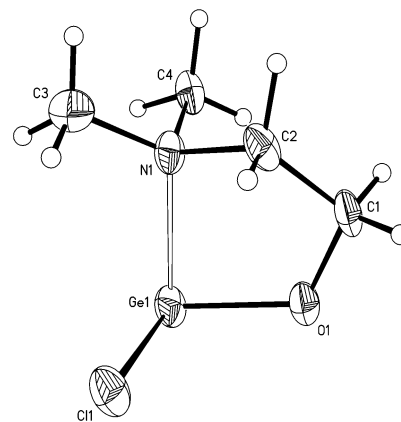
(3) (a) Khrustalev, V. N.; Borisova, I. V.; Zemlyanskii, N. N.; Ustynyuk, Yu. A.; Antipin, M. Yu. *Crystallogr. Rep.* **2002**, *47*, 616. (b) Zemlyansky, N. N.; Borisova, I. V.; Khrustalev, V. N.; Ustynyuk, Yu. A.; Nechaev, M. S.; Lunin, V. V.; Barrau, J.; Rima, *Organometallics* **2003**, *22*, 1675.



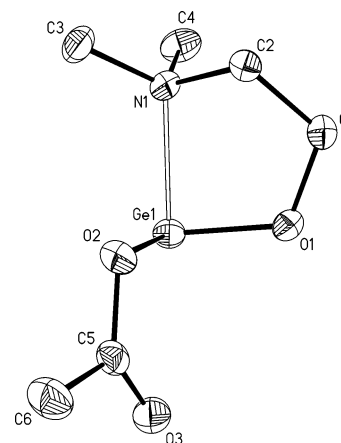
Both **1** and **2** are white crystalline substances that are very sensitive to traces of oxygen and moisture. They are moderately soluble in THF and dichloromethane and slightly soluble in ether and hexane. The  $^1\text{H}$  NMR spectra of **1** and **2** recorded in dichloromethane- $d_2$  at  $+40^\circ\text{C}$  contain sharp  $\text{A}_2\text{X}_2$  patterns of  $\text{CH}_2\text{CH}_2$  units and sharp singlets due to the  $\text{NMe}_2$  groups. This indicates that a fairly fast dynamic process occurs in solution, during which the  $\text{Ge}-\text{N}_{\text{sp}^3}$  coordination bonds break and re-form. In the  $^1\text{H}$  NMR spectra recorded at  $0^\circ\text{C}$  the triplets due to the  $\text{CH}_2\text{N}$  groups and  $\text{NMe}_2$  group singlets, as well as the singlets due to the  $\text{OCH}_2$  carbons in the  $^{13}\text{C}$  NMR spectra of both substances, are noticeably broadened due to retardation of this process. A similar process had been reported for the nitrogen- and oxygen-coordinated germanium(II) compounds  $(\text{Mamx})_2\text{Ge}$  [temperature range  $+80$  to  $-80^\circ\text{C}$ ;  $\text{Mamx} = 2,4\text{-Bu-}t\text{-}6\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_2$ ],<sup>2c</sup>  $(t\text{-Bomx})_2\text{Ge}$  [temperature range  $+80$  to  $-40^\circ\text{C}$ ;  $t\text{-Bomx} = 2,4\text{-Bu-}t\text{-}6\text{-(}t\text{-BuOCH}_2\text{)C}_6\text{H}_2$ ], and  $(i\text{-Pomx})_2\text{Ge}$  [temperature range  $\sim 20$  to  $-40^\circ\text{C}$ ;  $i\text{-Pomx} = 2,4\text{-Bu-}t\text{-}6\text{-(}i\text{-PrOCH}_2\text{)C}_6\text{H}_2$ ]<sup>2a</sup> and nitrogen-coordinated tin(II) compounds  $(\text{ArO})_2\text{Sn}$  ( $\text{Ar} = 2,4,6\text{-(Me}_2\text{NCH}_2\text{)}_3\text{C}_6\text{H}_2$ )<sup>2d,e</sup> and  $\text{RSnX}$  [ $\text{R} = \text{C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N-}2$ ,  $\text{X} = \text{Cl}$  or  $\text{N}(\text{SiMe}_3)_2$ ;<sup>2i</sup>  $\text{R} = \text{CH}(\text{SiMe}_3)\text{C}_9\text{H}_6\text{N-}8$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;<sup>2j</sup>  $\text{R} = 2,6\text{-(Me}_2\text{NCH}_2\text{)}_2\text{-C}_6\text{H}_3$ ,  $\text{X} = \text{Cl}$ ].<sup>2k</sup> We started the study of the NMR spectra of **1** and **2** in a wide range of temperatures and concentrations to obtain more detailed information about this dynamic process.

Previously unknown germanium(II) acetate,  $\text{Ge}(\text{OAc})_2$  (**5**), has been prepared by the reactions of triethyltin acetate,  $\text{Et}_3\text{SnOAc}$ , with  $\text{GeCl}_2\cdot\text{D}$  (**4**) or with  $\text{Ge}(\text{SBu})_2$ , which had been synthesized earlier<sup>5</sup> (Scheme 3). The reverse transformation of **5** into  $\text{Ge}(\text{SBu})_2$  can be effected easily by its reaction with  $\text{Me}_3\text{SiSBu}$ .

Acetate **5** is a white crystalline substance that is very sensitive to traces of oxygen and moisture. It is well soluble in pyridine, THF, and chloroform and practically



**Figure 1.** Molecular structure of **1** (50% probability ellipsoids).



**Figure 2.** Molecular structure of **2** (50% probability ellipsoids).

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

compound	<b>1</b> (R = Cl)	<b>2</b> (R = OCOMe)
Ge–O	1.820(4)	1.832(1)
Ge–R	2.330(2)	1.938(1)
Ge–N	2.093(5)	2.108(1)
O–Ge–R	98.0(2)	97.09(5)
N→Ge–R	92.9(2)	86.90(5)
N→Ge–O	84.7(2)	84.79(5)

insoluble in ether and hexane. We have not succeeded in preparing a crystal of **5** suitable for X-ray analysis. Our study of the synthesis and reactivity of the series of other germanium(II) acylates will be reported elsewhere.

Crystals suitable for an X-ray structure analysis were obtained from THF (for **1**) and  $\text{Et}_2\text{O}/\text{THF}$  (for **2**) solution. The molecular structures of **1** and **2** are shown in Figures 1 and 2. Selected bond lengths and angles are presented in Table 1, and crystallographic data are given in Table 2.

In the structures of **1** and **2** the germanium atom is three-coordinate, forming one  $\sigma$ -bond to each substituent and an additional  $\text{N}\rightarrow\text{Ge}$  coordination bond. The  $\text{Ge}-\text{N}$  bond length is 2.093(5) Å for **1** and 2.108(1) Å for **2**. These values are in the same range as those observed in previously studied amino-functionalized  $\text{Ge}(\text{II})$  compounds of this type (2.092(3)–2.165(5) Å<sup>2b,c,6</sup>). The alkoxide  $\text{Ge}-\text{O}$  bond lengths (1.820(4) Å in **1** and 1.832(1) Å in **2**) are shortened in comparison with that for  $\text{Ge}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$  (1.861(1)–1.870(1) Å<sup>3</sup>). The  $\text{Ge}-$

(4) (a) Silverman, L. D.; Zeldin, M. *Inorg. Chem.* **1980**, *19*, 272. (b) Lavayssière, H.; Dousse, G.; Satgé, J. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, *53*, 411. (c) Lavayssière, H.; Dousse, G.; Mazieres, S.; Satgé, J. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, *61*, 341. (d) Mazieres, S.; Lavayssière, H.; Dousse, G.; Satgé, J. *Inorg. Chim. Acta* **1996**, *252*, 25.

(5) Jutzi, P.; Stener, W. *Chem. Ber.* **1976**, *109*, 1575.

**Table 2. Crystallographic Data for 1 and 2**

	1	2
empirical formula	C <sub>4</sub> H <sub>10</sub> NOClGe	C <sub>6</sub> H <sub>13</sub> NO <sub>3</sub> Ge
fw	196.17	219.76
temperature (K)	110(2)	200(2)
cryst size (mm)	0.40 × 0.30 × 0.05	0.30 × 0.15 × 0.10
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	6.500(3)	12.8127(15)
<i>b</i> (Å)	11.203(4)	6.6734(8)
<i>c</i> (Å)	10.080(5)	11.5545(15)
α (deg)	90	90
β (deg)	94.453(9)	110.988(3)
γ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	731.8(5)	922.4(2)
<i>Z</i>	4	4
<i>d</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.781	1.582
<i>F</i> (000)	392	448
μ (mm <sup>-1</sup> )	4.462	3.285
θ range (deg)	2.72 to 26.06	3.41 to 28.06
index range	-8 ≤ <i>h</i> ≤ 7 -13 ≤ <i>k</i> ≤ 9 -12 ≤ <i>l</i> ≤ 11	-16 ≤ <i>h</i> ≤ 16 -8 ≤ <i>k</i> ≤ 8 -15 ≤ <i>l</i> ≤ 15
no. of reflns collected	4535	9088
no. of unique reflns	1403	2193
no. of reflns with <i>I</i> > 2σ( <i>I</i> )	890	1793
R1; wR2 ( <i>I</i> > 2σ( <i>I</i> ))	0.0487; 0.1052	0.0215; 0.0496
R1; wR2 (all data)	0.0852; 0.1170	0.0283; 0.0512
no. of data/restraints/ params	1403/0/113	2193/0/103
GOF on <i>F</i> <sup>2</sup>	0.921	0.953
max shift/error	0.001	0.001
largest diff peak/hole (e Å <sup>-3</sup> )	0.906/-0.916	0.359/-0.250
abs corr <i>T</i> <sub>max</sub> ; <i>T</i> <sub>min</sub>	0.800; 0.281	0.720; 0.398

Cl bond length in the structure **1** (2.330(2) Å) is equal to that in [Mamx]GeCl (2.3283(4) Å<sup>2b</sup>) or in [*t*-Bomx]-GeCl (2.333(1) Å<sup>2a</sup>). The acetate Ge–O bond length in **2** (1.938(1) Å) is equal to that in the salt [PPH<sub>3</sub>Pr<sup>IV</sup>]<sup>(+)</sup>[Ge(OCOMe)<sub>3</sub>]<sup>(-)</sup> (1.921(1)–1.948(1) Å<sup>7</sup>). However, it considerably exceeds the values of the lengths of other known Ge(II)–O bonds (1.765(6)–1.879(7) Å<sup>2b,6,8a-i</sup>).

The geometry at the germanium atom in the structures of **1** and **2** is worth mentioning. The angle α (O<sub>1</sub>–Ge–N) is smaller than 90° in both compounds (84.7(2)° in **1** and 84.79(5)° in **2**). The angle β (O<sub>1</sub>–Ge–X, X = Cl, O) is close to 90° (92.9(2)° in **1** and 86.90(5)° in **2**), and the angle γ (N–Ge–X, X = Cl, O) is larger than 90° (98.0(2)° in **1** and 97.09(5)° in **2**). The same distribution of the α, β, and γ bond angles (α < β ≈ 90° < γ) is characteristic of all previously investigated analogous Ge(II) compounds.<sup>2b,c,6</sup> The nitrogen atom is nearly perpendicular to the O–Ge–X (X = Cl, O) plane, allowing ideal interaction of its lone electron pair with the vacant Ge(p) orbital.

The five-membered heterocycles of **1** and **2** have envelope conformations with C(2) atom deviations from the mean-square planes through the rest of the atoms of 0.561 and 0.564 Å, respectively.

(6) Suh, S.; Hoffman, D. M. *Inorg. Chem.* **1996**, *35*, 6164.

(7) Khrustalev, V. N.; Antipin, M. Yu.; Zemlyansky, N. N.; Borisova, I. V.; Ustynyuk, Yu. A.; Lunin, V. V.; Izod, K. Unpublished results.

(8) (a) Çetinkaya, B.; Gümürkçü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088. (b) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939. (c) Hitchcock, P. B.; Lappert, M. F.; Thomas, S. A.; Thorne, A. J.; Carty, A. J.; Taylor, N. J. *J. Organomet. Chem.* **1986**, *315*, 27. (d) Veith, M.; Kafer, D.; Koch, J.; May, P.; Stahl, L.; Huch, V. *Chem. Ber.* **1992**, *125*, 1033. (e) Veith, M.; Mathur, C.; Huch, V. *Organometallics* **1996**, *15*, 2858. (f) Veith, M.; Mathur, C.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1997**, 995. (g) Veith, M.; Mathur, C.; Mathur, S.; Huch, V. *Organometallics* **1997**, *16*, 1292. (h) Hascall, T.; Rheingold, A. L.; Guzei, I.; Parkin, G. *Chem. Commun.* **1998**, 101. (i) McBurnett, B. G.; Cowley, A. H. *Chem. Commun.* **1999**, 17.

**Table 3. Calculated Geometry Parameters of Molecules 1a–c (interatomic distances in Å, valence angles in deg, deviations from X-ray data in parentheses)**

	1a	1b	1c
Ge–O	1.850 (+0.034)	1.843 (+0.023)	1.795
Ge–Cl	2.340 (+0.010)	2.351 (+0.021)	2.232
Ge–N	2.252 (+0.159)	2.093 <sup>a</sup> (0.000)	5.067
O–Ge–Cl	101.6 (+3.6)	100.9 (+2.9)	97.0
N–Ge–Cl	91.3 (+1.6)	92.2 (-0.7)	
N–Ge–O	81.4 (-3.3)	83.4 (-1.4)	

<sup>a</sup> Parameter fixed at the X-ray value in optimization.

In the crystal the molecules **1** and **2** show no intermolecular interactions.

### DFT Study of 1 and 2

The molecular and electronic structures of **1** and **2** have been studied using the DFT approach. The geometry optimizations have been carried out using generalized gradient functional PBE.<sup>9</sup> This functional has previously been extensively tested on a variety of types of molecules.<sup>10</sup> Triple-ζ valence basis sets including polarization functions TZ2P {3,1,1/3,1,1/1,1} for Ge, Cl, C, N, and O atoms and {3,1,1/1} for H atoms have been used.<sup>11</sup> Innermost electrons were treated using relativistic effective core potentials ECP-SBKJC.<sup>12</sup> All stationary points were characterized by calculation of Hessian matrices. In all cases no imaginary frequencies were found, which corresponds to local minima. Atomic partial charges were calculated using Hirshfeld's method.<sup>13</sup> All calculations have been performed using the "PRIRODA" program.<sup>14</sup> This approach and program have been successfully used by us earlier in the study of the structures and reactivities of organometallic betaines, compounds with multiple bonds R<sub>2</sub>M=X and heavier analogues of carbenes R<sub>2</sub>M: (M = Si, Ge, Sn; X = CR<sub>2</sub>, O, S, NR, Se; R = Alk, Ar).<sup>15</sup>

Although all calculations were performed for isolated molecules in the gas phase, calculated geometries **1a** and **2a** reproduced reasonably well the general features of **1** and **2** geometries in the crystalline state (Tables 3, 4; Figure 3). Rather large deviations from X-ray data for **1a** and **2a** were found, as expected for the relatively

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(10) (a) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029. (b) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

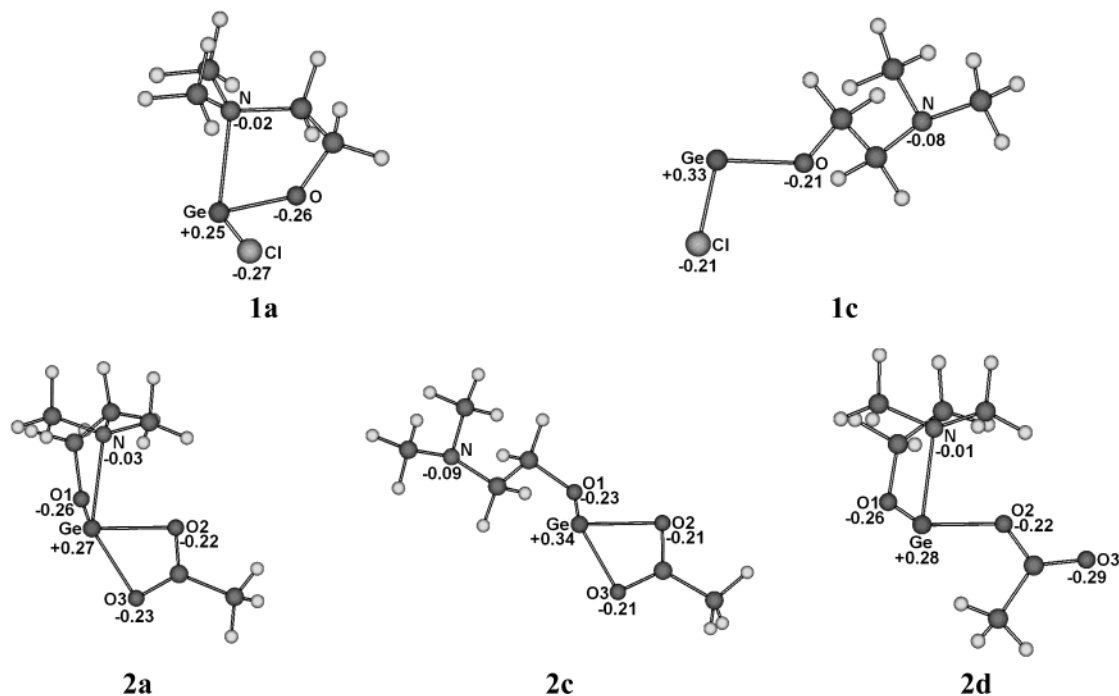
(11) Laikov, D. N. Ph.D. Dissertation, Moscow State University, Moscow, 2000.

(12) (a) Stevens, W. J.; Basch, H.; Krauss, M. J. *J. Chem. Phys.* **1984**, *81*, 6026. (b) Stevens, W. J.; Krauss, M. S.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 2. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.

(13) Hirshfeld, F. L. *Theor. Chim. Acta (Berlin)* **1977**, *44*, 129.

(14) Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151.

(15) (a) Nechaev, M. S.; Borisova, I. V.; Zemlyansky, N. N.; Laikov, D. N.; Ustynyuk, Yu. A. *Russ. Chem. Bull.* **2000**, *49*, 1823. (b) Borisova, I. V.; Zemlyansky, N. N.; Khrustalev, V. N.; Kuznetsova, M. G.; Ustynyuk, Yu. A.; Nechaev, M. S. *Russ. Chem. Bull.* **2001**, *50*, 1679. (c) Ustynyuk, Yu. A.; Nechaev, M. S.; Laikov, D. N.; Borisova, I. V.; Zemlyansky, N. N.; Chernyshev, E. A. *Russ. Chem. Bull.* **2001**, *50*, 771. (d) Borisova, I. V.; Nechaev, M. S.; Khrustalev, V. N.; Zemlyansky, N. N.; Ustynyuk, Yu. A. *Russ. Chem. Bull.* **2002**, *51*, 721.



**Figure 3.** Calculated molecular structures of **1a**, **1c**, **2a**, **2c**, and **2d** (numbers are calculated Hirshfeld's partial atomic charges).

**Table 4.** Calculated Geometry Parameters of Molecules **2a–d** (interatomic distances in Å, valence angles in deg, deviations from X-ray data in parentheses)

	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>2d</b>
Ge–O <sub>1</sub>	1.846 (+0.014)	1.850 (+0.018)	1.803	1.843
Ge–O <sub>2</sub>	2.077 (+0.139)	1.995 (+0.057)	2.090	1.925
Ge–N	2.389 (+0.281)	2.108 <sup>a</sup> (0.000)	5.097	2.211
Ge–O <sub>3</sub>	2.288 (–0.465)	2.753 <sup>a</sup> (0.000)	2.096	4.072
O <sub>1</sub> –Ge–O <sub>2</sub>	95.9 (–1.2)	98.0 (+0.9)	93.6	99.23
N–Ge–O <sub>2</sub>	83.2 (–3.7)	84.3 (–2.6)		84.2
N–Ge–O <sub>1</sub>	81.2 (–3.6)	83.5 (–1.3)		82.6

<sup>a</sup> Parameter fixed at the X-ray value in optimization.

weak Ge–N coordination bonds (+0.159 Å in **1** and +0.281 Å in **2**) and Ge–O<sub>3</sub> distance (–0.465 Å in **2**). The acetate group in isolated **2a** is bonded to the germanium atom as an unsymmetrical  $\eta^2$ -ligand, whereas in crystal **2** it clearly has  $\eta^1$ -coordination. To elucidate the reason for these deviations, we optimized the geometries of the structures **1b** and **2b**, in which the Ge–N and Ge–O<sub>3</sub> distances were fixed at the X-ray values. It was found that related energies of **1b** and **2b** differ from the corresponding values for **1a** and **2a** only by +1.7 and +2.9 kcal/mol, respectively (Table 5). This means that the potential energy surfaces (PES) of **1** and **2** in the region of minima are so flat that differences in calculated and X-ray structures of **1** and **2** are most probably due to crystal-packing effects.

The local minima that exist on the potential energy surfaces (PES) of **1** and **2** corresponded to isomeric structures **1c**, **2c**, and **2d**, in which Ge–N (structure **c**) or Ge–O<sub>3</sub> (structure **d**) coordination bonds are broken (Figure 3). Rupture of the Ge–N coordination bond in

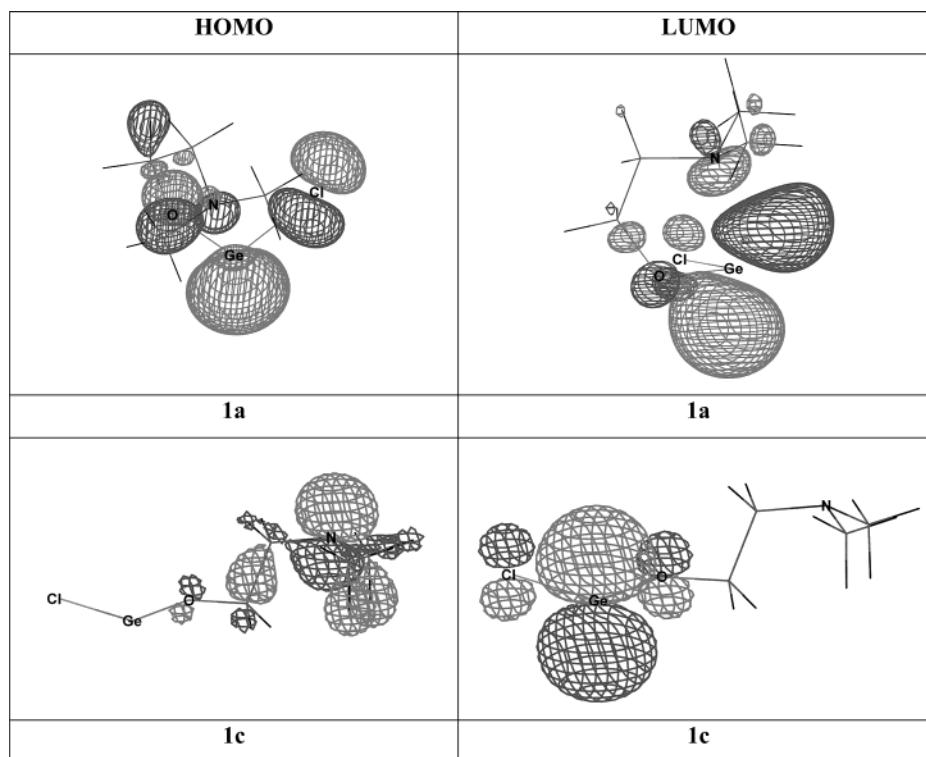
**Table 5.** Calculated Energies  $E$ ,  $E^0 = E + \text{ZPE}$  (au), and Related Energies  $\Delta E^0$  (kcal/mol) of Molecules **1a–c** and **2a–d**

molecule	$E$	$E^0$	$\Delta E^0$
<b>1a</b>	–73.47999	–73.33793	0.0
<b>1b</b>	–73.47759	–73.33517	+1.7
<b>1c</b>	–73.45257	–73.31251	+16.0
<b>2a</b>	–103.73236	–103.54260	0.0
<b>2b</b>	–103.72861	–103.53804	+2.9
<b>2c</b>	–103.71437	–103.52581	+10.5
<b>2d</b>	–103.72372	–103.53333	+5.8

**1a**, i.e., transition **1a** → **1c**, is related to the consumption of 16.0 kcal/mol (Table 5). In **1c** the bond lengths Ge–O and Ge–Cl and valence angle O–Ge–Cl are reduced with respect to **1a** (Table 3).

Rupture of the Ge–N coordination bond in **2a** results in the formation of isomer **2c** (Figure 3), which lies 10.5 kcal/mol higher in energy than **2a** (Table 5). The energy consumption for breaking the Ge–N bond in this case is partially compensated by strengthening of the coordination with the acetate ligand, which is manifested in the significant shortening of the Ge–O<sub>3</sub> distance in comparison with **2a**. The acetate  $\eta^2$ -coordination in **2c** becomes almost symmetrical; the Ge–O<sub>2</sub> and Ge–O<sub>3</sub> bonds differ only by 0.006 Å (Table 4). Rupture of the Ge–O<sub>3</sub> bond in **2a**, i.e., transition **2a** → **2d**, is associated with consumption of only 5.8 kcal/mol and accompanied by considerable shortening of the Ge–N bond in **2d**.

Population analysis shows that the HOMO in **1a**, **2a**, and **2d** are localized on the metal atoms and occupied by a lone electron pair (LEP) as shown for **1a** (Figure 4). In isomers **c** the HOMOs are localized on the nitrogen atoms of the NMe<sub>2</sub> groups, which are not included in the coordination. The LUMOs in **1a**, **1c**, **2c**, and **2d** are mainly localized on the germanium atoms and represented by a large contribution of the 4p<sub>z</sub> orbital of Ge and minor contributions of N and O atoms. The LUMO in **2a** is localized on the acetate ligand.



**Figure 4.** Shape of frontier molecular orbitals (HOMO and LUMO) in **1a** and **1c**.

**Table 6. Frontier Orbital Energies (eV) of 1a,c and 2a,c,d**

orbital	1a	1c	2a	2c	2d
LUMO	-1.27	-3.06	-0.79	-1.64	-1.28
HOMO	-5.66 <sup>a</sup>	-4.93	-5.13 <sup>a</sup>	-4.62	-5.38
HOMO-1	-6.06	-6.55 <sup>a</sup>	-5.93	-6.09 <sup>a</sup>	-5.82 <sup>a</sup>

<sup>a</sup> Lone electron pair on Ge atom.

The energies of molecular orbitals of LEP of metal atoms decrease in the order **2a** > **1a** > **2d** > **2c** > **1c** (Table 6). The loss of coordination at the Ge atom results in the lowering of LEP energy. We can conclude from the data presented that germylene **2** should be more nucleophilic than **1**.

Calculated charge distributions in isomers **1(2)a**, **b**, **c**, **d** (Figure 3) show an increase of the positive charge on the Ge atom and negative charge on the N atom with the rupture of the Ge–N coordination bonds (transitions **1(2)a** → **1(2)c**). Transition **2a** → **2d** leads to an increase of the negative charge on the O(3) atom. Changes in charges on the O(1) and O(2) atoms are insignificant.

### Conclusion

Data presented above show that one coordination Ge←N bond and two electronegative groups at the Ge(II) atom provide enough stabilization to make possible the existence of monomeric Ge(II) organic derivatives without steric protection of the Ge atom by bulky substituents. This fact opens new opportunities in the synthesis of stable, monomeric germylenes and related compounds.

### Experimental Section

**General Procedures.** All manipulations were carried out under purified argon atmosphere using standard Schlenk and high-vacuum-line techniques. Ge(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>,<sup>3b</sup> Et<sub>3</sub>–

GeOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>,<sup>3b</sup> GeCl<sub>2</sub>·dioxane,<sup>16</sup> Et<sub>3</sub>SnOAc,<sup>17</sup> Ge(SBu)<sub>2</sub>,<sup>5</sup> and Me<sub>3</sub>SiSBu<sup>18</sup> were synthesized as described earlier. The solvents commercially available were purified by conventional methods and distilled immediately prior to use. NMR spectra were recorded at 360.13 and 300.13 MHz (<sup>1</sup>H) and 90.55 and 75.47 MHz (<sup>13</sup>C) for the samples in CD<sub>2</sub>Cl<sub>2</sub> and THF-*d*<sub>6</sub>. Chemical shifts are relative to SiMe<sub>4</sub> for H, C or indirectly referenced to TMS via the solvent signals. Accuracy of the coupling constant determination is ±0.1 Hz; accuracy of the chemical shift measurements is ±0.01 ppm (<sup>1</sup>H) and ±0.05 ppm (<sup>13</sup>C).

**ClGeOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (1).** A solution of Ge(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (0.6729 g, 2.71 mmol) in THF (10 mL) was added at room temperature to a stirred solution of GeCl<sub>2</sub>·D (4) (0.6268 g, 2.71 mmol) in THF (30 mL). The mixture was refluxed for 0.5 h. The filtered solution was reduced in volume to about 10 cm<sup>3</sup> and kept at –12 °C to give white crystals of **1**. Yield: 0.79 g (74%); mp 74–75 °C with dec (in a sealed capillary). Anal. Calcd for C<sub>4</sub>H<sub>10</sub>ClGeNO: C, 24.49; H, 5.14; Cl, 18.07. Found: C, 25.05; H, 5.23. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.69 (s, 6H, Me<sub>2</sub>N, 2.96 (b, t, 2H, CH<sub>2</sub>N), 4.23 (t, 2H, CH<sub>2</sub>O, <sup>3</sup>J = 5.7 Hz). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 45.88 (Me<sub>2</sub>N), 61.32 (CH<sub>2</sub>N), 67.8 (br, CH<sub>2</sub>O).

**AcOGGeOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (2).** Et<sub>3</sub>GeOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (3.6355 g, 14.68 mmol) was added at room temperature to a stirred solution of Ge(OAc)<sub>2</sub> (5) (2.81 g, 14.74 mmol) in THF (50 mL). The mixture was refluxed for 0.5 h. The solvent was removed in vacuo, the residue was evaporated at 50–60 °C/1 Torr, and the volatiles were condensed in a liquid nitrogen cooled trap. The resulting crude product was crystallized from THF/Et<sub>2</sub>O at –12 °C, giving **2** as white crystals. Yield: 2.15 g (66.8%); mp 67–68 °C (in a sealed capillary). Anal. Calcd for C<sub>6</sub>H<sub>13</sub>GeNO<sub>3</sub>: C, 32.79; H, 5.96. Found: C, 33.04; H, 6.12. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.93 (s, 3H, MeCO), 2.63 (s, 6H, Me<sub>2</sub>N), 2.84 (b, t, 2H, CH<sub>2</sub>N), 4.11 (t, 2H, CH<sub>2</sub>O, <sup>3</sup>J = 5.7 Hz). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 23.36 (MeCO), 44.19 (Me<sub>2</sub>N), 60.50 (CH<sub>2</sub>N), 64.60 (b, CH<sub>2</sub>O), 177.01 (C=O).

(16) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(17) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, 60, 459.

(18) Schmeisser, M.; Miller, H. *Angew. Chem.* **1957**, 69, 781.

**Ge(OAc)<sub>2</sub> (5).** (a) A solution of Et<sub>3</sub>SnOAc (10.26 g, 38.8 mmol) in Et<sub>2</sub>O/THF (50 mL) (in ratio 1:1) was added at room temperature to a stirred solution of GeCl<sub>2</sub>·D (4) (4.49 g, 19.4 mmol) in Et<sub>2</sub>O/THF (50 mL). After 30 min the solvent was removed by distillation at normal pressure until the vapor temperature increased to 70 °C. The residue was evaporated at 100 °C/1 Torr. The volatiles were condensed in a liquid nitrogen cooled trap. The oil residue was treated with ether, and the precipitate was filtered off, washed, and dried in vacuo. The yield of **5** as a white solids is 2.22 g (60%); mp 109–110 °C (in a sealed capillary). Anal. Calcd for C<sub>4</sub>H<sub>6</sub>GeO<sub>4</sub>: C, 25.20; H, 3.17. Found: C, 25.43; H, 3.09. Distillation of liquid collected in the trap gave 8.21 g (87.8%) of Et<sub>3</sub>SnCl. **5**: <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N) δ 2.03 (Me, <sup>1</sup>J<sub>CH</sub> = 128.1 Hz); <sup>13</sup>C NMR (C<sub>5</sub>D<sub>5</sub>N) δ 23.24 (Me); 177.24 (C=O).

(b) A solution of Et<sub>3</sub>SnOAc (6.88 g, 26 mmol) in THF (50 mL) was added at room temperature to a stirred solution of Ge(SBu)<sub>2</sub> (3.255 g, 13 mmol) in THF (20 mL). After 20 min stirring the reaction mixture was worked up as in procedure (a). The yield of **5** is 6.1 g (90%), mp 109–110 °C (in a sealed capillary). A mixture of the probe and the substance obtained by procedure (a) melts without decomposition.

**Reaction of Ge(OAc)<sub>2</sub> with Me<sub>3</sub>SiSBu.** Solid Ge(OAc)<sub>2</sub> (0.6108 g, 3.21 mmol) was dissolved in Me<sub>3</sub>SiSBu (1.86 g, 11.5 mmol). This operation is exothermic. After that the reaction mixture was heated to boiling for 15 min and volatiles were evaporated in vacuo at 10<sup>-3</sup> Torr. Ge(SBu)<sub>2</sub> (0.802 g, 99.9%) was obtained as a residue. NMR spectra of the substance were identical to those of the compound described previously.<sup>5</sup>

**X-ray Structure Determination.** Data were collected on a Bruker SMART CCD 1000 diffractometer and corrected for Lorentz and polarization effects and for absorption.<sup>19</sup> For details see Table 2. The structures were determined by direct

methods and by full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms in **1** were objectively localized in the difference Fourier map and refined isotropically. The hydrogen atoms in **2** were placed in calculated positions and refined in a riding model with fixed thermal parameters. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.0) program.<sup>20</sup> Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 206357 and 206358, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

**Acknowledgment.** This work was financially supported by the Russian Foundation for Basic Research (Projects Nos. 00-03-32889a, 00-03-32807a, 00-15-97359) and by the Russian Academy of Sciences based on the subprogram "Theoretical and experimental study of chemical bonding and mechanisms of chemical reactions and processes". We thank Dr. M. G. Kuznetsova for providing us with multinuclear NMR measurements.

**Supporting Information Available:** Tables of atom coordinates, bond lengths and angles, and anisotropic displacement parameters for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM034068+

(19) Sheldrick, G. M. *SADABS*, V2.01; Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998.

(20) Sheldrick, G. M. *SHELXTL*, V5.10; Bruker AXS Inc.: Madison, WI 53719, 1997.