New tetrylenes based on substituted diethylenetriamines: synthesis and use as initiators for ε-caprolactone polymerization*

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The reactions of 3-benzyl-1,5-ditosyl-1,3,5-triazapentane (**1**) and 3-benzyl-1,5-dimesityl-1,3,5-triazapentane (**2**) with one equivalent of Lappert´s germylene or stannylene (M[N(SiMe₃)₂]₂, where M = Ge, Sn) produced germylenes and stannylenes of the general formula PhCH₂N(CH₂CH₂NR)₂M, where M = Ge, R = 4-MeC₆H₄SO₂— (**3**); 2,4,6-Me₃C₆H₂— (**5**); M = Sn, R = 4-MeC₆H₄SO₂— (**4**); 2,4,6-Me₃C₆H₂— (**6**), in satisfactory yields. According to NMR data (¹H, ¹³C, ¹¹⁹Sn), stannylenes **4** and **6** are monomeric in solution, and the coordination number of tin is four. The synthesized stannylenes exhibited very high (compound **4**) and moderate (compound **6**) activity as initiators for bulk polymerization of ε-caprolactone, resulting in the synthesis of high-molecular-weight polymers with relatively narrow molecular-weight distribution. Previously unknown triamine **2** was synthesized by benzylation of HN(CH₂CH₂N-HMes)₂ with benzyl chloride in the presence of K₂CO₃.

Key words: germanium, tin, germylenes, stannylenes, tetrylenes, ring-opening polymerization, poly-ε-caprolactone.

The field of main-group metal chemistry dealing with the synthesis of derivatives containing metals in low oxidation states has been extensively developed over several decades. Metal atoms in such compounds do not obey the Lewis octet rule, which has a significant effect on both stability and reactivity of these compounds. Examples of such compounds are derivatives of heavy Group 14 elements in oxidation state +2 — germylenes and stannylenes. Despite the fact that simplest inorganic compounds with oxidation state +2 have long been known for these elements (all these compounds have a polymeric structure), the chemistry of so-called molecular compounds started with pioneering studies by Lappert,[1] who prepared stannylene and germylene of the general formula M[N(SiMe₃)₂]₂. These derivatives are referred to in the literature as Lappert´s tetrylenes and are extensively used in the synthesis as precursors for the preparation of structurally diverse tetrylenes. There is now a significant number of rather stable heavier carbene analogs,[2—4] which can be handled under conditions typical of organometallic derivatives (standard Schlenk technique, inert gas atmo-

sphere). It was found that the following factors are responsible for stabilization of a low-valent center: bulky substituents in the vicinity of this center (kinetic stabilization) or donation of electron density to a vacant orbital of Group 14 metal (thermodynamic stabilization) both *via* transannular interaction and through bonding of the metal atom directly with a heteroatom containing a lone pair. Due to the possibility of controlling the effective charge and steric accessibility of a Group 14 metal by varying the ligand environment, such germylenes and stannylenes are very promising for use in catalysis.

The ring-opening polymerization of cyclic esters and related compounds is one of the most attractive reactions employing tetrylenes as initiators.[5,6] Currently, tin(+2) bis(2-ethylhexanoate) is the most popular industrially used initiator for the synthesis of polylactide.[6—9] Other tin derivatives in oxidation state +2 were also tested as initiators for ring-opening polymerization; however, these derivatives have received much less attention compared to Al and Zn complexes. This may be due to expected toxicity of the samples thus prepared because initiator residues are difficult to remove from the final polymer. Meanwhile, reliable data on toxicity of tin derivatives containing no Sn—Alk bonds are lacking in the literature. It could be expected that a low tin content in the resulting polymer

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would have no significant effect on its biocompatibility. Stannylenes tested as initiators for polymerization of lactide and ε-caprolactone, as well as for copolymerization of lactide and glycolide and copolymerization of lactide and trimethylene carbonate, include derivatives containing the following structural moieties with two-, three-, or four-coordinate tin(+2): SnN_2,[10] SnO_3,[10] SnO_2N,[10–13] SnN_2O,[10–18] SnN_3,[19] SnO_2N_2,[20,21] $SnOSN_2$,[21] $SnOPN_2$,[21] $SnON_3$,[18,21,22] and SnN_4.[23] Polymerization experiments showed that such complexes are promising for use in catalysis.

N,*N*′,*N*′′-Trisubstituted diethylenetriamines (R′N-(CH_2CH_2N(H)R)_2), which are tridentate diamidoamine ligands that form two covalent bonds with a metal atom, are among the most convenient compounds for stabilizing low-valent tin and germanium atoms and varying reactivity. Stannylenes and germylenes were synthesized based on these compounds and characterized.[19,24–27] One tin derivative, $MeN(CH_2CH_2NSiMe_3)_2Sn$, was tested as an initiator for copolymerization of (D,L)-lactide and glycolide.[19] Apparently, the diethylenetriamine structure is very promising for designing an efficient catalytic system because it provides the possibility to easily vary substituents (electronic properties and steric bulk) at the nitrogen atoms, which directly form bonds with the metal atom, *i.e.*, to directly influence the accessibility of the metal site for nucleophilic attack and its Lewis acidity. Therefore, studies aimed at extending the range of such tetrylenes and examining their catalytic activity are of importance.

The goal of this work is to synthesize new tetrylenes based on substituted diethylenetriamines and study the activity of the resulting stannylenes as initiators for ε-caprolactone polymerization.

Results and Discussion

Dialkylenetriamines are well-known tridentate dianionic ligands, which are extensively used in the synthesis of transition and main-group metal complexes.[28–34] The effective charge on the metal atoms can be to a certain extent controlled by varying the electronic nature of substituents at the nitrogen atoms, and the use of sufficiently bulky substituents enables the preparation of monomeric complexes. In this work, we synthesized new tetrylenes using 3-benzyl-1,5-ditosyl-1,3,5-triazapentane (**1**) containing strong electron-withdrawing groups at the terminal nitrogen atoms and 3-benzyl-1,5-dimesityl-1,3,5-triazapentane (**2**) containing electron-donating mesityl groups. In both compounds, the central nitrogen atom is bonded to the electron-donating benzyl group. Ditosyl ligand **1** was synthesized by cleavage of the three-membered ring of *N*-tosylaziridine with benzylamine according to a procedure described previpusly.[33] New dimesityl ligand **2** was synthesized by alkylation of $HN(CH_2CH_2N(H)Mes)_2$, which was prepared by Buchwald—Hartwig arylation.[34]

The reaction of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) with ligands **1** and **2** proceeds *via* transamination to give tetrylenes **3—6** (Scheme 1). The yields of the reaction products crucially depend on the nature of substituents at the terminal nitrogen atoms of the ligand. Thus, electron-withdrawing substituents increase the acidity of NH groups, thereby significantly increasing the yield.

Scheme 1
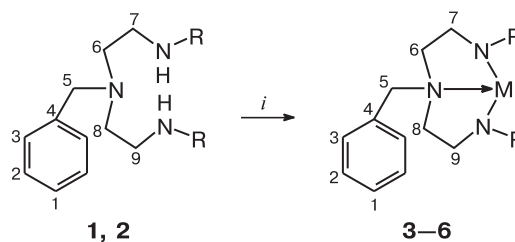
Compound	R	M	Yield (%)
1	Tos	—	—
2	Mes	—	—
3	Tos	Ge	91
4	Tos	Sn	83
5	Mes	Ge	28
6	Mes	Sn	30

Reagents and conditions: *i*. $M[N(SiMe_3)_2]_2$, toluene, 20 °C, 24 h, M = Ge, Sn.

The structures of all the new compounds were confirmed by NMR spectroscopy and elemental analysis. According to ^1H and ^{13}C NMR data, tetrylenes **3—6** are symmetrical, with two CH_2CH_2NR groups being equivalent in each compound. Unfortunately, we failed to grow crystals suitable for X-ray diffraction, but we studied the structures of stannylenes **4** and **6** in solution by ^{119}Sn NMR spectroscopy.

It is known that the chemical shift of the tin atom even with the same coordination number is very sensitive to both the nature of atoms bonded to tin and the nature of the solvent.[35] In this work, we found that the chemical shift of the tin atom in stannylene **4** bearing electron-withdrawing groups is −257 ppm (in C_6D_6), while this shift for compound **6** (electron-donating groups) is 33 ppm (in $CDCl_3$). The chemical shifts determined previously for stannylenes containing bonds only with nitrogen atoms are as follows (NMR data were obtained in C_6D_6 or $CD_3C_6D_5$): 771 ppm for $[(Me_3Si)_2N]_2Sn$ with CN = 2;[35] 158 ppm for $MeN(CH_2CH_2NPr^i)_2Sn$ with CN = 3;[24] 129 ppm for $MeN(CH_2CH_2NSiMe_3)_2Sn$;[24] 125 ppm for $[(Me_2N)_2Sn]_2$;[35] 126 ppm for $MeN(CH_2CH_2NC_6F_5)_2Sn$;[25] −223 ppm for $\{N(cyclo-C_6H_{11})C(CMe_3)N(cyclo-C_6H_{11})]_2Sn$ with CN = 4;[36] −227 ppm for $\{N(SiMe_2Ph)C(Ph)-N(SiMe_2Ph)]_2Sn$ with CN = 4;[14] −245 ppm for $\{N(SiMe_3)-C(Ph)N(SiMe_3)]_2Sn$ with CN = 4;[14] −258 ppm for $[NBu^tC(Ph)N(SiMe_3)]_2Sn$ with CN = 4;[37] −272 ppm for

{N(cyclo-C_6H_{11})C(Me)N(cyclo-C_6H_{11})]$_2$Sn.[36] A comparison of the chemical shift for stannylene **6** with the corresponding values for three-coordinate tin derivatives (158—126 ppm) suggests that stannylene **6** has a monomeric structure containing tin with coordination number of 3. By contrast, the signal of tin in stannylene **4** (−257 ppm) is shifted upfield compared to the values typical of three-coordinate tin derivatives. Apparently, stannylene **4** contains a tin atom in [3+1]-type coordination environment, which is formed, apart from strong N—Sn covalent bonds (two bonds) and one intramolecular donor-acceptor N→Sn bond, by a weaker donor-acceptor S=O→S bond due to an interaction with the tosyl group of another molecule. This compound apparently exists as an equilibrium monomer—dimer mixture (a process fast on the NMR time scale). Previously, a similar solid-state structure was established for related plumbylene [MeN(CH_2CPh_2O)(CH_2CPh_2NTs)Pb]$_2$.[38]

Stannylenes **4** and **6** were tested as initiators for ε-caprolactone polymerization. The reaction was performed in bulk in the presence of an external nucleophile (benzyl alcohol) at high temperature (conditions most commonly used in industry).[6] The compounds under consideration were shown to be active in this reaction (Table 1), stannylene **4** with electron-withdrawing tosyl groups being highly active. However, a relatively high polydispersity index indicates that the polymerization was uncontrolled. Compound **6** seems to be more promising despite the fact that it contains less electron-deficient metal center (the reaction is significantly slower). Nevertheless, the conversion in this reaction is almost 100% within 12 h, and the polydispersity index (1.16) is significantly smaller compared to that for the polymer synthesized using **4**.

To conclude, we synthesized four new tetrylenes based on substituted diethylenetriamines and showed that the new stannylenes are efficient initiators for ε-caprolactone polymerization.

Experimental

All manipulations with germanium and tin derivatives were performed under dry argon atmosphere using the standard Schlenk technique. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at 25 °C, unless otherwise indicated, on Bruker Avance

400 or Agilent 400 MR spectrometers operating at 400.13, 100.61, and 149.21 MHz, respectively, in $CDCl_3$ or C_6D_6. Chemical shifts are given with respect to Me_4Si or Me_4Sn. Elemental analysis was carried out on an Elementar Vario MicroCube analyzer (Department of Chemistry, M. V. Lomonosov Moscow State University). Gel permeation chromatography was performed on a HPLC chromatograph (Phenogel 10^4 Å column, refractometer detector), THF as the mobile phase, the flow rate was 1 mL min^{-1}, the sample concentration was 1%, the sample volume was 200 μL, the calibration was performed using polystyrene standards.

The solvents were purified according to standard procedures; $HN(CH_2CH_2NHMes)_2$,[31] ligand **1**,[32] and $M[N(SiMe_3)_2]_2$, where M = Ge, Sn,[1] were prepared by procedures described previously.

Bulk polymerization of ε-caprolactone. The monomer (in a ratio of 1 : 300) and benzyl alcohol (1 : 1) were added to the initiator under an inert atmosphere. The mixture was placed on an oil bath (100 °C). An aliquot was taken at a specified time, and the polymerization was terminated by the addition of methanol (1 mL). The solution was concentrated, and the residue was dissolved in dichloromethane. Methanol was added to the solution, the resulting solution was centrifuged and separated from the precipitate, and the residue was dried. The polymer was obtained as white solid.

3-Benzyl-1,5-dimesityl-1,3,5-triazapentane (2) Benzyl chloride (0.39 g, 3.1 mmol), $HN(CH_2CH_2NHMes)_2$ (1.00 g, 3.00 mmol), K_2CO_3 (2.1 g, 15.7 mmol), and anhydrous CH_3CN (20 mL) were mixed in a 100 mL Schlenk flask under argon atmosphere. The reaction mixture was heated for 18 h at 60 °C and then cooled. Water (30 mL) was added, and the aqueous and organic phases were separated. The aqueous phase was extracted with ethyl acetate (2S20 mL) and washed with a saturated NaCl solution. The organic phase was dried over $MgSO_4$ and then concentrated, resulting in the formation of dark-orange oil. The purification was performed using a column chromatography (Silufol, ethyl acetate—petroleum ether—triethylamine, 1 : 4 : 0.1, $R_f = 0.2$). Compound **2** was isolated as pale-yellow oil. Yield 0.39 g (31%).

^{1}H NMR ($CDCl_3$), δ: 2.22 (s, 18 H, MesC$\underline{H}_3$); 2.76 (t, 4 H, C(6)$\underline{H}_2$, J = 6.2 Hz); 3.08 (t, 4 H, C(7)$\underline{H}_2$, J = 6.2 Hz); 3.31 (br.s, 2 H, C(7)N$\underline{H}$); 3.72 (s, 2 H, C(5)$\underline{H}_2$N); 6.80 (s, 4 H, Mes); 7.25—7.39 (m, 5 H, C(5)$\underline{Ph}$). ^{13}C NMR ($CDCl_3$), δ: 18.5, 20.5 (Mes$\underline{C}H_3$); 46.0, 54.5, 58.9 ($\underline{C}$(6)H_2, $\underline{C}$(7)H_2); 127.1, 128.3, 129.1, 129.2, 129.4, 129.4, 130.8, 143.8 (carbon atoms of aromatic rings). Found (%): C, 80.88; H, 9.20; N, 9.29. $C_{29}H_{39}N_3$. Calculated (%): C, 81.07; H, 9.15; N, 9.78.

6-Benzyl-1,3-ditosyl-1,3,6,2-triazagerm(2+)ocane (3). A solution of 3-benzyl-1,5-ditosyl-1,3,5-triazapentane (**1**) (0.50 g,

Table 1. Ring-opening polymerization of ε-caprolactone initiated by stannylenes **4** and **6**^{a}

Run	Initiator	t/h	Conversion (%)	M_n (GPC)^b /g mol^{-1b}	M_w/M_n^{b}
1	**4**	1	100	7500	1.65
2	**6**	1	47	—	—
3	**6**	18	62	—	—
4	**6**	24	78	6170	1.16

^{a} The bulk polymerization: 100 °C, [caprolactone] : [cat] : [BnOH] = 300 : 1 : 1.
^{b} Determined by gel permeation chromatography taking into account the correction factor of 0.56.

1.00 mmol) in toluene (5 mL) was added dropwise to a stirred solution of germanium(II) bis(trimethylsilyl)amide (0.39 g, 1.00 mmol) in toluene (10 mL) under argon atmosphere at room temperature. The reaction mixture was stirred for 24 h at ~20 °C. The white precipitate that formed was separated by filtration and recrystallized from a minimum amount of toluene. Compound **3** was isolated as white powder. Yield 0.52 g (91%).

^{1}H NMR (CDCl$_3$), δ: 2.36 (s, 6 H, TosC$\underline{H}_3$); 2.68—2.80 (m, 2 H, C(6)H$_2$); 2.95—3.07 (m, 2 H, C(8)$\underline{H}_2$); 3.08—3.20 (m, 2 H, C(7)H$_2$); 3.35—3.46 (m, 2 H, C(9)H$_2$); 4.14 (s, 2 H, C(5)$\underline{H}_2$N); 7.18 (d, 4 H, S$\underline{Ph}$, *J* = 7.8 Hz); 7.27—7.41 (m, 5 H, C(5)$\underline{Ph}$); 7.74 (d, 4 H, S$\underline{Ph}$, *J* = 7.8 Hz). ^{13}C NMR (CDCl$_3$), δ: 21.4 (TosC$\underline{H}_3$); 46. 9, 58.1 ($\underline{C}$(6, 7, 8, 9)H$_2$); 63.6 ($\underline{C}$(5)H$_2$N); 127.0, 129.1, 129.4, 129.7, 131.3, 138.6, 142.3 (carbon atoms of aromatic rings, one signal is absent in the spectrum). Found (%): C, 52.38; H, 5.16; N, 6.99. C$_{25}$H$_{29}$GeN$_3$O$_4$S$_2$. Calculated (%): C, 52.47; H, 5.11; N, 7.34.

6-Benzyl-1,3-dimesityl-1,3,6,2-triazagerm(2+)ocane (5). A solution of 3-benzyl-1,5-dimesityl-1,3,5-triazapentane (**2**) (0.71 g, 1.65 mmol) in toluene (10 mL) was added to a stirred solution of germanium(II) bis(trimethylsilyl)amide (0.68 g, 1.73 mmol) in toluene (5 mL) under argon atmosphere at room temperature. The reaction mixture was stirred for 4 days at ~20 °C. Then volatile components were removed in high *vacuo*, and *n*-hexane (5 mL) was added. The precipitate was filtered off, additionally washed with hexane (3×2 mL), and dried in *vacuo*. Compound **5** was isolated as beige powder. Yield 0.23 g (28%).

^{1}H NMR (C$_6$D$_6$, 40 °C), δ: 2.25 (s, 6 H, MesC$\underline{H}_3$); 2.48 (s, 12 H, MesC$\underline{H}_3$); 2.16—2.24 (m, 4 H, C(6)$\underline{H}_2$); 2.66—2.80, 2.89—3.01 (m, 4 H, C(7)$\underline{H}_2$); 3.94 (s, 2 H, C(5)N$\underline{H}_2$); 6.94 (s, 4 H, $\underline{Mes}$); 7.02—7.14 (m, 5 H, C(5)$\underline{Ph}$). ^{13}C NMR (C$_6$D$_6$), δ: 20.9, 21.29 (MesC$\underline{H}_3$); 55.8, 60.0, 65.1 ($\underline{C}$(6)H$_2$, $\underline{C}$(7)H$_2$); 128.6, 128.8, 129.8, 131.3, 131.6, 133.6, 148.0 (carbon atoms of aromatic rings). Found (%): C, 68.95; H, 7.32; N, 8.23. C$_{29}$H$_{37}$GeN$_3$. Calculated (%): C, 69.63; H, 7.45; N, 8.40.

6-Benzyl-1,3-ditosyl-1,3,6,2-triazastann(2+)ocane (4). 3-Benzyl-1,5-ditosyl-1,3,5-triazapentane (**1**) (0.44 g, 1.00 mmol) dissolved in toluene (10 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.50 g, 1.00 mmol) in toluene (5 mL) under argon atmosphere at room temperature. Upon the addition of the ligand, the orange mixture turned colorless. The reaction mixture was stirred for 24 h at ~20 °C. Then volatile components were removed in high *vacuo*. The resulting compound was recrystallized from toluene. Compound **4** was isolated as white powder. Yield 0.51 g (83%).

^{1}H NMR (CDCl$_3$), δ: 2.36 (s, 6 H, TosC$\underline{H}_3$); 2.72—2.82 (m, 2 H, C(6)H$_2$); 3.05—3.17 (m, 4 H, C(8)$\underline{H}_2$,C(7)H$_2$); 3.35—3.42 (m, 2 H, C(9)$\underline{H}_2$); 4.03 (s, 2 H, C(5)$\underline{H}_2$N); 7.17 (d, 4 H, *J* = 7.8 Hz); 7.25—7.32, 7.35—7.42 (m, 5 H); 7.75 (d, 4 H, *J* = 7.8 Hz); (m, 13 H, protons of aromatic rings). ^{13}C NMR (CDCl$_3$), δ: 21.4 (TosC$\underline{H}_3$); 45.0, 57.1 ($\underline{C}$(6, 7, 8, 9)H$_2$); 61.8 ($\underline{C}$(5)H$_2$N); 125.3, 127.1, 129.1, 129.4, 129.7, 131.2, 138.7, 142.0 (carbon atoms of aromatic rings, one signal is absent in the spectrum). ^{119}Sn NMR (C$_6$D$_6$), δ: −257 (S). Found (%): C, 48.43; H, 4.55; N, 6.82. C$_{25}$H$_{29}$N$_3$O$_4$S$_2$Sn. Calculated (%): C, 48.56; H, 4.73; N, 6.80.

6-Benzyl-1,3-dimesityl-1,3,6,2-triazastann(2+)ocane (6). 3-Benzyl-1,5-dimesityl-1,3,5-triazapentane (**2**) (0.30 g, 0.70 mmol) dissolved in toluene (10 mL) was added dropwise to a stirred solution of tin(II) bis(trimethylsilyl)amide (0.30 g, 0.70 mmol) in toluene (5 mL) under argon atmosphere at room temperature.

The reaction mixture was stirred for 24 h at ~20 °C. Then volatile components were removed in high *vacuo*, and *n*-hexane (5 mL) was added. The precipitate was filtered off, additionally washed with hexane (3×2 mL), and dried in *vacuo*. The resulting compound was recrystallized from toluene. Compound **6** was isolated as white powder. Yield 0.12 g (30%).

^{1}H NMR (CDCl$_3$), δ: 2.19 (s, 18 H, MesC$\underline{H}_3$); 2.68—2.77 (m, 4 H, C(6)$\underline{H}_2$); 3.01—3.09 (m, 4 H, C(7)$\underline{H}_2$); 3.69 (s, 2 H, C(5)N$\underline{H}_2$); 6.77 (s, 4 H, $\underline{Mes}$); 7.27—7.35 (m, 5 H, C(5)$\underline{Ph}$). ^{13}C NMR (CDCl$_3$), δ: 18.4, 20.4 (MesC$\underline{H}_3$); 46.0, 54.4 ($\underline{C}$(6)H$_2$, $\underline{C}$(7)H$_2$); 58.8 ($\underline{C}$(5)H$_2$N); 127.0, 128.2, 128.9, 129.0, 129.3, 130.5, 138.7, 143.8 (carbon atoms of aromatic rings). ^{119}Sn NMR (CDCl$_3$), δ: 33 (S). Found (%): C, 63.84; H, 6.91; N, 7.60. C$_{29}$H$_{37}$N$_3$Sn. Calculated (%): C, 63.75; H, 6.83; N, 7.69.

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