Germylenes and stannylenes based on aminobisphenolate ligands: insertion into the C—Br bond

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A reaction of previously synthesized germylenes and stannylenes based on aminobisphenols $RN\{CH_2[(5-R´)(3-Bu^t)C_6H_2(2-O—)]\}_2M^{II}$, M = Ge, R = CH_2(2-Py), R´ = Bu^t (**1**); M = Ge, R = Et, R´ = Me (**2**); M = Sn, R = CH_2(2-Py), R´ = Bu^t (**3**); M = Sn, R = Et, R´ = Me (**4**), containing (tetrylenes **1** and **3**) or not containing (tetrylenes **2** and **4**) a group capable of additional donation, with allyl bromide leads to the products of the insertion of tetrylenes into the C—Br bond: $RN\{CH_2[(5-R´)(3-Bu^t)C_6H_2(2-O—)]\}_2M(Br)All$, M = Ge, R = CH_2(2-Py), R´ = Bu^t (**5**); M = Ge, R = Et, R´ = Me (**6**); M = Sn, R = CH_2(2-Py), R´ = Bu^t (**7**); M = Sn, R = Et, R´ = Me (**8**). The structures of obtained derivatives were confirmed by NMR spectroscopy and elemental analysis. The structures of compounds **4**, **5**, and **7** were studied by X-ray crystallography. Stannylene **4** was found to be monomeric in the solid phase: the coordination number of the Sn atom is 3. The insertion products **5** and **7** are characterized by the coordination number 6 for the central atom.

Key words: germanium, tin, germylenes, stannylenes, tetrylenes, insertion.

At the present time, the studies of the Group 14 divalent element (Si, Ge, Sn, Pb) derivatives is one of the rapidly developing directions of organometallic chemistry. These "heavy carbenes", for which lately the term "tetrylenes" is actively used in the English-language scientific literature, can be a starting point for the synthesis of various organometallic compounds and intermediates, for example, complexes with transition metals and clusters, compounds with multiple metal—carbon and metal—heteroatom bonds, small metallacycles, radicals, and ions.[1] Apart from that, stannylenes are used in organic synthesis as intermediates for different versions of Stille reaction,[2] while germylenes are used as starting compounds for the development of nanomaterials based on germanium.[3] Note that earlier these derivatives were regarded as unstable molecules. At the present time, it is known that when the corresponding factors stabilizing the "heavy carbene" molecule are present, these compounds become stable.

Relatively recently it was shown that dialkanolamines, pyridine-containing dialcohols, and diethylenetriamines are the ligands which efficiently stabilize the low-valent state (the oxidation state +2) of germanium and tin atoms.[4—12] The stabilization of the electron-deficient center in germylenes and stannylenes using these ligand can

be effected by two pathways. Kinetic stabilization suggests the introduction of the inert bulky substituents as groups bonded to the metal atom, hindering the approach to the reaction center of the molecule. Thermodynamic stabilization is effected by the donation of the electron density of the lone electron pairs of the substituent to the vacant orbital of the metal atom. In this case, the stabilized compound formally is not an analog of carbene, since the electron environment of the metal atom obeys the octet rule. An important factor in the study of germylenes and stannylenes based on dialkanolamines and diethylenetriamines is a degree of their oligomery. Such derivatives can be monomeric, dimeric, and oligomeric. The determination of the oligomery degree seems an important issue, since it should exert influence on the reactivity of "heavy carbenes".

Despite the fact that stable germylenes and stannylenes have been studied for more than 40 years and by the present moment a large enough amount of these compounds have been synthesized, there are just few literature works devoted to the study of their reactivity. Such studies are very important because of the possibility of application of germylenes and, especially, stannylenes in organic synthesis.

The purpose of the present work is the study of the behavior of germylenes and stannylenes synthesized earli-

er based on aminobisphenols in the reaction of insertion into an activated C—Br bond using allyl bromide as an example.

Results and Discussion

One of the main types of the reaction of Group 14 low-valent element compounds are the reactions proceeding with the increase in the oxidation state. Among these processes, an important place is taken by the insertion reaction into the σ-bonds of tetrylenes, including the C—Hal bonds. Methyl iodide was commonly used as a substrate for the study of the insertion of dioxygen-containing tetrylenes $M(OR)_2$.[11-17] It was found[13] that the compound having a polymeric structure, for example, $(PhO)_2Sn$, did not react with methyl iodide upon reflux of the reaction mixture for 7 h. At the same time, the monomeric compounds $(2\text{-EtOOCC}_6H_4O)_2Sn$ (the structure of the monomer was not established, but the presence of additional intramolecular interactions of the tin atom with ethoxycarbonyl groups can be suggested)[13] and sterically hindered $(Bu^t_3CO)_2Sn$[14] insert into the C—I bond with the formation of the expected product. Note that when a nitrogen atom is present in the ligand molecule, the insertion reaction can be accompanied by the quaternization reaction of the nitrogen atom. Thus, treatment of methyl iodide with $(ArO)_2Ge$ (Ar = $2,4,6\text{-}(Me_2NCH_2)_3C_6H_2$) characterized by the presence of the transannular Ge—N interaction leads, instead of the insertion product, to the mixture of different insoluble solid compounds with ionic structure, for which the authors[15] suggested an ammonium structure. At the same time, the intermolecular complex of dimesityloxygermylene with TMEDA at room temperature in the reaction with methyl iodide gives an insertion product into the C—I bond.[16] Recently, a new possible direction of the reaction of tetrylenes with methyl iodide was discovered:[17] the reaction of $(Me_2NCH_2CH_2O)_2Ge$ with MeI gives an ionic complex $[(Me_2NCH_2CH_2O)_2GeMe]^+I^-$. Related germylenes and stannylenes based on diethanolamines in the reaction with methyl iodide give an insertion product into the C—I bond[11] in the case of the starting monomeric tetrylene $MeN(CH_2CPh_2O)(CHMeCH\text{-}PhO)Ge$ and a mixture of difficult to identified products in the case of dimeric tetrylenes $[MeN(CH_2CH_2O)_2M]_2$, M = Ge, Sn.[11,12]

In the course of this work, four monomeric tetrylenes **1—4** obtained by us earlier[18] were studied in the reaction with allyl bromide (Scheme 1). By the present time, the insertion of tetrylenes into the C—Br bond in allyl bromide have been studied for the complex of dibromogermane with dioxane and dimethylgermane.[19,20] Note that according to the X-ray diffraction data, germylene **1** is monomeric in the solid phase, with the coordination number (N) of the germanium atom being equal to three due to the formation of an intramolecular Ge←N bond of the

germanium atom with the nitrogen atom of the $N(CH_2)_3$ group. The nitrogen atom of the pyridine ring does not form a bond with the germanium atom.[18] We suggested that compound **2** is also monomeric and Ge has N = 3. Stannylene **3** is monomeric according to the X-ray diffraction data, the tin atom has N equal to four due to the formation of two intramolecular Sn←N interactions.[18] Compound **4** was studied by X-ray diffraction in the course of this work (Fig. 1): the stannylene **4** is monomeric, Sn has N = 3. The insertion was carried out upon heating (70 °C) a mixture of reagents in toluene for prolong time. In all the cases, insertion products were isolated, the yields varied from low to satisfactory. The structure of complexes **5—8** was confirmed by the ^1H and ^{13}C NMR spectroscopy data (in the case of compound **7** also by ^{119}Sn NMR). The NMR spectroscopy data indicate the presence in the solution of the $M\leftarrow N(CH_2)_3$ intramolecular coordination. For compounds **5** and **7**, it was impossible to unambiguously determine the presence in the solution of the $M\leftarrow N_{Py}$ interaction, which is present in the solid phase. Thus, it was confirmed that monomeric tetrylenes in the insertion into the C—Hal bond give the products with the expected structure.
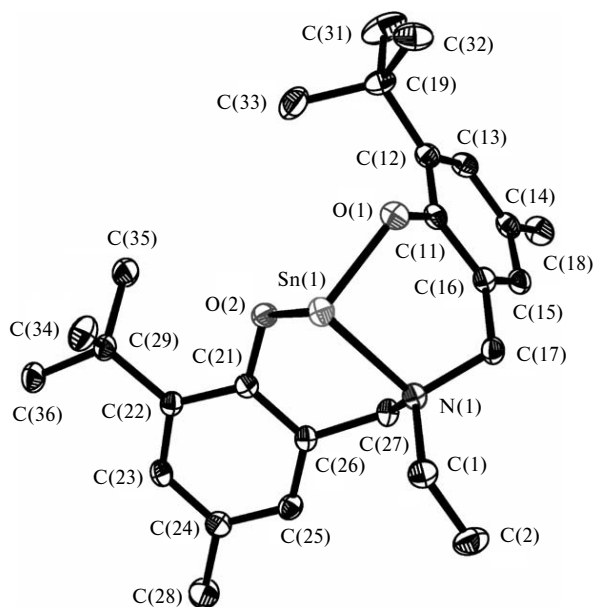
Scheme 1
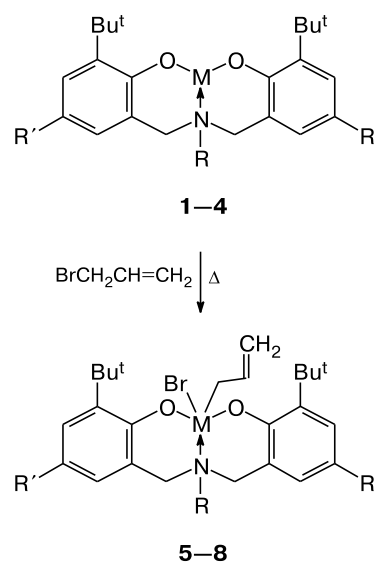
The structures of compounds **5** and **7** were studied by X-ray diffraction (Tables 1 and 2, Figs 2 and 3).

The coordination polyhedron of the germanium and the tin atom is a distorted octahedron, in which the Group 14 element atom is bonded by covalent bonds with two
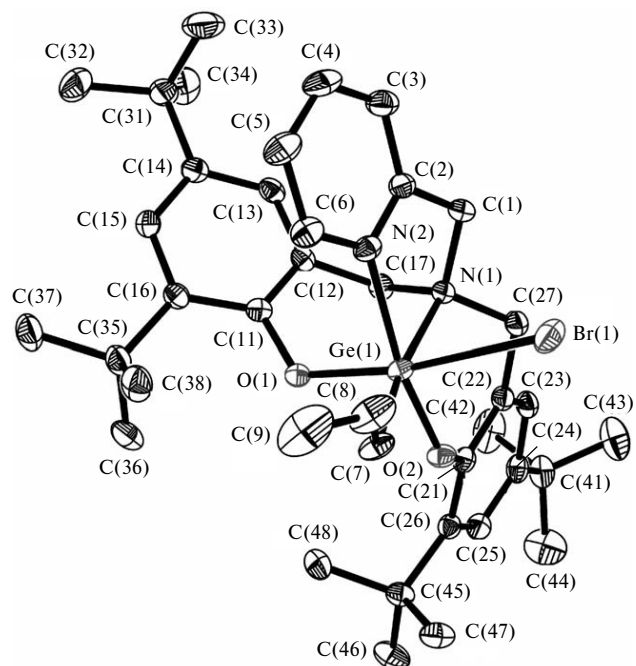
Fig. 1. Molecular structure of compound **4**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted.

Table 1. Principal interatomic distances (*d*) in the structures **4**, **5**, and **7**

Bond	*d*/Å		
	4	**5**	**7**
$M{\leftarrow}N_{Py}$	—	2.1499(15)	2.2976(16)
$M{\leftarrow}N(CH_2)_3$	2.3155(12)	2.0970(16)	2.2816(15)
M—O	2.0395(10)	1.8523(12)	2.0282(12)
	2.0693(10)	1.8704(13)	2.0503(12)
M—Br	—	2.7009(3)	2.6681(2)
M—C	—	1.9903(19)	2.1866(17)

**Table 2.** Principal bond angles (ω) in the structures **4**, **5**, and **7**

Angle	ω/deg		
	4	**5**	**7**
O—M—C	—	90.21(7)	99.95(6)
		96.55(8)	91.90(6)
O—M—N(CH₂)₃	88.26(4)	89.57(6)	85.60(5)
	85.52(4)	93.49(6)	87.03(5)
O—M—N_Py	—	166.49(6)	159.47(5)
		87.96(6)	85.62(5)
O—M—Br	—	93.83(4)	92.37(4)
		170.53(4)	170.25(4)
O—M—O	95.36(4)	95.36(6)	94.94(5)
C—M—N(CH₂)₃	—	169.93(8)	174.42(6)
C—M—N_Py	—	102.44(7)	100.54(6)
N_Py—M—N(CH₂)₃	—	77.14(6)	73.92(5)
Br—M—N(CH₂)₃	—	84.30(4)	87.10(4)
Br—M—N_Py	—	82.57(4)	85.28(4)
C—M—Br	—	85.68(7)	93.19(5)

Fig. 2. Molecular structure of compound **5**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted.

oxygen atoms, bromine and carbon atoms, as well as with two dative bonds with the nitrogen atoms. The bond distance values Ge←N in **5** and Sn←N in **7** (see Table 1) unambiguously indicate the presence of two strong enough M—N transannular interactions in both compounds. Note that in germylene **1** studied earlier, the germanium center is not attractive enough for the formation of two transannular interactions, obviously, due to the presence of a lone electron pair on the germanium atom (Ge—O 1.8516(13), 1.8607(13), Ge←N(CH₂)₃ 2.1614(15) Å). At the same time, in stannylene **3** studied earlier, the two transannular bond are present (Sn—O 2.0415(13), 2.1136(13), Sn←N(CH₂)₃ 2.3192(15), Sn←N_Py 2.7059(17) Å).[18] As it was expected, an increase in the oxidation state and the coordination number of the central atom on going from a tetrylene to the insertion product into the C—Br bond leads to the strengthening of the dative bonds, and, at the same time does not exert noticeable influence on the properties of the covalent M—O bonds.

The structure of the starting stannylene **4** containing a tin atom with a coordination number 3 was studied by X-ray diffraction (see Fig. 1, Tables 1 and 2). The coordination polyhedron of the tin atom is a distorted tetrahedron, in which one of the vertices is occupied by the unshared pair of electrons. A comparison of bond distances in **4** with similar bonds in stannylene **3**[18] (Sn—O 2.0415(13), 2.1136(13), Sn←N(CH₂)₃ 2.3192(15), Sn←N_Py 2.7059(17) Å) indicates that the formation of an additional Sn←N_Py bond in **3** does not exert noticeable influence on the properties of other bond of the tin atom.
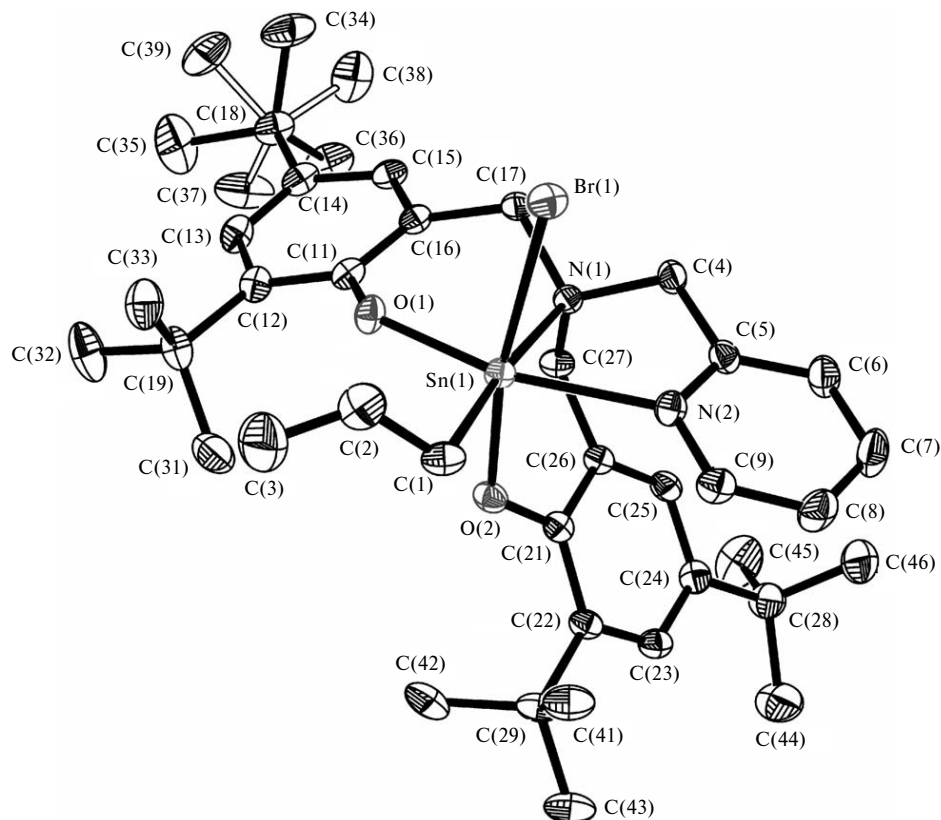
Fig. 3. Molecular structure of compound **7**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted. The minor component of disordering is shown in hollow lines.

In conclusion, in the course of these studies we demonstrated a possibility of application of germylenes and stannylenes based on sterically bulky aminobisphenolate ligands in the synthesis of germanium and tin compounds in the oxidation state +4. New tin and germanium complexes were obtained and structurally characterized.

Experimental

All the manipulations with germanium and tin derivatives were carried out under dry argon using standard Schlenk technique. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Bruker Avance 400 or Agilent 400 MR spectrometers (400.13, 100.61, 149.21 MHz, respectively) at room (25 °C) temperature in CDCl$_3$ or C$_6$D$_6$; signals of residual protons of the deuterated solvents were used as references; chemical shift are given relative to Me$_4$Si. Elemental analysis was carried out in the Laboratory of Organic Microanalysis of the Chemical Department of the Moscow State University. The structure of compound **7** was confirmed by ESI-HRMS. ESI-HRMS was carried out at the Chemical Department of the Moscow State University. The sample were syringed into an OrbitrapElite high resolution mass spectrometer with electrospray ionization, the flow rate was 1—3 μL min^{-1}.

Solvents were purified according to the standard procedures. Toluene and hexane were refluxed and distilled over metallic sodium. Allyl bromide was distilled before use in the reaction.

Compounds **1**—**4** were obtained according to the procedures described earlier.[18]

Synthesis of 6-allyl-6-bromo-2,4,8,10-tetra(*tert*-butyl)-13-(pyridin-2-ylmethyl)-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-germadibenzo[*a,f*]cyclodecadiene (5). Allyl bromide (0.06 mL, 0.70 mmol) was added to a solution of compound **1** (0.33 g, 0.54 mmol) in toluene (10 mL) using a syringe. A white precipitate was formed after stirring for 4 days at room temperature and 10 h at 60 °C. Another portion of allyl bromide (0.6 mL, 6.9 mmol) was added to the reaction mixture and then the reaction mixture was additionally heated for 8 h at 70 °C. Then, the solution over the precipitate was decanted, the solid compound was washed with a mixture of toluene—*n*-hexane (1 : 1) (2 mL) and dried to obtain complex **5** as a white powder. The yield was 0.11 g (28%). ^{1}H NMR (CDCl$_3$), δ: 1.11 (s, 18 H, C(CH$_3$)$_3$); 1.38 (s, 18 H, C(CH$_3$)$_3$); 3.41 (d, 2 H, C̲H$_2$CH=CH$_2$, *J* = 7.8 Hz); 4.44 (d, 2 H, NCH$_2$, *J* = 13.1 Hz); 5.15—5.29 (m, 2 H, CH$_2$CH=C̲H$_2$); 5.68 (br.s, 2 H, NC̲H$_2$Py); 6.25—6.40 (m, 1 H, CH$_2$C̲H=CH$_2$); 6.77—6.85 (m, 2 H, H$_{Ar}$); 7.08—7.15 (m, 3 H, H$_{Ar}$ and H$_{Py}$); 7.55 (d, 1 H, H$_{Py}$, *J* = 8.1 Hz); 7.63—7.71 (m, 1 H, H$_{Py}$); 8.15 (d, 1 H, H$_{Py}$, *J* = 5.3 Hz). A signal for one of the CH$_2$ groups is absent in the spectrum. ^{13}C NMR (CDCl$_3$), δ: 29.97, 31.44 (C(C̲H$_3$)$_3$); 34.16, 34.94 (C̲(CH$_3$)$_3$); 40.57 (C̲H$_2$CH=CH$_2$); 61.51, 61.81 (NC̲H$_2$Ar and NC̲H$_2$Py); 99.98, 118.32, 119.71, 122.84, 124.24, 124.57, 125.15, 132.31, 140.61, 142.85, 143.85, 150.62, 170.91 (Py, Ar and C̲H=C̲H$_2$). Found (%): C, 63.72; H, 7.40; N, 3.85. C$_{39}$H$_{55}$N$_2$O$_2$GeBr. Calculated (%): C, 63.61; H, 7.53; N, 3.80.

Synthesis of 6-allyl-6-bromo-4,8-di(*tert*-butyl)-13-ethyl-2,10-dimethyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-germa-dibenzo[*a,f*]cyclodecadiene (6). Freshly distilled allyl bromide (0.8 mL, 9.24 mmol) was added to a solution of compound **2** (0.42 g, 0.90 mmol) in toluene (10 mL) using a syringe. The mixture was stirred for 70.5 h at 70 °C, then the solvent was half evaporated *in vacuo* to decrease the volume to about 2 mL and hexane (2 mL) was added. A precipitate formed was separated from the orange solution, washed with a small amount of a mixture of hexane—toluene (6 : 1), and dried *in vacuo* to obtain compound **6** as a light beige powder. The yield was 0.26 g (49%). ^{1}H NMR (C$_6$D$_6$), δ: 0.35 (t, 3 H, CH$_2$C$\underline{H}_3$, J = 6.8 Hz); 1.73 (s, 18 H, C(C$\underline{H}_3$)$_3$); 2.18 (s, 6 H, C$\underline{H}_3$—Ar); 2.34 (m, 2 H, C$\underline{H}_2$CH$_3$); 2.75 (d, 2 H, C$\underline{H}_2$CH=CH$_2$, J = 7.1 Hz); 3.11, 3.63 (both d, 4 H, NC$\underline{H}_2$Ar, J = 14.4 Hz); 5.02—5.14 (m, 2 H, CH$_2$CH=C$\underline{H}_2$); 6.33 (m, 2 H, H$_{Ar}$); 6.39—6.53 (m, 1 H, CH$_2$C$\underline{H}$=CH$_2$); 7.20 (m, 2 H, H$_{Ar}$). ^{13}C NMR (C$_6$D$_6$), δ: 4.99 (CH$_2\underline{C}$H$_3$); 20.81 ($\underline{C}$H$_3$—Ar); 30.07 (C($\underline{C}$H$_3$)$_3$); 35.18 ($\underline{C}$(CH$_3$)$_3$); 39.46 (br, $\underline{C}$H$_2$CH=CH$_2$); 46.71 ($\underline{C}$H$_2$CH$_3$); 54.55 (br, N$\underline{C}$H$_2$Ar); 117.69, 119.04, 127.27, 128.63, 128.87, 131.98, 140.55, 154.53 (Ar and CH=CH$_2$). Found (%): C, 59.04; H, 7.44; N, 2.33. C$_{29}$H$_{42}$NO$_2$GeBr. Calculated (%): C, 59.12; H, 7.18; N, 2.38.

Synthesis of 6-allyl-6-bromo-2,4,8,10-tetra(*tert*-butyl)-13-(pyridin-2-ylmethyl)-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-stannadibenzo[*a,f*]cyclodecadiene (7). Allyl bromide (0.08 mL, 0.92 mmol) was added to a solution of compound **3** (0.27 g, 0.41 mmol) in toluene (9 mL) using a syringe. After stirring for 66 h at 70 °C, a precipitate was formed on the flask bottom. The solution over the precipitate was decanted, the solid compound

was washed with toluene (4 mL) and dried to obtain compound **7** as a white solid compound. The decanted solution contained an insertion product as a main compound with a small amount of side difficult to identify compounds. The yield was 0.16 g (50%). ^{1}H NMR (CDCl$_3$), δ: 1.25, 1.45 (both s, 36 H, C(CH$_3$)$_3$); 2.95 (d, 2 H, C$\underline{H}_2$CH=CH$_2$, J = 12.8 Hz); 3.02—3.11, 3.49—3.56, 3.78—3.85, 4.56—4.62, 5.01—5.07, 6.03—6.09 (all m, 6 H, 3 NC$\underline{H}_2$); 5.13—5.15 and 5.32—5.35 (both m, 2 H, CH$_2$CH=C$\underline{H}_2$); 6.50—6.52 (m, 1 H, Ar); 6.50—6.58 (m, 1 H, CH$_2$C$\underline{H}$=CH$_2$); 6.82—6.85 (m, 2 H, Ar); 6.99 (d, 1 H, Py, J = 7.9 Hz); 7.12—7.16 (m, 1 H, Py); 7.27—7.29 (m, 1 H, Ar); 7.57—7.61 (m, 1 H, Py); 8.30 (d, 1 H, Py, J = 5.1 Hz). ^{13}C NMR (CDCl$_3$), δ: 29.71, 31.65 (C($\underline{C}$H$_3$)$_3$); 34.70, 35.16 ($\underline{C}$(CH$_3$)$_3$); 38.03 ($\underline{C}$H$_2$CH=CH$_2$); 59.10, 63.03 (N$\underline{C}$H$_2$Ar, N$\underline{C}$H$_2$Py); 114.75, 122.79, 124.02, 124.18, 124.23, 124.32, 124.50, 124.68, 136.18, 140.03, 145.33, 150.86 (Ar and Allyl). One signal for the carbon atom (an aromatic or at the double bond) is absent in the spectrum. ^{119}Sn NMR (CDCl$_3$), δ: −528.49. ESI-HRMS, found (%): [M − Br]$^+$ = 703.3251. Calculated (%): [M − Br]$^+$ = = 703.3280.

Synthesis 6-allyl-6-bromo-4,8-di(*tert*-butyl)-13-ethyl-2,10-dimethyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-stannadibenzo-[*a,f*]cyclodecadiene (8). Freshly distilled allyl bromide (0.13 mL, 1.4 mmol) was added to a solution of compound **4** (0.36 g, 0.70 mmol) in toluene (15 mL) using a syringe. The mixture was stirred for 120 h at 70 °C, a yellow solution obtained was concentrated. The residue was recrystallized from toluene, filtered through the layer of celite, the filtrate was concentrated. The compound was isolated as a yellowish green solid residue, which,

Table 3. Details of X-ray diffraction studies of compounds **4**, **5**, and **7**

Compound	4	5	7
Molecular formula	C$_{26}$H$_{37}$N$_1$O$_2$Sn$_1$	C$_{39}$H$_{55}$Br$_1$Ge$_1$N$_2$O$_2$	C$_{39}$H$_{55}$Br$_1$N$_2$O$_2$Sn$_1$
F*w*	514.26	736.35	782.45
Crystal size/mm	0.30×0.25×0.20	0.38×0.10×0.10	0.30×0.20×0.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Temperature/K	150	183	150
Space group	$P2_1/n$	$C2/c$	$Pna2_1$
a/Å	9.2668(5)	29.278(3)	12.4165(8)
b/Å	11.5055(6)	12.5632(12)	22.5676(14)
c/Å	23.4166(13)	21.963(2)	13.7922(9)
β/deg	95.1405(8)	108.910(2)	90
V/Å^3	2486.6(2)	7642.5(13)	3864.7(4)
Z	4	8	4
d_{calc}/g cm^{-3}	1.374	1.280	1.345
μ/mm^{-1}	1.048	1.881	1.728
F(000)	1064	3088	1616
θ Range of scanning	2.30—30.00	2.46—26.00	2.38—29.00
Number of reflections			
measured	29335	32782	42407
independent (R_{int})	7239	7523	10204
with $I \geq 2\sigma(I)$	6790	6311	9777
Number of refined parameters	280	418	449
R_1 [$I \geq 2\sigma(I)$]	0.0225	0.0264	0.0198
wR_2 (for all reflections)	0.0547	0.0685	0.0457
Reliability on F^2	1.115	1.031	1.035
Residual electron density (max/min)/e Å^{-3}	0.549/−0.769	0.478/−0.314	0.526/−0.274

according to the spectrum, contained a considerable amount of the ligand and the insertion product **8**. An analytically pure sample cannot be obtained because of the hydrolytic instability of the product. The yield of the solid residue was 0.3 g. ^{1}H NMR of compound **8** (C_6D_6), δ: 0.38 (t, 3 H, CH$_2$CH$_3$, *J* = 7.0 Hz); 1.66 (s, 18 H, C(CH$_3$)$_3$); 2.24 (s, 6 H, CH$_3$—Ar); 2.53—2.64 (m, 2 H, CH$_2$CH$_3$); 2.69—2.79 (m, 2 H, CH$_2$CH=CH$_2$); 3.01, 3.90 (both d, 4 H, NCH$_2$Ar, *J* = 13.7 Hz); 5.06 (d, 1 H, CH$_2$CH=CH$_2$, *J* = 10.6 Hz); 5.24 (d, 1 H, CH$_2$CH=CH$_2$, *J* = 17.2 Hz); 6.24—6.35 (m, 1 H, CH$_2$CH=CH$_2$); 6.42 (d, 2 H, Ar, *J* = 1.6 Hz); 7.25 (d, 2 H, Ar, *J* = 2.4 Hz).

X-ray diffraction study of compounds 4, 5, and 7 was carried out on a Bruker SMART APEX II automated diffractometer (Mo-*K*α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan technique). Crystals of **4** were obtained by a slow evaporation of the solvent from the solution in a mixture of toluene—hexane, crystals of **5** from the solution in a mixture of THF—toluene, crystals of **7** from a solution in toluene. Correction for absorption was made based on the measurements of equivalent reflection intensities.[21] The structures were solved by direct method; all the nonhydrogen atoms were refined by the full-matrix least squares method with anisotropic parameters with respect to F^2 (SHELXTL[22]). In compound **7**, the *tert*-butyl group C(18)Me$_3$ was found to be rotationally disordered over two position with the ratio of occupancies 0.54/0.46. This group was refined imposing limitations on the C—Me distances (SADI). In all the structures, all the hydrogen atoms were placed in calculated positions and refined using a riding scheme. The experimental details are given in Table 3.

The structures **4**, **5**, and **7** were deposited with the Cambridge Crystallographic Data Center (CCDC 1517031, 1517033, and 1517032, respectively).

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