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New Stable Germylenes, Stannylenes, and Related Compounds. 1. Stable Germanium(II) and Tin(II) Compounds $M(OCH_2CH_2NMe_2)_2$ (M = Ge, Sn) with Intramolecular Coordination Metal−Nitrogen Bonds. Synthesis and Structure

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New stable monomeric germanium(II) and tin(II) compounds $M(OCH_2CH_2NMe_2)_2$ (M = Ge (**1**); M = Sn (**2**)), stabilized by two intramolecular coordination $M \leftarrow N$ bonds and containing no bulky groups on the metal atoms, were synthesized. The molecular and crystal structures of these compounds, and that of the previously synthesized compound $(ArO)_2Sn$ (**3**; Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$), were determined by X-ray diffraction analysis. The electronic structures of **1** and **2** were studied by the DFT method.

Introduction

In the past decade, considerable progress has been made in the chemistry of stable organic derivatives of divalent germanium and tin.[1] Compounds of the type R_2M, containing hydrocarbon groups on the metal atoms, are heavier congeners of carbenes (the true germylenes and stannylenes). Their kinetic stability afforded by bulky substituents R rests exclusively on steric factors. Another and rather special group of divalent species consists of the sterically hindered compounds $(RX)_2M$, in which the organic substituent R is attached to the element through an electronegative heteroatom (X = O, S, N).[1b,2] In all of these compounds the frontier orbitals are strongly perturbed by interactions with the orbitals of lone electron pairs of the heteroatoms. Accordingly, their structures and reactivities are quite unique and different from those of intrinsic singlet carbene analogues. Lappert and coworkers were the first to prepare and structurally characterize the sterically stabilized, monomeric aryloxy compounds $(ArO)_2M$ (M = Ge, Sn; Ar = C_6H_2Me-4-*t*-Bu_2-2,6).[2a] The diverse alkoxy derivatives $(RO)_2M$ (M = Ge, Sn) also have been described; depending on the size of the RO groups, they are usually found to be cyclodimeric (R = *t*-Bu)[3] or oligomeric (R = Me, Et, *i*-Pr),[1b] associated through intermolecular $M \leftarrow O$ coordination, and, less frequently, monomeric (R = *t*-Bu_3C).[2c] Furthermore, it is noteworthy that the series of divalent compounds of group 14 elements R_2M and $(RX)_2M$ have been thermodynamically stabilized in monomeric form by $M \leftarrow Y$ (Y = N, O) intramolecular coordination of donor atom substituted sidearms of the bulky groups R. In the chemistry of germanium(II) and tin(II) this is documented by various stable aryl derivatives with one

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or two intramolecular coordination bonds[4] and by some examples of aryloxy compounds.[5] It is doubtless of interest to obtain more information on the relative contributions of the different factors (thermodynamic and kinetic) to the stabilization of germanium(II) and tin(II) compounds. Herein we report the synthesis and structures of stable, sterically nonhindered bis[2-(dimethylamino)ethoxy]germanium and -tin $\mathrm{M(OCH_2CH_2NMe_2)_2}$ (M = Ge (**1**); M = Sn (**2**)) compounds with intramolecular coordination M←N bonds. The electronic and molecular structures of these compounds is also analyzed by density functional theory, and the M←N binding energies are calculated. The X-ray study of the previously synthesized bis{2,4,6-tris[(dimethylamino)methyl]phenoxy}tin (**3**)[5c−f] also is reported.

Results and Discussion

Synthesis of Bis[2-(dimethylamino)ethoxy]germanium (1) and -tin (2). Bis[2-(dimethylamino)ethoxy]germanium (**1**) and -tin (**2**) were prepared by two methods. The redistribution of the functional groups between the divalent species $\mathrm{MCl_2}$ and $\mathrm{Et_3MOCH_2CH_2NMe_2}$ (M = Ge, Sn) readily occurs at room temperature in THF or diethyl ether (eq 1), giving moderate yields of compounds **1** and **2** as white, crystalline solids, which are soluble in standard organic solvents, stable under anaerobic conditions, and easily sublimed in vacuo.

$$\mathrm{MCl_2 + 2Et_3M'OCH_2CH_2NMe_2 \rightarrow \underset{\mathbf{1,\,2}}{\ddot{M}(OCH_2CH_2NMe_2)_2} + 2Et_3M'Cl} \quad (1)$$

1: $\mathrm{MCl_2 = GeCl_2{\cdot}(dioxane),\ M' = Ge}$

2: $\mathrm{M,\ M' = Sn}$

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−3

	1[a]	**2**[b]	**3**
M−O	1.868(1), 1.864(1); 1.861(1), 1.870(1)	2.056(2)	2.071(2), 2.073(2)
M←N	2.329(2), 2.337(2); 2.324(2), 2.346(2)	2.458(2)	2.427(3), 2.478(3)
O−M−O	98.79(6); 98.91(7)	96.52(11)	91.89(9)
N→M←N	156.38(6); 156.11(6)	145.78(9)	156.56(8)
O−M←N	80.48(6), 80.78(6), 83.89(6), 84.21(6); 80.22(6), 81.00(6), 83.85(6), 84.00(6)	76.71(6), 80.68(6)	80.75(8), 81.18(9), 81.55(9), 84.10(8)

[a] For the two independent molecules. [b] The molecule occupies a special position on the 2-fold axis (C_2).

A more convenient method for the synthesis of **1** and **2** is the alcoholysis of Lappert's metal amides $\mathrm{M[N(SiMe_3)_2]_2}$ (M = Ge, Sn)[2e] by (dimethylamino)ethanol, which occurs rapidly and in almost quantitative yield (eq 2). This method has been used previously for the

$$\mathrm{\ddot{M}(NSiMe_3)_2 + 2HOCH_2CH_2NMe_2 \rightarrow \underset{\mathbf{1,\,2}}{\ddot{M}(OCH_2CH_2NMe_2)_2} + 2HN(SiMe_3)_2} \quad (2)$$

preparation of bis{2,4,6-tris[(dimethylamino)methyl]phenoxy}tin (**3**) and its germanium and lead analogues.[5c] In the ^{1}H NMR spectra of compounds **1** and **2**, recorded at room temperature in benzene-d_6 or toluene-d_8 solutions, the $\mathrm{OCH_2CH_2N}$ signals appear as triplets and those of the methyl groups on the nitrogen atoms as singlets. The signals in the spectrum of **1** are noticeably broadened, suggesting that a fairly rapid process occurs in solution, during which the M←N coordination bonds open and close (see below). The study of the dynamic NMR spectra over a wide temperature interval is now in progress.

Molecular and Crystal Structures of Bis[2-(dimethylamino)ethoxy]germanium (1) and -tin (2). The X-ray diffraction study showed that compounds **1** and **2** are monomers. These are the first structurally characterized monomeric germanium(II) and tin(II) compounds stabilized by only two intramolecular Ge←N coordination bonds in the absence of steric shielding of the metal atoms (Figures 1 and 2). The $\mathrm{M^{II}}$←N bond lengths are 2.329(2), 2.337(2) Å and 2.324(2), 2.346(2) Å for two independent molecules of **1** and 2.458(2) Å for **2** (Table 1). The $\mathrm{Ge^{II}}$−N bond lengths for **1** are considerably larger than the lengths of all the previously known $\mathrm{Ge^{II}}$←N coordination bonds[6] (except for the diazogermylene $\mathrm{ArGeC(N_2)SiMe_3}$ [Ar = 2,6-($\mathrm{iPr_2NCH_2)_2}$-$\mathrm{C_6H_3}$]).[7] In contrast, the $\mathrm{Sn^{II}}$← N bond lengths in **2** are much shorter than the previously reported lengths of axial $\mathrm{Sn^{II}}$←N bonds (range of values 2.516(3)−2.660(3) Å).[4b,c,5a,8a,b] The $\mathrm{M^{II}}$−O bond lengths (1.864(1), 1.868(1), and 1.861(1), 1.870(1) Å for two independent molecules of **1** and 2.056(2) Å for **2** (Table 1)) are typical

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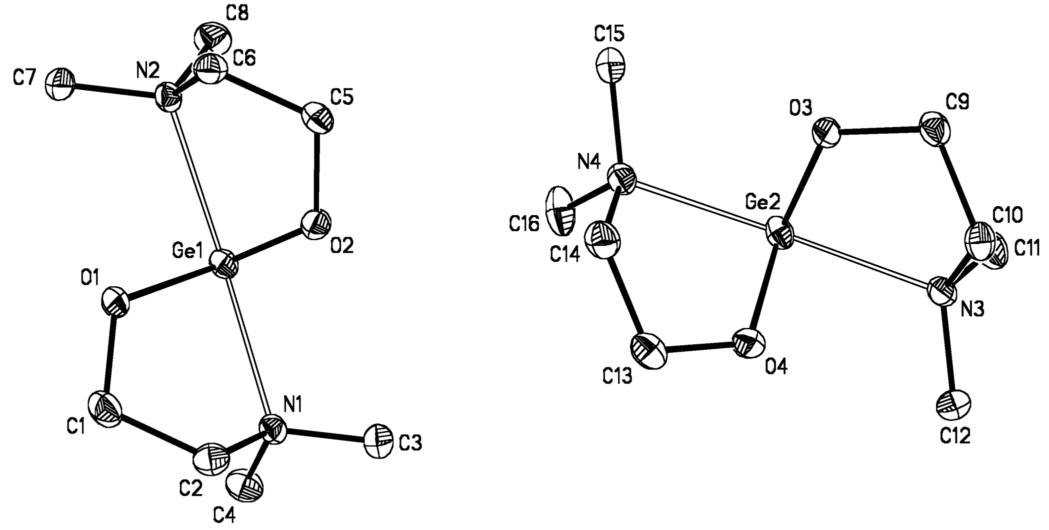

Figure 1. Molecular structure of compound **1**. The two crystallographically independent molecules presenting chiral enantiomers are shown (ellipsoids are drawn at the 50% probability level).

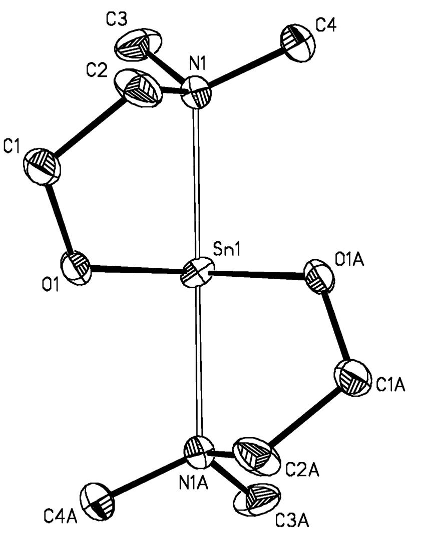

Figure 2. Molecular structure of compound **2** (ellipsoids are drawn at the 50% probability level).

M−O distances for M(OR)$_2$ compounds (range of values for Ge−O bond lengths[2b,4e,9a] 1.765(6)−1.878(4) Å; range of values for Sn−O bond lengths[2b,5a,b,f−i,9a,b] 1.956(7)−2.202(6) Å). The O−M−O bond angles (98.79(6) and 98.91(7)° for two independent molecules of **1** and 96.52(11)° for **2** (Table 1)) are somewhat greater than that observed for the sterically hindered compound **3** (see below), indicating the absence of steric strain. The central M(II) atom in **1** and **2** has a distorted-trigonal-bipyramidal configuration (Table 1) with a lone electron pair in the equatorial position. It occupies a spiro position between two five-membered heterocycles in the envelope conformation.

Both compounds **1** and **2** are chiral. The enantiomers cocrystallize in noncentrosymmetric space groups $P2_12_12_1$ (**1**) and $Aba2$ (**2**). The molecular packings in crystals of **1** and **2** are layered along the direction [001]. Note that, due to the equality of the M^{II}←N bonds, molecules **1** and **2** (unlike molecule **3**; see below), have intrinsic symmetry C_2, and the layers formed by them have symmetry *pba*2. However, the symmetry of the layers is retained only in the case of **2**, in the crystal of which the layers are congruently imposed on each other (with retention of the polar axis). In the crystal structure of **1**, the layers are incongruently imposed on each other with the turning at 180°; the polar axis is lost due to that.

A wide set of pseudo-symmetric operations, which are manifested as absences of the corresponding reflections (see the Supporting Information), takes place in crystals **1** and **2** due to the characteristic shifts of the layers relative to each other. The crystal structures of compounds **1** and **2** represent one more striking example for the layer-in-layer three-dimensional packing of molecules described recently by Britton[10] determining the appearance of different pseudo-symmetric operations in crystals of compounds, which have, as a rule, intrinsic symmetry elements.

The intramolecular Sn←N coordination bonds, which in compounds **1**−**3** result in the appearance of chirality and favor crystallization of compounds **1** and **2** in noncentrosymmetric space groups, could be used as an important factor in the design of new materials with some important physical properties (piezo- and segnetoelectrics, nonlinear optical materials, etc.).

Molecular Structure of Bis{2,4,6-tris[(dimethylamino)methyl]phenoxy}tin (3). The X-ray structural study of **3** shows that the tin atom has a distorted-trigonal-bipyramidal coordination, showing unambiguously that the stabilizing effect of the aryloxy ligand in the compound is due to the formation of two stable intramolecular Sn←N coordination bonds. The lone electron pair and the oxygen atoms occupy the equatorial positions, and the nitrogen atoms are in the axial positions. As for **2**, the Sn←N bond lengths (2.427(3) and 2.478(3) Å; Table 1 and Figure 3) are much shorter than those reported for analogous bonds; however, in contrast to that observed for **2** these two Sn−N bonds have significantly different lengths, although from the formal point of view these bonds should be chemically equiva-

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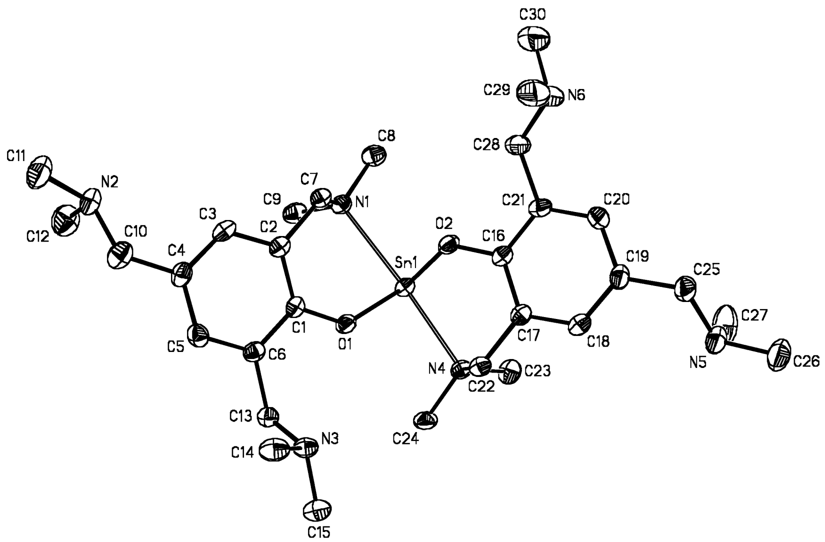
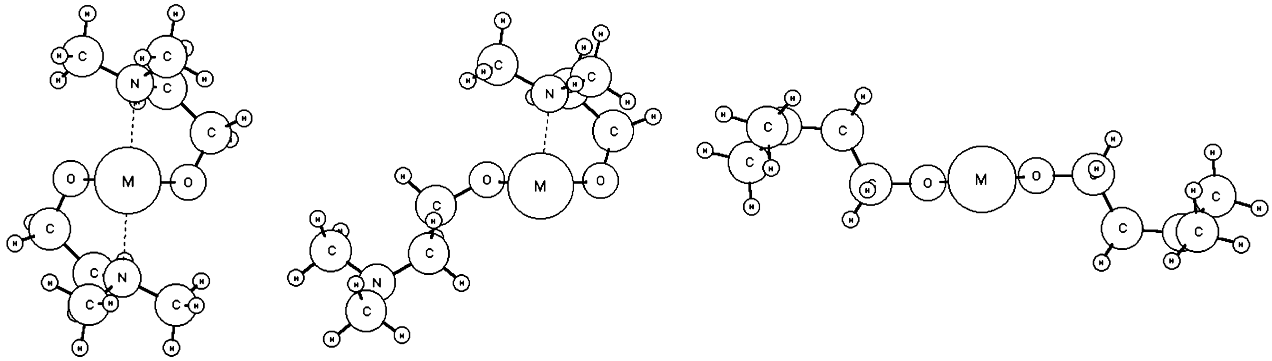


Figure 3. Molecular structure of compound **3** (ellipsoids are drawn at the 50% probability level).



1, 2 **1a, 2a** **1b, 2b**

Figure 4. DFT calculated structures of molecules **1**, **2**, **1a**, **2a**, **1b**, and **2b**.

lent. A search of the Cambridge Crystallographic Database[6] revealed that such nonequivalency is characteristic of tin(II) compounds with Sn−N donor−acceptor bonds; however, the bond lengths in them equalize if the lone electron pair of the Sn(II) atom is involved in coordination with acceptors such as BH_3[11a] or in binding to transition metals.[4b,c,11b,c] The additional interactions of both types have no substantial effect on the coordination Sn←N bond lengths (range of values 2.456(2)−2.608(4) Å, mean value 2.543 Å). The Sn^{II}−O bond lengths (2.071(2) and 2.073(2) Å; Table 1) in **3** compare well with the range found in the previously studied alkoxy- and aryloxytin(II) compounds[2b,5a,b,f−i,9a,b] (range of values 1.956(7)−2.202(6) Å). The O−Sn−O bond angle 91.89(9)° (Table 1) is close to 90° due to the presence of two intramolecular coordination bonds and steric effects.

Compound **3** is chiral, as are **1** and **2**. Both of its enantiomers are cocrystallized in the centrosymmetric space group $P2_1/n$. The packing of molecules **3** in a crystal is stacked along the y axis. The molecules are arranged at their van der Waals distances.

Study of the Structure of Bis[2-(dimethylamino)ethoxy]germanium (1) and -tin (2) by the DFT Method. The structures of **1** and **2** were studied by the density functional (PB E functional, ECP for innermost electrons and TZ2p basis set for valence shell) using the PRIRODA program.[12] This approach and this program have been used earlier by us successfully to study the structure of organoelement betaines, compounds with multiple bonds $R_2M{=}X$ and R_2M: (M = Si, Ge, Sn; X = CR_2, O, S, NR, Se).[13a−d]

The calculations satisfactorily reproduce the structure and geometric parameters of molecules **1** and **2** (Table 2, Figure 4). On the potential energy surfaces of **1** and **2** we also found local minima for isomeric structures **1a**, **1b**, **2a**, and **2b**, in which one (structures **a**) and both coordination bonds (structures **b**) are open. Opening of the first coordination M←N bond (transitions **1** → **1a** and **2** → **2b**) requires 7.6 and 10.2 kcal/mol for **1** and **2**,

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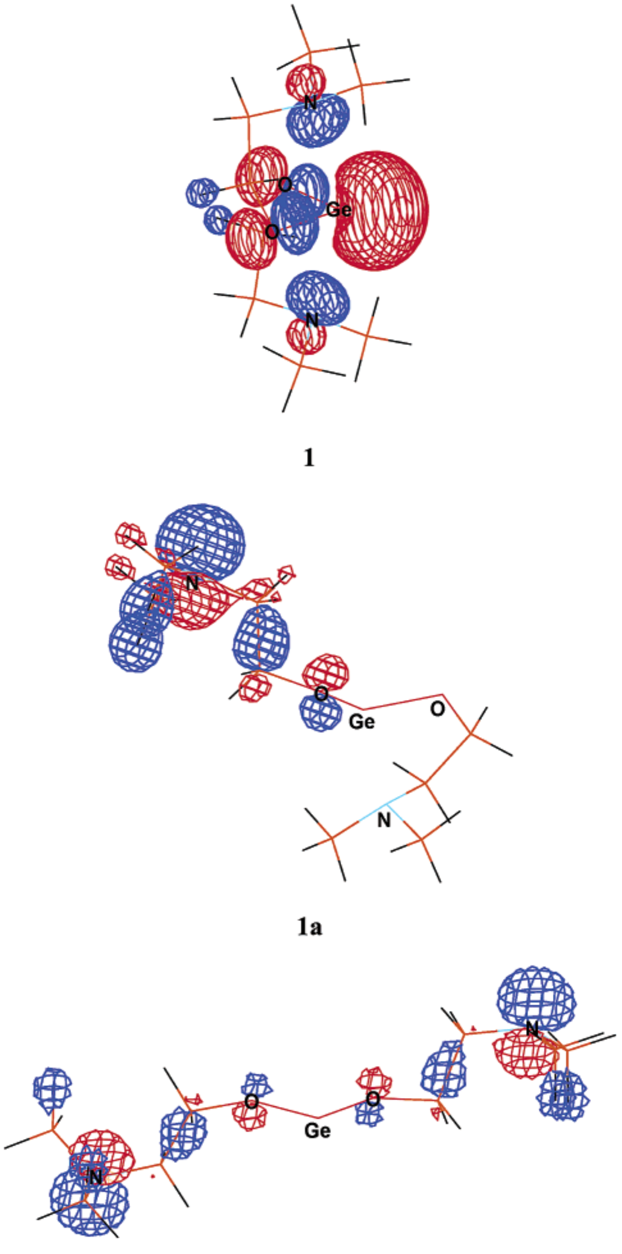
Table 2. Geometry Parameters of Molecules 1, 1a, 1b, 2, 2a, and 2b According to DFT Calculations[a]

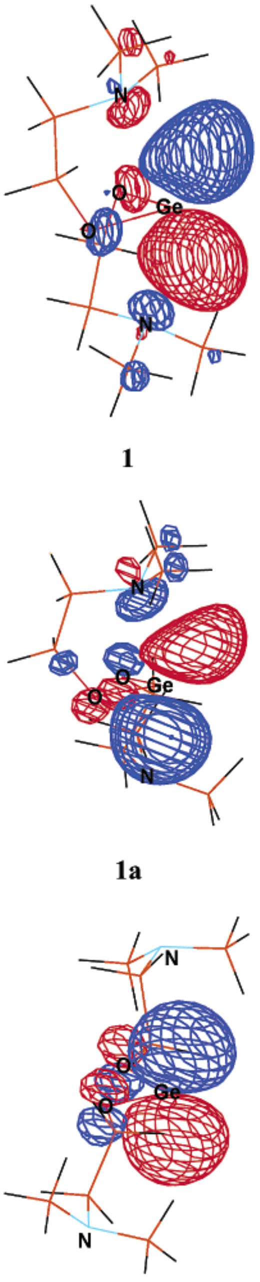
param	1	2	1a	2a	1b	2b
M−O1	1.896	2.082	1.844	2.035	1.799	1.989
M−O2	1.896	2.082	1.861	2.048	1.799	1.989
M−N1	2.428	2.556	2.280	2.435	5.081	5.222
M−N2	2.428	2.556	5.097	5.420	5.081	5.222
O1−M−O2	98.4	96.3	99.0	97.8	94.3	91.9
O1−M−N1	80.1	76.0	80.7	76.5		

[a] Internuclear distances in Å, and valence angles in deg.



1b

Figure 5. HOMO's in the molecules **1**, **1a**, and **1b** (the HOMO's in **2**, **2a**, and **2b** have similar shapes).



1b

Figure 6. LUMO in the molecules **1**, **1a**, and **1b** (the LUMO's in **2**, **2a**, and **2b** have similar shapes).

respectively, and is accompanied by considerable shortening of the second bond (by 0.148 Å in **1a** and 0,121 Å in **2 a**). The lengths of both M−O bonds are simultaneously shortened, and the M−O bonds in the chelate cycle remain shorter. The cleavage of the second chelate cycle (transitions **a** → **b**) requires 11.6 kcal/mol in the case of **1** and 16.4 kcal/mol in the case of **2**. Thus, as could be expected, the coordination bonds in isomers **1a** and **2a** are stronger than those in isomers **1** and **2**. Analysis of the populations shows that the HOMO's in **1** and **2** are localized on the metal atoms and occupied by a lone electron pair, as shown for **1** (Figure 5). In isomers **a** the HOMO's are localized on the nitrogen atoms of the NMe_2 groups, which are not involved in coordination, and in isomers **b** they are localized on the oxygen and nitrogen atoms. The energies of the molecular orbitals of the lone electron pair of the metal atoms regularly decrease in the order **1** (**2**) > **1a** (**2a**) > **1b** (**2b**) (Table 3). The LUMO's in all isomers of **1** and **2** are localized on the metal atoms (Figure 6). In **b** isomers they represent pure $4p_z$ and $5p_z$ atomic orbitals of germanium and tin in **1b** and **2b**, respectively. In isomers **1** (**2**) and **1a** (**2a**) the LUMO's contain additional

Table 3. Frontier Orbital Energies (eV) for 1, 1a, 1b, 2, 2a, and 2b

orbital	1	1a	1b	2	2a	2b
LUMO	−0.11	−0.88	−2.36	−0.43	−1.46	−2.72
HOMO	−4.36[a]	−4.33	−4.64	−4.57[a]	−4.76	−4.57
HOMO − 1	−5.00	−5.18[a]	−4.70	−4.91	−5.25[a]	−4.65
HOMO − 2	−5.52	−5.78	−6.03[a]	−5.42	−5.41	−5.86[a]

[a] Lone electron pair (LEP) orbital localized on metal atom.

Table 4. Hirtschfeld Atomic Charges (au) in Molecules 1, 1a, 1b, 2, 2a, and 2b

atom	1	1a	1b	2	2a	2b
M	+0.22	+0.25	+0.32	+0.29	+0.35	+0.42
O1	−0.26	−0.27	−0.22	−0.28	−0.29	−0.25
N1	−0.03	−0.02	−0.09	−0.04	−0.03	−0.09
O2	−0.26	−0.24	−0.22	−0.28	−0.27	−0.25
N2	−0.03	−0.09	−0.09	−0.04	−0.09	−0.09

contributions from the MO of nitrogen. The energies of the LUMO's also regularly decrease in the order **1** (**2**) > **1a** (**2a**) > **1b** (**2b**) (Table 3). It follows from the data presented for the energies of frontier orbitals that the reactivity of **1** and **2** in the series **1** (**2**) → **1a** (**2a**) → **1b** (**2b**) decreases with respect to electrophilic reactants but increases with respect to nucleophiles. Charge distribution in isomers **1** (**2**), **1a** (**2a**), and **1b** (**2b**) (Table 4) shows that positive charges on the metal atoms increase somewhat with opening of the coordination bonds in the series **2** (**3**) > **2a** (**3a**) > **2b** (**3b**), according to expectations. Changes in charges on the oxygen atoms are insignificant. The negative charge on the nitrogen atom increases when the coordination bond is cleaved.

Conclusion

These results show that two powerful stabilizing electronic effects such as the formation of the $M^{II} \leftarrow N$ coordination bonds and the σ-acceptor ability of the oxygen atoms in the alkoxy and aryloxy derivatives of divalent tin and germanium are sufficient to allow the existence of monomer species **1** and **2** at standard temperature and under anaerobic conditions without substantial steric shielding of the metal atoms. Other compounds of this type will be described elsewhere.

Experimental Section

General Procedures. All manipulations were carried out under a purified argon atmosphere using standard Schlenk and high-vacuum-line techniques. The commercially available solvents were purified by conventional methods and distilled immediately prior to use. Et_3GeOEt,[14] Et_3SnOMe,[15] $Ge[N(SiMe_3)_2]_2$,[5c] $Sn[N(SiMe_3)_2]_2$,[5c] and $GeCl_2 \cdot$(dioxane)[16] were prepared according to the procedures described in the literature. NMR spectra were recorded on a Bruker AM-360 NMR spectrometer at 360.134 MHz (^{1}H), 90.555 MHz (^{13}C), and 111.92 MHz (^{119}Sn) for the samples in C_6D_6, except where indicated. Chemical shifts are relative to $SiMe_4$ for H and C or indirectly referenced to TMS via the solvent signals and relative to $SnMe_4$ for ^{119}Sn. The accuracy of the coupling constant determination is ±0.1 Hz, and the accuracy of chemical shift measurements is ±0.01 ppm (^{1}H), ±0.05 ppm (^{13}C), and ±0.2 ppm (^{119}Sn).

[(Dimethylamino)ethoxy]triethylgermanium, $Et_3GeOCH_2CH_2NMe_2$. To a solution of ethoxytriethylgermanium (8.95 g, 43.7 mmol) in 10 mL of benzene was added a solution of (dimethylamino)ethanol (3.92 g, 44 mmol) in 5 mL of benzene. The mixture was heated at reflux for 2 h. After removal of the volatiles the colorless residue was distilled in vacuo to give $Et_3GeOCH_2CH_2NMe_2$. Yield: 6.9 g, 64%. Bp: 73−74 °C/1 Torr. $n_D^{20} = 1.4494$. ^{1}H NMR: δ 0.88 (q, 6H, $GeCH_2$-CH_3, $^3J_{HH} = 7.6$ Hz), 1.00 (t, 9H, $GeCH_2CH_3$, $^3J_{HH} = 7.6$ Hz), 2.18(s, 6H, NMe_2), 2.36 (t, 2H, NCH_2, $^3J_{HH} = 6.7$ Hz), 3.61 (t, 2H, OCH_2, $^3J_{HH} = 6.7$ Hz). Anal. Calcd for $C_{10}H_{25}GeNO$: C, 48.45; H, 10.16; N, 5.65. Found: C, 48.33; H, 10.09; N, 5.51.

[(Dimethylamino)ethoxy]triethyltin, $Et_3SnOCH_2CH_2NMe_2$. In a similar way the reaction of methoxytriethylstannane (13.44 g, 56.8 mmol) with (dimethylamino)ethanol (5.32 g, 59.8 mmol) afforded $Et_3SnOCH_2CH_2NMe_2$ as a colorless liquid. Yield: 11.68 g (70%). Bp: 88−89 °C/1 Torr. $n_D^{20} = 1.4838$. ^{1}H NMR: δ 0.79−1.1 m, 6H, $SnCH_2CH_3$), 1.1−1.43 (m, 9H, $SnCH_2CH_3$), 2.14 (s, 6H, Me_2N), 2.34 (t, 2H, CH_2N, $^3J_{HH} = 5.5$ Hz), 3.85 (t, br, 2H, CH_2O, $^3J_{HH} = 5.5$ Hz). ^{13}C NMR: δ 6.33 ($SnCH_2CH_3$, $^1J_{^{119/117}Sn} = 381.5/364.5$ Hz), 10.18 ($SnCH_2CH_3$, $^2J_{^{119/117}Sn} = 23.14$), 46.30 ($Me_2N$), 64.01 ($CH_2N$), 65.06 ($CH_2O$). Anal. Calcd for $C_{10}H_{25}NOSn$: C, 40.85; H, 8.57; N, 4.76. Found: C, 41.07; H, 8.52; N, 4.64.

Bis[(dimethylamino)ethoxy]germanium, $Ge(OCH_2CH_2NMe_2)_2$ (1). (a) The mixture of $Et_3GeOCH_2CH_2NMe_2$ (6.46 g, 26.1 mmol) and $GeCl_2 \cdot$(dioxane) (3.02 g, 13.0 mmol) in 40 mL of THF was kept at ambient temperature for 12 h. The solvent was removed by distillation until the vapor temperature reached 78 °C. Et_3GeCl from the residual viscous oil was distilled at 50−60 °C/1 Torr into a trap cooled by liquid nitrogen. The residue in the distillation flask after recrystallization from hexane at −12 °C gave **1** as white crystals. Yield: 2.23 g (69%). Mp: 67−68 °C. The substance can be purified additionally by sublimation at 70 °C/10^{-3} Torr. ^{1}H NMR: δ 2.22 (s, 12H, Me_2N), 2.38 (t, br, 4H, CH_2N, $^3J_{HH} = 5.2$ Hz), 4.14 (t, 4H, CH_2O, $^3J_{HH} = 5.6$ Hz). ^{13}C NMR: δ 43.48 (Me_2N), 60.41 (CH_2N), 63.08 (br, CH_2O). Because of the extremely high sensitivity of compound **1** to moisture and oxygen, a satisfactory elemental analysis was not obtained. A second distillation of the liquid collected in the trap gave 3.88 g (76%) of Et_3GeCl.

(b) A 0.75 g (8.4 mmol) portion of (dimethylamino)ethanol was added to 1.62 g (4.1 mmol) of bis[bis(trimethylsilyl)amino]germanium(II). The exothermic reaction was complete in several minutes. After that hexamethyldisilazane was removed in vacuo. The residue was recrystallized from hexane at −12 °C or sublimed at 70 °C/10^{-3} Torr. Yield: 1.01 g (98%). The melting point and NMR parameters of this product were identical with those described above.

Bis[(dimethylamino)ethoxy]tin, $Sn(OCH_2CH_2NMe_2)_2$ (2). (a) A mixture of $Et_3SnOCH_2CH_2NMe_2$ (5.56 g, 18.9 mmol) and $SnCl_2$ (1.77 g, 9.3 mmol) in 50 mL of ether was kept at ambient temperature for 12 h. After removal of the solvent by distillation (until the vapor temperature rose to 78 °C) Et_3SnCl from the residue was distilled at 50−60 °C/1 Torr and condensed in the trap cooled by liquid nitrogen. The solid residue in the distillation flask after recrystallization from hexane at −12 °C gave **2** as white crystals. Yield: 1.3 g (47%). Mp: 45−46 °C. **3** sublimes at 50−70 °C/10^{-3} Torr. Distillation of the liquid collected in the trap gave 4.3 g (95%) of Et_3SnCl. ^{1}H NMR ($C_6D_5CD_3$): δ 2.30 (s, 12H, Me_2N), 2.53 (t, 4H, CH_2N, $^3J_{HH} = 5.5$ Hz), 4.18 (t, 4H, CH_2O, $^3J_{HH} = 5.5$ Hz). ^{13}C NMR: δ 44.51 (Me_2N), 62.79 (CH_2N), 63.14 (CH_2O). ^{119}Sn NMR ($C_6D_5CD_3$): δ −309.9. Anal. Calcd for $C_8H_{20}N_2O_2Sn$: C, 32.58; H, 6.83; N, 9.50. Found: C, 32.24; H, 6.63; N, 9.40.

(b) (Dimethylamino)ethanol (1.39 g, 15.6 mmol) was added to bis[bis(trimethylsilyl)amino]tin(II) (3.39 g, 7.7 mmol). After the exothermic reaction was completed, hexamethyldisilazane was removed in vacuo. The residue was recrystallized from hexane at −12 °C or sublimed at 50−60 °C/10^{-3} Torr. Yield:

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Table 5. Crystallographic Data for 1−3

	1	**2**	**3**
empirical formula	$C_8H_{20}N_2O_2Ge$	$C_8H_{20}N_2O_2Sn$	$C_{30}H_{52}N_6O_2Sn$
fw	248.85	294.95	647.47
temp (K)	110(2)	110(2)	148(2)
cryst size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.2 × 0.2	0.3 × 0.3 × 0.2
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$Aba2$	$P2_1/n$
a, Å	10.1606(12)	11.7705(18)	23.355(6)
b, Å	11.2693(14)	10.1142(18)	6.260(2)
c, (Å)	20.387(2)	10.061(2)	23.778(6)
α (deg)	90	90	90
β (deg)	90	90	106.18(2)
γ (deg)	90	90	90
V (Å^3)	2334.3(5)	1197.8(4)	3338.6(16)
Z	8	4	4
d_c (Mg m^{-3})	1.416	1.636	1.288
F(000)	1040	592	1360
μ (mm^{-1})	2.601	2.110	0.799
θ range (deg)	2.06−30.02	4.03−30.06	2.16−27.06
index ranges	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-28 \leq l \leq 28$	$-16 \leq h \leq 16$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$	$-10 \leq h \leq 27$ $-8 \leq k \leq 7$ $-30 \leq l \leq 29$
no. of rflns collected	27535	6714	7074
no. of unique rflns	6786	1709	6894
no. of rflns with $I > 2\sigma(I)$	5412	1625	5482
R1; wR2 ($I > 2\sigma(I)$)	0.0230; 0.0436	0.0190; 0.0464	0.0367; 0.0814
R1; wR2 (all data)	0.0330; 0.0449	0.0202; 0.0472	0.0563; 0.1052
no. of data/restraints/params	6786/0/395	1709/1/100	6847/0/560
GOF on F^2	0.887	1.060	1.046
Flack param	0.003(7)	0.48(4)	none
max shift/error	0.001	0.001	0.001
largest diff peak/hole (e Å^{-3})	0.436/−0.354	0.865/−0.576	1.151/−0.633
abs cor T_{max}; T_{min}	0.862; 0.483	0.656; 0.425	none

2.1 g (92%). The melting point and NMR parameters of this product were identical with those described above. Using method b for the preparation of **1** or **2**, one has to give special attention to the purification of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) from highly volatile $LiN(SiMe_3)_2$. In the presence of the latter, compounds **1** and **2** form the ate complexes $LiM(OCH_2CH_2NR_2)_3$, which will be described elsewhere. In the reaction of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) with $LiN(SiMe_3)_2$ and (dimethylamino)ethanol at an equimolar ratio of the reactants these complexes are formed in quantitative yield.

Crystallography. Data were collected on a Bruker SMART CCD 1000 diffractometer (compounds **1** and **2**) and a Syntex $P2_1$ four-circle automated diffractometer (compound **3**); the reflection intensities in the case of compounds **1** and **2** were corrected for absorption.[17] For details see Table 5. The structures were solved by direct methods and by full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The absolute structure of the compound **1** was objectively determined by the refinement of the Flack parameter, which was 0.003(7). The value of the Flack parameter for compound **2**, 0.48(4), indicates that the absolute structure in this case cannot be determined unambiguously due to the specific centrosymmetric arrangement of heavy atoms Sn(II). The hydrogen atoms were objectively localized in the difference Fourier map and were refined isotropically. All calculations were carried out by use of the SHELXTL (PC version 5.10) program.[18]

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Supporting Information Available: Tables of atom coordinates, bond lengths and angles, and anisotropic displacement parameters for **1**−**3** and tables of the space group determinations for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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