Tetrylenes based on 1,10-phenanthroline-containing diol: the synthesis and application as initiators of ε-caprolactone polymerization

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Treatment of 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline with two equivalents of *p*-*tert*-butylphenol in the presence of K_2CO_3 afforded 4,7-di(4-*tert*-butylphenoxy)-2,9-dimethyl-1,10-phenanthroline (**1**). Monolithiation of **1** with lithium diisopropylamide followed by treatment with benzophenone resulted in 1-(4,7-bis-*p*-*tert*-butylphenoxy-9-methyl-1,10-phenanthrolin-2-yl)methyl-1,1-diphenylethanol (**2**). 1-(4,7-Bis-*p*-*tert*-butylphenoxy-9-hydroxy(diphenyl)methyl-1,10-phenanthrolin-2-yl)-1,1-diphenylethanol (**3**), a tetradentate ONNO ligand, was prepared analogously from **2**. The interaction of **3** with 1 eq. of Lappert's germylene or stannylene $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) led to the corresponding germylene **4** and stannylene **5** in moderate yields. According to ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy data, stannylene **5** is monomeric in solution and the coordination number of tin atom is 4. Tetrylenes **4** and **5** demonstrated high activity as initiators of bulk polymerization of ε-caprolactone which leads to high-molecular-weight polymers with relatively narrow molecular weight distribution.

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

In the last decades, polymers based on olefins derived from petrochemicals have become important materials for various areas of human activity. Although having many obvious advantages, polyolefins have a major drawback, *viz.*, they are almost not biodegradable. Recently, biodegradable polymers have become an alternative to the "classical" ones.[1] The most widely used biodegradable polymers include polylactide, polyglycolide, and poly-ε-caprolactone that contain lactic, glycolic, and 6-hydroxyhexanoic acid residues, respectively, as monomer units. Ring-opening polymerization (ROP) of cyclic esters (lactide, glycolide, and ε-caprolactone) with tin bis(octanoate) as initiator is the main method for commercial production of these compounds.[2] The drawbacks of the technique include, first, toxicity of tin compounds (production technology does not guarantee a complete removal of metal traces from the end product) and, second, a relatively low activity of the initiator.[3,4] At present, there is considerable research activity aimed at searching for new organoinitiators and initiators based on electron-deficient complexes of less toxic metals. An important avenue of this research is to design novel ligand systems, including those for tin compounds, that will allow one to vary the Lewis acidity of the metal center and, in some cases, to stabilize the polymerization-convenient molecular geometry, thus noticeably enhancing the activity of the initiator.[5]

Among potential initiators of polymerization, particular attention has been paid to tetrylenes, that are, heavier carbene analogues including stannylenes[1,5] (in spite of relatively high toxicity of tin derivatives) and germylenes (especially, taking into account the low toxicity of germanium derivatives).[6,7] Recently, it was shown that tri- and tetradentate aminodiols that efficiently stabilize the low-valence state of germanium and tin atoms (oxidation state is +2) are convenient ligands for the synthesis of tetrylenes.[8—13]

The aim of this work was to synthesize novel tetrylenes based on a previously unknown diol of the phenanthroline series and to study their behavior as initiators of ε-caprolactone polymerization.

Results and Discussion

At present, mononuclear complexes of most elements are thought to be the best initiators.[1] The key factor in the design of corresponding efficient catalytic systems is to use ligands whose structure simultaneously precludes dimer-

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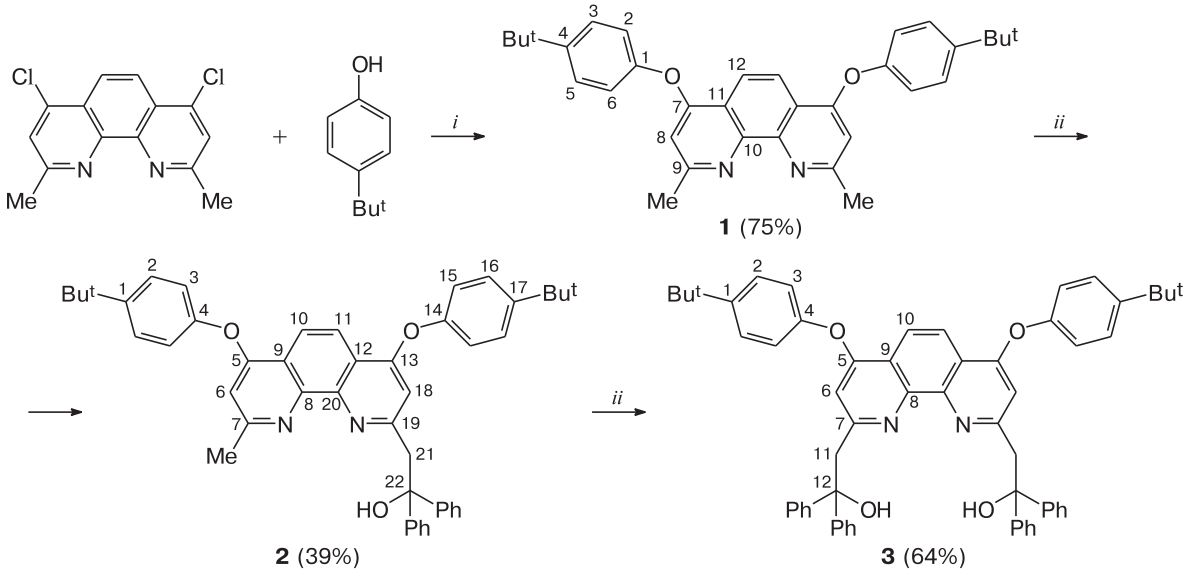
Scheme 1



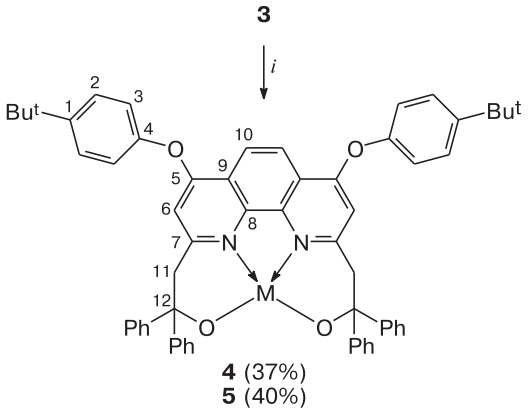
Reagents and conditions: *i*. K_2CO_3, 130 °C; *ii*. 1) $LiNPr^i_2$, THF, –80 °C, 2) Ph_2CO, THF, –20 °C, 3) NH_4Cl, H_2O.

ization (oligomerization) of the complex on the one hand and retains the accessibility of the electrophilic metal center to an ester molecule on the other hand. In this respect, heteroaromatic systems bonded to the metal center through both covalent and coordination bonds should be rather efficient. Earlier, 2,6-di(hydroxyalkyl)pyridines were used as ligands in aluminum complexes.[14] To extend the range of substituted pyridine ligands, we synthesized 1-(4,7-*p*-*tert*-butylphenoxy-9-hydroxy(diphenyl)methyl-1,10-phenanthrolin-2-yl)-1,1-diphenylethanol (**3**). Emphasize that the procedure presented in Scheme 1 allows one to vary substituents both at positions 4 and 7 of the phenanthroline system and in the hydroxyalkyl moieties.

The starting 4,7-dichloro-2,9-dimethyl-1,10-phenanthroline was obtained following a known procedure.[15] Treatment of this compound with two equivalents of 4-*tert*-butylphenolate anion leaded to efficient replacement of chlorine atoms by phenoxy groups to give phenanthroline **1**. Compound **1** was successively treated with lithium diisopropylamide and benzophenone to give an intermediate monoalcohol **2** using a procedure proven earlier taking related pyridine derivatives as examples. To obtain compound **3**, the procedure was repeated. Treatment of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) with ligand **3** afforded tetrylenes **4** (M = Ge) and **5** (M = Sn), respectively (Scheme 2).

The structures of all compounds synthesized were confirmed by NMR spectroscopy and elemental analysis. According to ^1H and ^{13}C NMR spectroscopy data, tetrylenes **4** and **5** have symmetric structures. Each compound bears equivalent oxaalkyl groups and six-membered nitro-

Scheme 2



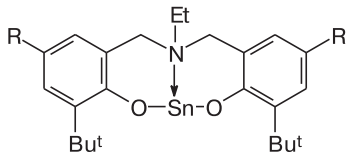
Reagents and conditions: *i*. $M[N(SiMe_3)_2]_2$, toluene.

gen-containing aromatic rings. Unfortunately, we failed to grow crystals suitable for X-ray study; however, the structure of stannylene **5** in solution was studied by ^{119}Sn NMR spectroscopy.

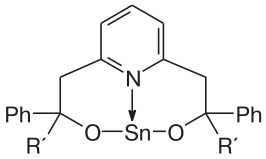
The chemical shift of a tin atom even with the same coordination number (CON) is extremely sensitive to the nature of the solvent and the atoms bonded to the Sn atom.[16] In this work we established that the signal of tin atom in stannylene **5** in C_6D_6 is observed at δ –448. To determine the coordination number of tin atom in **5**, we had to analyze the chemical shifts of tin atom in related compounds. Table 1 lists the chemical shifts of tin atoms in the stannylenes studied to date by ^{119}Sn NMR spectro-

scopy. In these compounds, tin atoms have a CON of at least 2 and form chemical bonds with at least one nitrogen atom (data for dimeric $[(Bu^tO\text{-}\mu)(Ph_3SiO)Sn]_2$ and for monomeric Lappert´s stannylene are given for comparison).[8,13,16–25] From these data it follows that the chemical shift also depends strongly on the nature of the entire ligand. For instance, replacement of donor isopropyl moiety by electron-withdrawing pentafluorophenyl one in the diethylenetriamine-based stannylene leads to a large difference (~300 ppm). A comparison of the chemical shifts of tin atom in stannylene **5** (this work) and in tin-containing compounds (published data) suggests that compound **5** is monomeric in solution and two coordination bonds Sn←N in its molecule seem not to be strong.

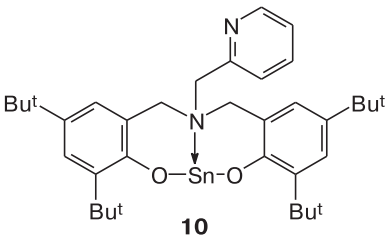
Tetrylenes **4** and **5** synthesized in this work were tested as initiators of ε-caprolactone polymerization. The reaction was conducted in bulk, in the presence of external nucleophile (benzyl alcohol) at high temperature; these are the most appropriate conditions for commercial production. The compounds studied appeared to be efficient initiators (Table 2). In both cases, conversion reached nearly 100% after 12 h. However, the polydispersity index



6, **7**



8, **9**



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R = Me (**6**), Bu^t (**7**); R´ = Me (**8**), Ph (**9**)

Table 1. Chemical shifts of tin atoms in stannylenes with N,O-surrounding

Compound	CON[a]	Stannylene form	Ligand type[b]	X-ray data availability	Solvent	δ	Reference
$[(Me_3Si)_2N]_2Sn$	2	Monomer	NN	+[16]	$C_6D_5CD_3$	771	16
$MeN(CH_2CH_2NPr^i)_2Sn$	3	Monomer	NNN	—	C_6D_6	158	17
$MeN(CH_2CH_2NSiMe_3)_2Sn$	3	Monomer	NNN	+[17]	C_6D_6	129	17
$(Me_2N)_2Sn$	3	Dimer	NNN	+[19]	$C_6D_5CD_3$	125	16
$(Me_3Si)_2N(Pr^iO\text{-}\mu)Sn$	3	Dimer	NOO	—	$C_6D_5CD_3$	41	16
$(Me_2N)(Pr^iO\text{-}\mu)Sn$	3	Dimer	NOO	—	$C_6D_5CD_3$	30	16
$(Me_2N)(Ph_3SiO\text{-}\mu)Sn$	3	Dimer	NOO	—	$C_6D_5CD_3$	−38	16
$MeN(CH_2CH_2NC_6F_5)_2Sn$	3	Monomer	NNN	—	C_6D_6	−126	18
$(Bu^tO\text{-}\mu)(Ph_3SiO)Sn$	3	Dimer	OOO	+[20]	C_6D_6	−226	20
MeN[CH(*S*-Me)CH(*R*-Ph)O]$(CH_2CPh_2O)Sn$	3 or 4	Monomer or dimer	ONO or OONO	—	C_6D_6	−254	13
$Bu^tN(CH_2CH_2O)_2Sn$	4	Dimer	OONO	—	$CDCl_3$	−271	21
$MeN(CH_2CH_2O)_2Sn$	4	Dimer	OONO	+[22]	CD_2Cl_2	−303	21
						(−328—−314)[c]	22
$MeN(CH_2CPh_2O)(CH_2CH_2NSO_2\text{-}p\text{-}Tol)Sn$	4	Monomer	OONO[d]	—	DMSO-d_6	−310	23
$MeN(CH_2CH_2O)(CH_2CH_2NSO_2\text{-}p\text{-}Tol)Sn$	4	Dimer	OONO	—	$CDCl_3$	−363, −379[e]	23
6	3	Monomer	ONO	+[24]	C_6D_6	−420	25
7	3	Monomer	ONO	—	C_6D_6	−423	25
8	4	Dimer	OONO	—	THF-d_8	−444	8
5	4	Monomer	ONNO	—	C_6D_6	−448	This work
9	4	Dimer	OONO	+[8]	C_6D_6	−486	8
10	4	Monomer	ONNO	+[25]	C_6D_6	−514	25

[a] Tentative CN of Sn atom.
[b] Atom participating in the coordination bond with tin atom is underlined.
[c] Solid phase.
[d] Coordination to oxygen atom of DMSO-d_6.
[e] Two isomers.

Table 2. Ring-opening polymerization of ε-caprolactone initiated by tetrylenes **4** and **5**[a]

Run	Initiator	[Complex] : [BnOH]	*t*/h	*C* (%)	M_n/g mol^{-1}		M_w/M_n
					GPC[b]	Calculated[c]	
1	**4**	1 : 1	12	98	6546	33665	1.77
2	**5**	1 : 1	12	>99	10457	34008	1.70

[a] Bulk polymerization conditions: 100 °C, [caprolactone] : [catalyst] = 300 : 1.
[b] Determined from GPC data with a correction factor of 0.56 applied.
[c] Calculated using expression M_n(theor) = 114.14 • ([caprolactone]:[catalyst]) • *C* + 108.14.

(>1.7) and a large difference between the experimentally determined and calculated molecular weights of polymers demonstrate that polymerization is complicated by side processes. Further tests of polymerization activity are in progress.

Summing up, we synthesized two novel tetrylenes based on the previously unknown phenanthroline-containing diol and established that they are efficient initiators of ε-caprolactone polymerization.

Experimental

All operations with germanium and tin derivatives were carried out in dry argon atmosphere using conventional Schlenk techniques. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Bruker Avance 400 or Agilent 400 MR spectrometers operating at 400.13, 100.61, and 149.21 MHz, respectively, at ~25 °C. The solvents were $CDCl_3$, CD_2Cl_2, and C_6D_6; residual protons of the deuterated solvents were used as internal standards. The chemical shifts are given relative to Me_4Si and Me_4Sn. Elemental analysis was carried out at the Laboratory of Organic Microanalysis (Department of Chemistry, Lomonosov Moscow State University). The solvents were purified following conventional procedures. 4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline[15] and compounds $M[N(SiMe_3)_2]_2$ (M = Ge,[26] Sn[26]) were synthesized as reported earlier.

Synthesis of 4,7-di(4-*tert*-butylphenoxy)-2,9-dimethyl-1,10-phenanthroline (1). 2,9-Dimethyl-4,7-dichloro-1,10-phenanthroline (1.50 g, 5.4 mmol), *p-tert*-butylphenol (5.00 g, 33.3 mmol), and potassium carbonate (0.69 g, 5.0 mmol) were placed in a 25-mL Schlenk flask in argon atmosphere. The mixture was stirred at 130 °C for 48 h; the reaction was monotired by TLC (Silufol, EtOAc : methanol = 10 : 1). After completion of the reaction the mixture thus obtained was dissolved in methylene chloride (50 mL) and then washed with 2 *M* NaOH (500 mL). The organic phase was concentrated to dryness and compound **1** was obtained as white powder. M.p. 164—166 °C. The yield was 1.94 g (71%). ^{1}H NMR (CD_2Cl_2), δ: 1.30 (s, 18 H, C(1)Bu^t); 2.68 (s, 6 H, C(7)Me); 6.69 (s, 2 H, C(6)H); 7.12 (d, 4 H, C(3)H, *J* = 8.6 Hz); 7.48 (d, 4 H, C(2)H, *J* = 8.6 Hz); 8.24 (s, 2 H, C(10)H). ^{13}C NMR (CD_2Cl_2), δ: 26.27 (C(7)Me); 31.08 (C(1)CMe_3); 35.04 (C(1)CMe_3); 107.59, 118.95, 120.88 127.73, 147.32, 149.13, 152.84, 160.36, 162.58 (aromatic ring carbons). Found (%): C, 81.98; H, 7.23; N, 5.59. $C_{34}H_{36}N_2O_2$. Calculated (%): C, 80.92; H, 7.19; N, 5.55.

Synthesis of 1-[4,7-di(4-*tert*-butylphenoxy)-9-methyl-1,10-phenanthrolin-2-yl]-1,1-diphenylethanol (2). Diisopropylamine was preliminarily distilled over calcium hydride in argon atmosphere, b.p. 84 °C (760 Torr). To a solution of diisopropylamine (2.79 g, 27.6 mmol) in anhydrous tetrahydrofuran (15 mL), a 2.5 *M* solution of *n*-butyllithium in hexane (11 mL, 27.5 mmol) was added with stirring in argon atmosphere at −25 °C and the reaction mass was stirred at this temperature for 30 min. To lithium diisopropylamide thus obtained, a solution of compound **1** (4.58 g, 9.1 mmol) in THF (70 mL) was added dropwise with stirring in argon atmosphere at −80 °C and the mixture was stirred at this temperature for 20 min. Then, the mixture was warmed to −20 °C, stirred at this temperature for an additional 1 h, and diphenyl ketone (4.14 g, 22.7 mmol) dissolved in anhydrous tetrahydrofuran (20 mL) was added dropwise. The reaction mass was stirred for 16 h. After completion of the reaction the mixture was treated with saturated NH_4Cl solution (100 mL). Then, extraction with ethyl acetate (3×80 mL) was performed. The combined organic extracts were dried over Na_2SO_4. Volatiles were removed *in vacuo*. Ethanol was added to orange oil thus obtained, and a residue precipitated. The residue was filtered off and dried. Compound **2** was isolated as beige powder. M.p. 198—200 °C. The yield was 2.44 g (39%). ^{1}H NMR ($CDCl_3$), δ: 1.38, 1.40 (both s, 18 H, C(1)Bu^t, C(17)Bu^t); 2.78 (s, 3 H, C(7)Me); 3.85 (s, 2 H, C(21)H_2); 6.55 (s, 1 H, C(18)H); 6.73 (s, 1 H, C(6)H); 6.94 (d, 2 H, C(15)H, *J* = 8.3 Hz); 7.15—7.11 (m, 4 H, aromatic ring protons); 7.20 (t, 4 H, aromatic ring protons, *J* = 7.6 Hz); 7.45—7.50 (m, 8 H, aromatic ring protons); 8.15 (d, 1 H, C(11)H, *J* = 9.1 Hz), 8.23 (d, 1 H, C(10)H, *J* = 9.1 Hz). No proton signal from OH group was observed. ^{13}C NMR ($CDCl_3$), δ: 26.20 (C(7)Me); 31.46 (C(1)CMe_3); 34.53 (C(1)CMe_3); 48.06 (C(21)H_2); 78.50 (C(22)(Ph_2)); 107.35, 108.47, 118.00, 119.08, 119.86, 119.99, 120.24, 126.28, 126.43, 126.52, 127.01, 127.09, 127.65, 127.73, 127.83, 147.35, 148.38, 152.04, 152.16, 160.39, 160.47, 161.79, 161.82, 162.13 (aromatic ring carbons). Found (%): C, 82.21; H, 6.77; N, 4.11. $C_{47}H_{46}N_2O_3$. Calculated (%): C, 82.18; H, 6.75; N, 4.08.

Synthesis of 1-(4,7-di(4-*tert*-butylphenoxy)-9-hydroxydi-(phenyl)methyl-1,10-phenanthrolin-2-yl)-1,1-diphenylethanol (3). Diisopropylamine was preliminarily distilled over calcium hydride in argon atmosphere, b.p. 84 °C (760 Torr). To a solution of diisopropylamine (0.89 g, 8.8 mmol) in anhydrous tetrahydrofuran (5 mL), a 2.5 *M* solution of *n*-butyllithium in hexane (3.28 mL, 8.2 mmol) was added with stirring in argon atmosphere at −25 °C and the reaction mixture was stirred at this temperature for 30 min. To lithium diisopropylamide thus obtained, a solution of compound **2** (2.00 g, 2.90 mmol) in THF (20 mL) was added dropwise in argon atmosphere at −80 °C and the mixture was stirred at this temperature for 20 min. Then, the mixture was warmed to −20 °C, stirred at this temperature for an additional 1 h, and diphenyl ketone (1.33 g, 7.3 mmol) in anhydrous tetra-

hydrofuran (10 mL) was added dropwise at −20 °C. The reaction mass was stirred for 16 h. After completion of the reaction the mixture was treated with saturated NH_4Cl solution (100 mL). Then, extraction with ethyl acetate (3×60 mL) was performed. The combined organic extracts were dried over Na_2SO_4. Volatiles were removed *in vacuo*. Ethanol was added to orange oil thus obtained, and a white residue precipitated. The solid residue was filtered off and recrystallized from an ethyl acetate—petroleum ether mixture. Compound **3** was isolated as beige powder. M.p. 179—181 °C. The yield was 1.62 g (64%). ^{1}H NMR ($CDCl_3$), δ: 1.41 (s, 18 H, C(1)Bu^t); 3.88 (s, 4 H, C(11)H_2); 6.52 (s, 2 H, C(10)H); 6.91 (d, 4 H, C(3)H, J = 7.4 Hz); 7.14 (m, 4 H, aromatic ring protons); 7.20—7.23 (m, 8 H, aromatic ring protons); 7.46 (d, 4 H, C(2)H, J = 8.6 Hz); 7.53 (m, 8 H, aromatic ring protons); 8.16 (s, 2 H, C(10)H). No proton signal from OH group was observed. ^{13}C NMR ($CDCl_3$), δ: 29.66 (C(1)CMe_3); 31.46 (C(1)CMe_3); 34.55 (C(11)H_2); 48.58 (C(12)Ph_2OH); 108.84, 118.80, 120.03, 120.09, 126.29, 126.37, 127.10, 127.79, 147.17, 147.21, 148.53, 151.78, 160.76, 162.08 (aromatic ring carbons). Found (%): C, 82.89; H, 6.45; N, 3.18. $C_{60}H_{56}N_2O_4$. Calculated (%): C, 82.92; H, 6.49; N, 3.22.

Synthesis of germylene 4. To a solution of germanium(II) bis(trimethylsilyl)amide (0.1130 g, 0.29 mmol) in toluene (10 mL), ligand **3** (0.2500 g, 0.29 mmol) dissolved in toluene (5 mL) was added dropwise with stirring in argon atmosphere at ~25 °C. The mixture turned red. The reaction mass was stirred at ~25 °C for 24 h and then volatiles were removed in high vacuum. The substance thus obtained was recrystallized from toluene. Compound **4** was isolated as light-red powder. The yield was 0.10 g (37%). ^{1}H NMR (C_6D_6), δ: 1.25 (s, 18 H, C(1)Bu^t); 3.53 (s, 4 H, C(11)H_2); 6.53 (s, 2 H, C(10)H), 6.92—7.01 (m, 8 H, aromatic ring protons); 7.12—7.16 (m, 8 H, aromatic ring protons); 7.35 (d, 4 H, C(2)H, J = 8.6 Hz); 7.72 (d, 8 H, aromatic ring protons, J = 7.4); 8.05 (s, 2 H, C(10)H). ^{13}C NMR (C_6D_6), δ: 31.87 (C(1)CMe_3); 34.91 (C(1)CMe_3); 49.11 (C(11)H_2); 79.01 (C(12)Ph_2OSn); 109.42, 119.31, 120.87, 121.10, 126.80, 127.43, 127.87, 128.45, 146.23, 148.77, 148.08, 153.01, 162.12, 162.62 (aromatic ring carbons). ^{13}C NMR (C_6D_6), δ: 162.62, 162.12, 153.01, 148.08, 148.77, 146.23, 128.45, 127.87, 127.43, 126.80, 121.10, 120.87, 119.31, 109.42 (Ar); 79.01 (C(Ph_2)OH); 34.91 (CH_2); 31.87 ((CH_3)$_3$C); 31.87 ((CH_3)$_3$C). Found (%): C, 77.02; H, 6.11; N, 2.74. $C_{62}H_{56}GeN_2O_4$. Calculated (%): C, 76.69; H, 5.79; N, 2.92.

Synthesis of stannylene 5. To a solution of tin(II) bis-(trimethylsilyl)amide (0.2720 g, 0.62 mmol) in toluene (10 mL), ligand **3** (0.5387 g, 0.62 mmol) dissolved in toluene (7 mL) was added dropwise with stirring in argon atmosphere at ~25 °C. The mixture turned dark-green. The reaction mass was stirred at ~25 °C for 24 h and then volatiles were removed in high vacuum. The substance thus obtained was recrystalized from toluene. Compound **5** was isolated as green powder. The yield was 0.25 g (40%). ^{1}H NMR (C_6D_6), δ: 1.28 (s, 18 H, C(1)Bu^t); 3.56, 3.80 (both d, 4 H, C(11/13)H_2, J = 13.6 Hz); 6.50 (s, 2 H, C(10)H), 6.96 (d, 8 H, aromatic ring protons, J = 8.8 Hz); 7.22—7.28 (m, 5 H, aromatic ring protons); 7.40 (d, 4 H, C(2)H, J = 8.8 Hz); 7.53 (m, 5 H, aromatic ring protons); 7.85 (d, 4 H, aromatic ring protons, J = 7.3 Hz); 7.96 (d, 4 H, aromatic ring protons, J = 7.3 Hz). ^{13}C NMR (C_6D_6), δ: 31.87 (C(1)CMe_3); 34.99 (C(1) CMe_3); 50.14 (C(11)H_2); 79.00 (C(12)Ph_2OSn); 110.38, 118.97, 120.98, 127.39, 127.63, 127.86, 130.56, 132.43, 149.71, 152.36, 152.61, 153.89, 162.08, 163.01 (aromatic ring carbons). ^{119}Sn NMR (C_6D_6), δ: −448.02. Found (%): C, 73.55; H, 5.93; N, 2.69. $C_{62}H_{56}SnN_2O_4$. Calculated (%): C, 73.10; H, 5.52; N, 2.84.

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