

Reviews

Tetrylenes based on tri- and tetradentate ONO-, NNO-, NNN-, and ONNO-type ligands: synthesis, structure, and reactivity*

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The review discusses the results of the authors' research aimed at the synthesis of stable tetrylenes (germylenes and stannylenes) and the determination of the structure of these compounds, including their oligomeric degree. Substituted dialkanolamines, dialkylenetriamines, aminobisphenols, pyridine and phenanthroline-containing dialcohols, and some other derivatives were used as the ligands for the synthesis. The reactivity of monomeric and dimeric tetrylenes in the reactions proceeding with both the change and the retention of the oxidation state of the metal atom (2+) is discussed in detail, as well as the influence of the oligomeric degree on the reactivity. The use of tetrylenes in synthetically useful reactions as ligands for catalytically active transition metal complexes, as well as initiators for ring-opening polymerization of cyclic esters, is analyzed.

Key words: germanium, tin, germylenes, stannylenes, tetrylenes, ring-opening polymerization, X-ray diffraction analysis, NMR spectroscopy, cross-coupling.

In 1916, G. N. Lewis formulated the so-called "octet rule", which states that atoms of non-transition elements when forming bonds in a molecule tend to form an 8-electron valence shell through sharing electrons.¹ Since compounds containing atoms with the number of valence electrons less than 8 tend to increase this number, they are extremely reactive. Among such compounds, a special

place is taken by tetrylenes (the name comes from the word "tetrel" meaning the heavy analogs of carbon and the suffix "ylene" meaning a group 14 divalent atom), derivatives of group 14 elements in the formal oxidation state 2+. The existence of heavy analogs of carbenes (carbenes themselves are not the subject of this review) as stable compounds, which can be handled under conditions typical for organometallic compounds (at least for Si and Ge) has been disputed for a long time. Of course, the simplest inorganic compounds of germanium and tin in

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the oxidation state 2+ have been known for a long time (all of them have a polymer structure in the solid phase),^{2,3} while compounds of lead in the oxidation state 2+ are more stable than those in the oxidation state 4+. Note that lead derivatives, as well as carbon compounds, differ significantly in their properties from the derivatives of the central triad of this group, namely, silicon, germanium, and tin. Stable compounds of group 14 divalent elements with organic substitutes were mentioned for the first time in 1956 when dicyclopentadienyltin (Cp_2Sn)³ was synthesized in the E. O. Fisher group. However, a breakthrough research study in the field of molecular tetrylenes became a series of works of the M. F. Lappert group on the synthesis of $\text{M}[\text{CH}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Sn}, \text{Pb}$),⁴ $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$, and $\text{M}[\text{N}(\text{SiMe}_3)(\text{CMe}_3)]_2$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$)⁵ published in 1970s. From this point on, the study of derivatives of group 14 metals in a low-valent state has become a broad area of research in modern chemistry. There is a fairly large number of review papers on this subject, which, however, either were published quite a long time ago,^{6–12} or consider only one of the sections of this field of chemistry.^{13–21} The number of publications on heavy analogs of carbenes has long exceeded a thousand, which makes it impossible to overview all sections of this field of chemistry at the present time.

It is known that tetrylenes are present as intermediates in many reactions of silicon, germanium, and tin derivatives. In certain cases, they may be stable enough to be handled at room temperature with the usual precautions used in organometallic chemistry. The use of various ligands to increase the stability of heavy carbenes has been under intensive study, and over the past three decades the factors stabilizing a low-valent center have been established: this is either the presence of bulky substituents near the low-valent center (kinetic stabilization), or the donation of electron density to the vacant orbital of the group 14 metal atom (thermodynamic stabilization) both through the transannular interaction, and in the case when the atom of the element is directly bonded to the heteroatom containing an unshared electron pair (*i.e.*, the ligand is an n - or a π -donor).^{11,12}

As mentioned above, tetrylenes are highly reactive. They are characterized by several types of reactions, which proceed with both the change in the formal oxidation state (usually from 2+ to 4+) and the retention of the oxidation state 2+. The first type of reactions are oxidative addition (the insertion of a metal atom into a σ -bond),²¹ [1+2] and [1+4] cycloaddition.^{7,9} A typical example of the reaction with retention of the oxidation state is the formation of a complex with a group 14 element \rightarrow transition metal bond, in which tetrylene acts as a Lewis base, donating the lone pair of electrons of the group 14 atom to the vacant orbital of the transition metal atom.^{18–20} A large number of nucleophilic substitution reactions at the group 14 element atom are also known.¹⁷ A special type of tetrylene reactions

is the dimerization with the formation of a $\text{M}=\text{M}$ double bond, which is often a combination of two dative bonds, and in such cases the dimerization is reversible.¹³ It should be noted that the nature of substituents bonded to the group 14 element atom has a critical effect on both the structure of tetrylene and its chemical properties.

The review analyzes the results obtained by the authors over the last 10 years in the field of synthesis, studies of the structure and reactivity of germynes and stannylenes based on the tri- and tetradentate ONO- , NNO- , NNN- , and ONNO- type ligands.^{22–37} In addition, we also present comparative data on related derivatives.

1. Synthesis of tetrylenes

Our research was focused on the synthesis and study of properties of tetrylenes based on the ligands bound to the metal atom by two covalent bonds through oxygen and/or nitrogen atoms and capable of forming one or two more intramolecular coordination bonds. Such ligands, on the one hand, provide sufficient stabilization of the low-valent center, and on the other hand, leave the possibility for its attack by various reagents.

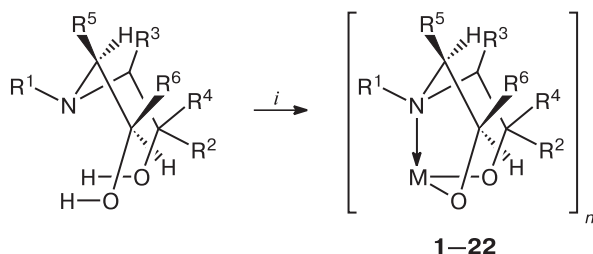
1.1. The N, O, O-type ligands*

The most common ligands of this type are diethanolamines. For the synthesis of tetrylenes on their basis, the most suitable is the reaction of Lappert's tetrylenes, $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$,⁵ with free ligands, which under mild conditions (a prolonged mixing in toluene at room temperature) leads to the target products usually in high yields. The synthesis of germynes **1–13** and stannylenes **14–22** based on substituted diethanolamines is presented^{24,26} in Scheme 1.

The yields in this case are 29–96 and 40–94% for germanium and tin derivatives, respectively. Such a broad range of values is associated with the ligand structure and the solubility of a particular product under the isolation and purification conditions. The yield of germylene is almost always lower than the yield of the corresponding stannylene, which is obviously explained by the greater thermodynamic stability of the latter. It should be noted that one germylene (**2**)³⁸ and two stannylenes (**14** and **15**)³⁹ (see Scheme 1) were synthesized before the beginning our research: germylene **2** was obtained by treatment of $\text{Ge}(\text{OC}_2\text{H}_5)_2 \cdot x\text{C}_2\text{H}_5\text{OH}$ with a free ligand,³⁸ while stannylenes **14** and **15**, like related $\text{Sn}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ ($\text{R} = \text{H}, \text{Et}, \text{Bu}$), were obtained from $\text{Sn}(\text{OR}')_2$ ($\text{R}' = \text{Me}, \text{Bu}$)³⁹ or from SnCl_2 by treatment with the ligand disodium salt (**14** and $\text{Sn}(\text{OCH}_2\text{CH}_2)_2\text{NBu}^{\text{I}}$).⁴⁰

* Here and below the underlined is an atom capable of forming only a coordination bond with a metal atom.

Scheme 1



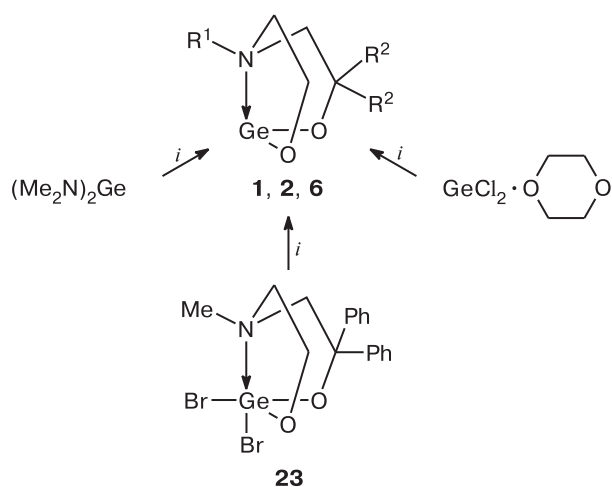
M = Ge (**1–13**), Sn (**14–22**); $n = 1, 2$

Compound	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	Isomer
1, 14	Me	H	H	H	H	H	—
2, 15	Ph	H	H	H	H	H	—
3, 16	Bn	H	H	H	H	H	—
4, 17	Me	H	H	Me	H	H	—
5, 18	Me	H	H	Ph	H	H	—
6, 19	Me	Ph	H	Ph	H	H	—
7, 20	Me	Ph	Ph	H	H	H	<i>erythro</i>
8	Me	Ph	Ph	H	H	H	<i>threo</i>
9	Me	Ph	Ph	H	Ph	Ph	<i>erythro</i> , <i>threo</i>
10, 21	Me	Ph	H	Ph	(S)-Me	(R)-Ph	—
11	Me	C ₃ H ₆	H	H	H	H	<i>threo</i>
12, 22	Me	C ₄ H ₈	H	H	H	H	<i>threo</i>
13	Me	CH ₂ (C ₆ H ₄)	H	H	H	H	<i>threo</i>

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C, 24 h (M = Ge, Sn).

In addition to the methods described above, we studied several alternative approaches to the target dialkanolamine-based germlylenes (Scheme 2).²⁶

Scheme 2



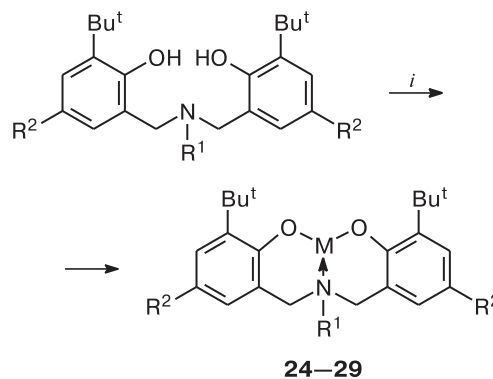
R¹ = Me, R² = H (**1**); R¹ = Ph, R² = H (**2**); R¹ = Me, R² = Ph (**6**)

Reagents and conditions: *i.* MeN(CH₂CH₂OH)₂, toluene, 20 °C (for **1**); PhN(CH₂CH₂O)₂GeMe₂, toluene, 20 °C (for **2**); K₂C₈, THF, 20 °C (for **6**).

The use of Ge(NMe₂)₂ instead of Lappert's germlylene gives germlylene **1** in almost the same yield (92% instead of 89%), however, here one should take into account the much lower availability of Ge(NMe₂)₂ as compared to Lappert's germlylene. A rather unusual reaction leading to germlylene **2** in 60% yield is the treatment of Me₂Ge(OCH₂CH₂)₂NPh with germanium dichloride dioxanate. The driving force of this reaction is the formation of intramolecular and intermolecular donor-acceptor interactions in compound **2** (see Section 2); note that such bonds are absent in Me₂Ge(OCH₂CH₂)₂NPh. It was shown that dibromogermocane **23** is reduced by potassium naphthalenide, giving germlylene **6**, but the yield is relatively low in this case, too (66%). Besides, the last two reactions are of limited use because of the poor availability of starting materials.

Thus, the most convenient method for the synthesis of tetrylenes based on the ONO ligands is the alkoxydeamination reaction of Lappert's tetrylene by a free ligand. This was the approach used for the synthesis of Ge, Sn, and Pb derivatives **24–29** based on aminobisphenols (Scheme 3)³³ and germlylenes and stannylenes **30–35** based on 2,6-bis(hydroxyalkyl)pyridines (Scheme 4).²² The yields were 42–79 and 31–74%, respectively. Such tetrylenes were unknown earlier. The yields of derivatives **34** and **35** based on unsymmetric dialcohol turned out to be much lower than for the symmetric ligands. Apparently, in this case, due to the different steric and electronic properties of CR₂OH and CR'₂OH groups, intermolecular processes which do not lead to the target product can compete with intramolecular cyclization.

Scheme 3

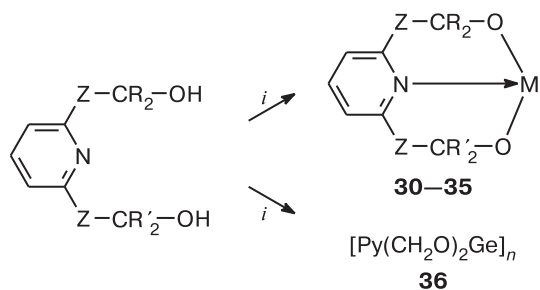


Compound	M	R ¹	R ²	Compound	M	R ¹	R ²
24	Ge	Et	Me	27	Sn	Et	Bu ^t
25	Ge	Et	Bu ^t	28	Pb	Et	Me
26	Sn	Et	Me	29	Pb	Et	Bu ^t

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C (M = Ge, Sn, Pb).

Note that compound **36** is insoluble in the used organic solvents and, apparently, is a polymeric product

Scheme 4



Compound	M	Z	R	R'	Compound	M	Z	R	R'
30	Ge	—	Ph	Ph	33	Sn	—	Ph	Ph
31	Ge	CH ₂	Ph	Ph	34	Sn	CH ₂	Ph	Ph
32	Ge	CH ₂	Ph	Me	35	Sn	CH ₂	Ph	Me

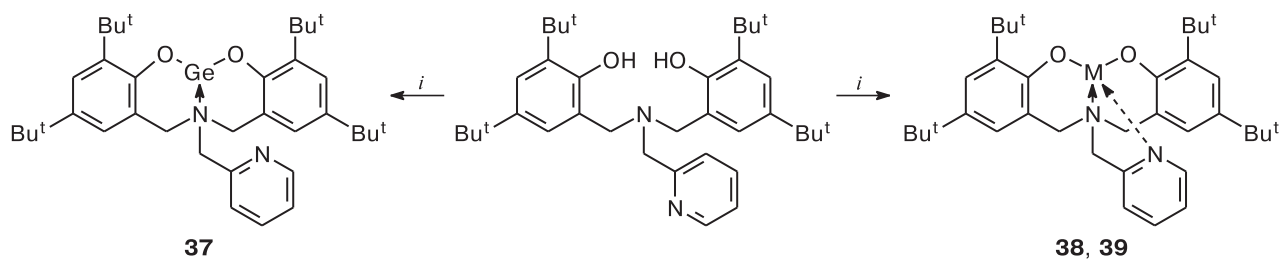
Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C (M = Ge, Sn).

[2,6-Py(CH₂O)₂Ge]_n. Moreover, this derivative is not a coordination polymer, since it does not react with bromine, which should lead to a Ge(4+) derivative.

1.2. The N,N,O,O-type ligands

One of the important moments in the chemistry of tetrylenes is their oligomeric degree (see Section 2). Derivatives based on the N,O,O-type ligands quite often exist in the form of dimers. In order to reduce the tendency of tetrylenes to dimerization, we synthesized derivatives based on the N,N,O,O-type ligands of two classes: tetrylenes **37–39** derived from aminobisphenol containing a 2-pyridylmethyl substituent (Scheme 5)³³ and germynes and stannylenes **40–51** derived from 2,9-bis-(hydroxyalkyl)phenanthrolines (Scheme 6).^{35,36} The yields were 67–87 and 37–65%, respectively.

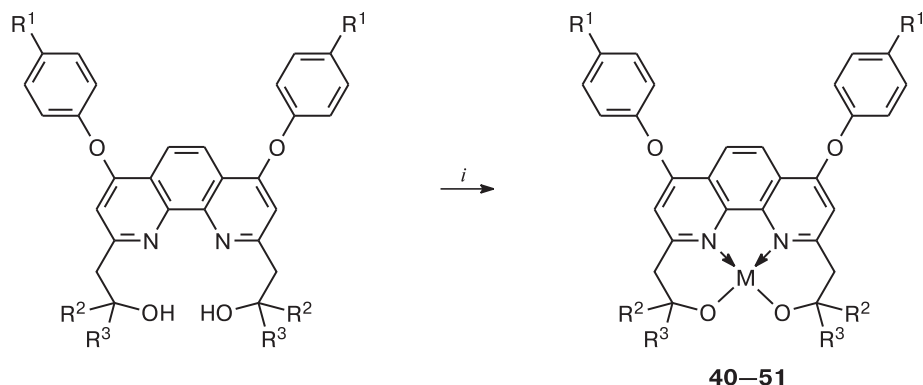
Scheme 5



M = Sn (**38**), Pb (**39**)

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C (M = Ge, Sn, Pb).

Scheme 6

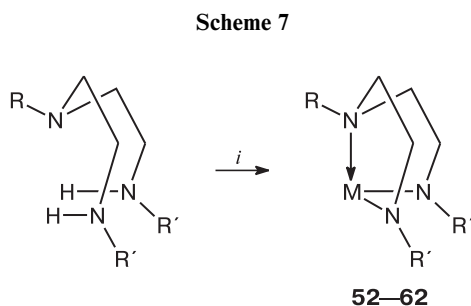


Compound	M	R ¹	R ²	R ³	Compound	M	R ¹	R ²	R ³	Compound	M	R ¹	R ²	R ³
40	Ge	Me	Me	Me	44	Ge	Bu ^t	(CH ₂) ₅		48	Sn	Bu ^t	Ph	Ph
41	Ge	Bu ^t	Me	Me	45	Ge	Me	2,2-adamantylene		49	Sn	Me	(CH ₂) ₅	
42	Ge	Bu ^t	Ph	Ph	46	Sn	Me	Me	Me	50	Sn	Bu ^t	(CH ₂) ₅	
43	Ge	Me	(CH ₂) ₅		47	Sn	Bu ^t	Me	Me	51	Sn	Me	2,2-adamantylene	

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C (M = Ge, Sn).

1.3. The *N,N,N*- and *S,N,N*-type ligands

Substituted diethylenetriamines (1,3,5-trisubstituted 1,3,5-triazaheptans) capable of forming two covalent bonds and one coordination bond with a metal atom are one of the most commonly used classes of ligands in coordination chemistry. Their advantage is that the metal atom is directly bonded to three nitrogen atoms, the variation of substituents on which allows one to alter both the electronic properties of the central atom and its steric availability (it should be noted that the synthesis of diethylenetriamines containing substituents differing in electronic properties and sizes is possible, although in some cases it poses a problem). The synthesis of tetrylenes **52**–**62** based on the indicated ligands is presented in Scheme 7.



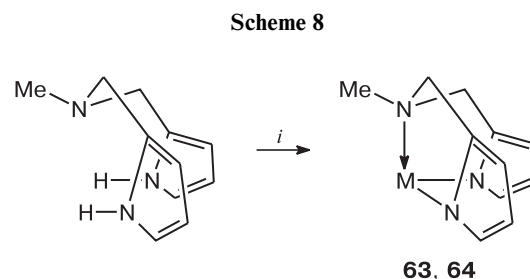
Compound	M	R	R'	Compound	M	R	R'
52	Ge	Me	C ₆ F ₅	58	Sn	Me	C ₆ F ₅
53	Ge	Bn	C ₆ F ₅	59	Sn	Bn	C ₆ F ₅
54	Ge	Bn	Ts	60	Sn	Bn	Ts
55	Ge	Bn	Mes	61	Sn	Bn	Mes
56	Ge	Bn	SiMe ₃	62	Sn	SiMe ₃	SiMe ₃
57	Ge	SiMe ₃	SiMe ₃				

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C, 24 h (M = Ge, Sn).

Substituents R' range from donor (mesityl and SiMe₃) to acceptor groups (tosyl and pentafluorophenyl). Compounds **52**–**62** were synthesized by transamination of Lappert's tetrylene with a free ligand.^{27,29,37} The yields vary from 18 to 91% and strongly depend on the nature of substituents on the terminal nitrogen atoms of the ligand: acceptor substituents increase the acidity of the NH groups, which greatly increases the yield.

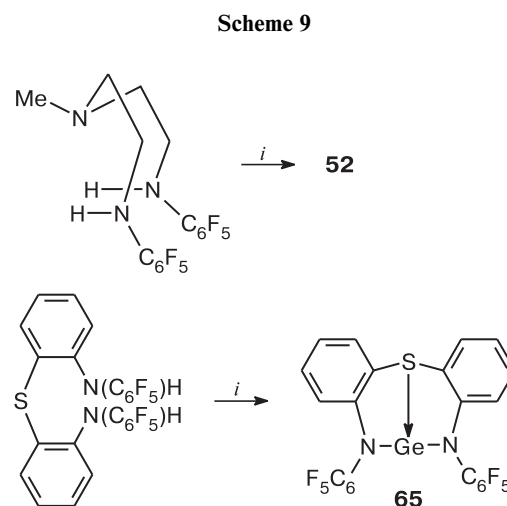
A similar transamination reaction was used to obtain related derivatives **63** and **64** based on a dipyrrole compound (Scheme 8).^{27,29} The yields were 36 and 46%, respectively.

An alternative pathway for the synthesis of tetrylenes based on diamidoamine ligands, which consists in the treatment of MHal₂ with the ligand dilithium salt generated *in situ*, was tested on the example of germylene **52** (Scheme 9).²⁷



M = Ge (**63**), Sn (**64**)

Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C (M = Ge, Sn).



Reagents and conditions: *i.* 1) LiN(SiMe₃)₂·Et₂O, THF, –78 °C, 1 h, 20 °C; 2) GeCl₂·C₄H₈O₂, THF, –78 °C, 24 h, 20 °C.

However, this approach gives the target product in a lower yield (24%), including due to the necessity to purify it from the liberated salt. In addition, attempted synthesis of compound **65** by transamination did not give the target product (the spectrum showed the presence of only the signals of the starting compounds even after prolonged reflux), while germylene **65** was isolated in 67% yield when germanium dichloride dioxanate was treated with the ligand dilithium salt.²⁷

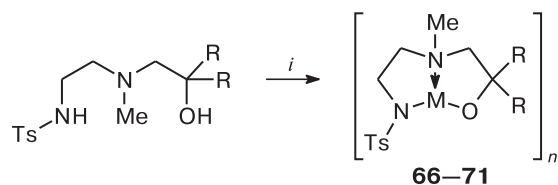
1.4. The *N,N,O*-type ligands

Asymmetric ligands, namely, amino alcohols containing NH and OH groups also were used for the synthesis of tetrylenes. The Lappert's tetrylenes treated with free ligands gave³¹ germylenes **66** and **67**, stannylenes **68** and **69**, plumbylenes **70** and **71** (Scheme 10).

The yields in all cases are good enough (67–90%), which correlates with the relatively high acidity of the N(Tos)H group.

Thus, it can be concluded that the most suitable method for the synthesis of tetrylenes of the indicated

Scheme 10



M = Ge, R = H, $n = 1$ (**66**); M = Ge, R = Ph, $n = 1$ (**67**);
 M = Sn, R = H, $n = 2$ (**68**); M = Sn, R = Ph, $n = 1$ (**69**);
 M = Pb, R = H, $n = 2$ (**70**); M = Pb, R = Ph, $n = 1$ (**71**)

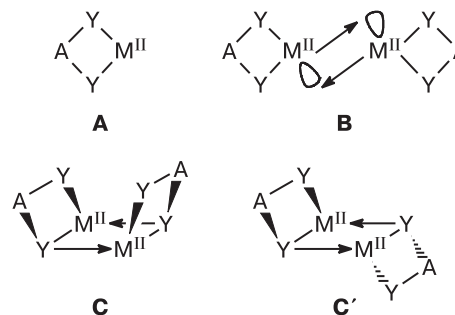
Reagents and conditions: *i.* M[N(SiMe₃)₂]₂, toluene, 20 °C, 12 h.

types is the treatment of Lappert's tetrylene with a free ligand.

2. Structure of tetrylenes

The main structural question arising in the analysis of the structure of relatively stable tetrylenes is the oligomeric degree of the molecule. From general considerations confirmed by quantum chemical calculations for the simplest germylenes and stannylenes, it follows that tetrylenes can exist in the form of three different structures (A–C), in which the oxidation state of +2 is retained for each atom of element M.

Compounds of the types indicated in the review exist either as monomeric molecules (A), in which one or two additional metal–N(S) intramolecular bonds are present, stabilizing the low-valent center, or as dimeric molecules, in which a metal–N(S) intramolecular bond is present in



each monomeric cell, and the dimerization occurs due to the formation of two additional interactions between metal atoms and Y heteroatoms bonded to the metal atom (C). This conclusion was also made based on the data obtained by DFT studies of the structure of a large set of compounds.²³ It was found that one of two possible dimers C, in which dimerization is realized due to the formation of an additional interaction between the metal atom and the oxygen (nitrogen) atom of the other monomeric cell, is the most stable for the majority of compounds. Quantum chemical calculations showed that the existence of type B dimers due to the formation of a metal–metal bond is almost impossible for these structures. The main factor affecting the comparative stability of the monomer or dimers is the steric size of the ligand: its reduction causes the dimerization of tetrylenes.

The experimental study of the structure of the synthesized compounds was performed by X-ray diffraction (solid phase) and NMR spectroscopy (including ¹¹⁹Sn and ²⁰⁷Pb NMR). The data on the main structural parameters of tetrylenes obtained by X-ray diffraction are given in Table 1.

Table 1. Tetrylenes, whose structure was studied by X-ray diffraction

Compound	Ligand type	CN ^a	Oligomeric degree	Coordination type ^b	M	Ref.
1	Diethanolamine	4	Dimer	<u>O</u> ONO	Ge	26
2	Diethanolamine	4	Dimer	<u>O</u> ONO	Ge	26
6	Diethanolamine	4	Dimer	<u>O</u> ONO	Ge	26
10	Diethanolamine	3	Monomer	<u>O</u> NO	Ge	26
14	Diethanolamine	4	Dimer	<u>O</u> ONO	Sn	24
32	2,6-Bis(2-hydroxyethyl)pyridine	3	Monomer	<u>O</u> NO	Ge	22
34	2,6-Bis(2-hydroxyethyl)pyridine	4	Dimer	<u>O</u> ONO	Sn	22
26	Aminobisphenol	3	Monomer	<u>O</u> NO	Ge	32
37	Aminobisphenol	3	Monomer	<u>O</u> NO	Ge	32
38	Aminobisphenol	4	Monomer ^c	<u>O</u> NNO	Sn	32
53	Diethylenetriamine	3	Monomer	<u>N</u> NN	Ge	27
58	Diethylenetriamine	3	Monomer	<u>N</u> NN	Sn	29
59	Diethylenetriamine	3	Monomer	<u>N</u> NN	Sn	29
66	(2-Hydroxyethyl)ethylenediamine	3	Monomer	<u>N</u> NO	Ge	31
70	(2-Hydroxyethyl)ethylenediamine	4	Dimer	<u>N</u> NOO	Pb	31
71	(2-Hydroxyethyl)ethylenediamine	3	Monomer	<u>N</u> NO	Pb	31

^a Coordination number of atom M.

^b The underlined atom is bound to the metal atom by a coordination bond.

^c The ligand contains an additional Py group.

As noted above, the oligomeric degree of tetrylene depends, first of all, on the ligand size, especially on the size of the part which is bonded to the metal atom, and also on the metal nature. Among the compounds under study, stannylenes are more prone to dimerization. Thus, sterically nonbulky ligands in germylenes **1**, **2**, and **6** do not interfere with the dimerization in the solid phase of tetrylene, while the related germylene **10** based on more substituted dialkanolamine is monomeric in the solid phase. Germylene **32** based on substituted 2,6-bis(2-hydroxyethyl)pyridine is monomeric, while stannylene **34** based on even bulkier ligand is dimeric. All the studied tetrylenes based on diethylenetriamines and aminobisphenols, which contain bulky groups in close proximity to the metal atom, are monomeric.

The coordination polyhedron of the central atom for tricoordinated derivatives is a distorted tetrahedron, in which one of the coordination positions is occupied by a metal atom lone pair of electrons having a pronounced *s*-character. The coordination polyhedron of metal atoms in dimers is a distorted trigonal bipyramid, in which two substituents covalently bonded to the metal atom and the lone pair electrons occupy equatorial positions.

The ^{119}Sn NMR spectroscopy is a fairly convenient tool allowing one to determine the coordination number of this atom and, therefore, analyze the structure of tetrylene in solution. However, the chemical shift value of the tin atom even with the same coordination number is very sensitive to both the nature of the atoms bonded to it and the solvent nature,⁴¹ which should be taken into account in such an analysis. The chemical shift values of the tin

atom in the stannylenes studied in our works are given in Table 2. Based on the known data (see, for example, Ref. 35), a conclusion on the oligomeric degree in solution of the synthesized stannylenes was drawn.

The structure of plumbylene **71** in solution was studied by ^{207}Pb NMR spectroscopy. According to the data obtained, the compound contains a tetracoordinated lead atom.³¹ The oligomeric degree can also be studied by DOSY NMR experiment. Two stannylenes (**68** and **69**) and two plumbylens (**70** and **71**) were investigated³¹ in CDCl_3 and DMSO-d_6 solutions. The compounds based on a less bulky ligand in the non-coordinating solvent exist as dimers, while compounds **69** and **71** form monomeric adducts with DMSO-d_6 .

3. Reactivity of tetrylenes

In the study of the reactivity of tetrylenes, we focused on the reactions changing the oxidation state of the central atom. The systematic study of their reactivity was directed on the determination of the influence of structural factors, namely, the oligomeric degree, on the reaction pathways of heavy carbenes.

3.1. Reactions changing the oxidation state of metal atom from 2+ to 4+

This type of reactions can follow three main directions: insertion into a σ -bond, cycloaddition, and oxidation. In all the cases, the central atom increases its oxidation state, and in the reaction products the octet rule for it is abided.

Table 2. The ^{119}Sn NMR spectroscopy data of studied stannylenes

Compound (monomeric cell)	Suggested CN of Sn atom	Oligomeric degree	Coordination type ^a	XRD data	Solvent	δ	Ref.
61	3	Monomer	<u>NNN</u>	—	CDCl_3	33	37
58	3	Monomer	<u>NNN</u>	—	C_6D_6	-126	29, 30
49	4	Monomer	<u>ONNO</u>	—	C_6D_6	-130	36
21	4	Dimer	<u>OONO</u>	—	C_6D_6	-254	24
60	3	Monomer	<u>NNN</u>	—	CDCl_3	-257	37
50	4	Monomer	<u>ONNO</u>	—	CDCl_3	-280	36
14	4	Dimer	<u>OONO</u>	+	CD_2Cl_2	-303	24
18	4	Dimer	<u>OONO</u>	—	C_6D_6	-305	24
69	4	Monomer	<u>OONO</u> ^b	—	DMSO-d_6	-310	33
47	4	Monomer	<u>ONNO</u>	—	C_6D_6	-350	36
51	4	Monomer	<u>ONNO</u>	—	C_6D_6	-365	36
68	4	Dimer	<u>OONO</u>	—	CDCl_3	-363, -379 ^c	33
26	3	Monomer	<u>ONO</u>	+	C_6D_6	-420	31, 32
27	3	Monomer	<u>ONO</u>	—	C_6D_6	-423	31
35	4	Dimer	<u>OONO</u>	—	THF-d_8	-444	22
48	4	Monomer	<u>ONNO</u>	—	C_6D_6	-448	35
34	4	Dimer	<u>OONO</u>	+	C_6D_6	-486	22
38	4	Monomer	<u>ONNO</u>	+	C_6D_6	-514	31, 32

^a The underlined atom is bound to the tin atom by a coordination bond.

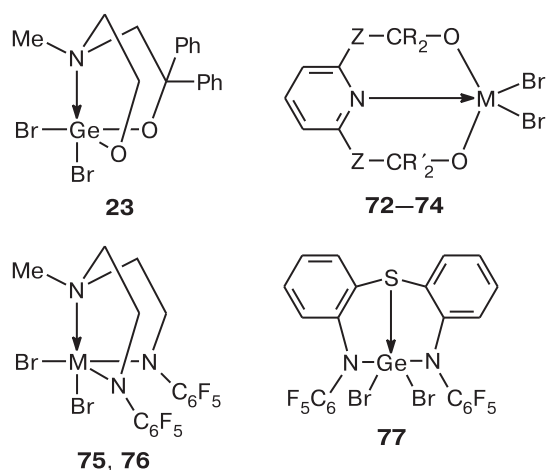
^b Coordination with the oxygen atom of DMSO-d_6 .

^c Two isomers.

3.1.1. Insertion reactions into a σ -bond

The early studies showed that the more electropositive substituents are bonded to the atom of group 14 element, the easier proceeds the insertion reaction.⁴² In general, all the target derivatives synthesized by us contain bonds of the group 14 element with electronegative atoms, which, together with the intramolecular stabilization of the low-valent center present in the tetrylene molecule, can lead to the absence of the indicated reactions. A reaction of tetrylenes with halogens is one of the most studied for all types of these compounds. The reactions were carried out at room temperature. In all the cases studied (Scheme 11), except for compound **36** (see below), the expected dibromides (M^{4+}) were formed.^{22,26,27,29}

Scheme 11



M = Ge, Z is absent, R = R' = Ph (**72**);
 M = Ge, Z = CH₂, R = R' = Ph (**73**);
 M = Sn, Z is absent, R = R' = Ph (**74**);
 M = Ge (**75**), Sn (**76**)

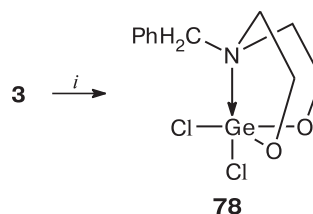
Reagents and conditions: *i.* Br₂, THF (for **23**), toluene (for **72–77**), 20 °C.

Note that the reaction of stannylene **14** with Cl₂, Br₂, and I₂ was described earlier,⁴³ which also led to the expected insertion products. Thus, the oligomeric degree of tetrylene has not a decisive influence on the course of the reaction, both monomeric and dimeric derivatives can be involved in it. At the same time, derivative **36** in the reaction with Br₂ does not give the expected product, which, apparently, confirms its polymeric nature.²² We studied the mechanism of the insertion of tetrylene into the Br–Br bond using DFT quantum chemical calculations.²⁶ The dimeric germanium derivative **1** and the monomer of this compound were chosen as the objects of study. In addition, a dicoordinated germanium derivative, di(*tert*-

butoxy)germylene, was studied for comparison. All the studied reactions are thermodynamically favorable. It should be noted that the bromination of (Bu^tO)₂Ge is accompanied by a greater energy gain than the bromination of monomer **1**. This is obviously due to the stabilizing effect of the additional intramolecular germanium–nitrogen interaction in molecule **1**. The activation energies of these reactions are small and significantly decrease with increasing coordination number of germanium and tin atoms, which correlates with the assumption on the increase in the effective positive charge on the metal atom as the coordination number increases with the oxidation state remaining unchanged. The transition state of the bromination reaction is characterized by the interaction of one of the lone electron pairs of the bromine atom and a suitable orbital of the germanium atom.

Germylene **3** was involved into the reaction with interhalide KICl₂, but the only product with germanium atom isolated from this reaction was dichloride **78** (Scheme 12).²⁶

Scheme 12

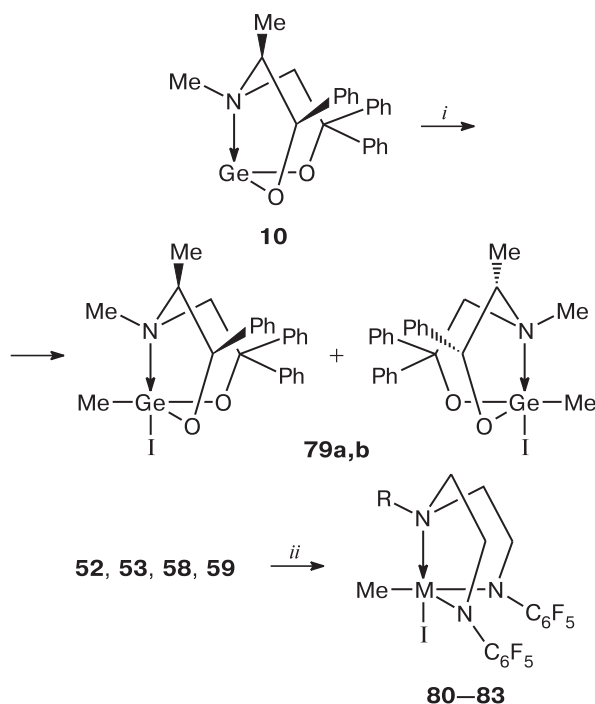


Reagents and conditions: *i.* KICl₂, toluene, reflux, 15 h.

In contrast to the insertion of tetrylenes into the Br–Br bond, a similar reaction with methyl iodide turned out to be more selective (Scheme 13).^{24,26,27,29}

Monomeric derivative of germanium **10** based on di-alkanolamine,²⁶ like germanium and tin monomeric derivatives based on diethylenetriamines,^{27,29} leads to the expected insertion products (derivative **79** is formed as a mixture of two diastereomers). At the same time, dimeric germylene **1** (see Ref. 26) and stannylene **14** (see Ref. 24) do not give the expected insertion products into the C–I bond, rather leading to a mixture of difficult-to-identify products. Earlier, similar results were obtained in the study of dialkoxy(aroxy)- and diamino germylenes and -stannylenes, indicating that the direction of the reaction is determined by the tetrylene structure. Monomeric derivatives in this reaction almost always give the target products. The reaction of the oxidative addition of MeI to the monomeric (2-EtOOC(C₆H₄O))₂Sn was studied, which upon heating for 3 h gave the insertion product.⁴⁴ Monomeric dimesityloxygermylene complexes react similarly with TMEDA⁴⁵ and (Me₂NCH₂CH₂O)₂Ge,⁴⁶ with the latter giving the ionic complex [(Me₂NCH₂CH₂O)₂GeMe]⁺I[–] as the product. It was found⁴⁷ that monomeric sterically hindered

Scheme 13



M = Ge, R = Me (**80**); M = Ge, R = Bn (**81**);
M = Sn, R = Me (**82**); M = Sn, R = Bn (**83**)

Reagents and conditions: *i.* MeI, THF, -60°C . *ii.* MeI, toluene, 20°C .

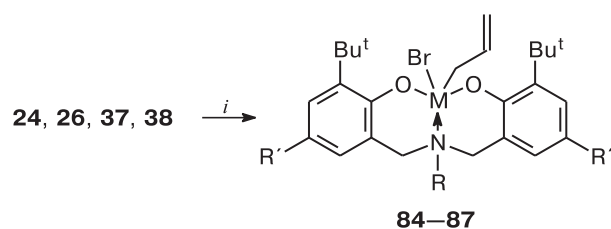
tin alkoxide $(\text{Bu}^t\text{CO})_2\text{Sn}$, containing no additional intramolecular interactions, also undergoes insertion into the C—I bond. Conversely, polymeric $(\text{PhO})_2\text{Sn}$ does not react with methyl iodide upon reflux of the reaction mixture for 7 h.⁴⁴ It should be noted, however, that the monomeric $(\text{ArO})_2\text{Ge}$ ($\text{Ar} = 2,4,6-(\text{Me}_2\text{NCH}_2)_3\text{C}_6\text{H}_2$), which is characterized by the presence of a germanium—nitrogen transannular interaction, adds MeI, but, instead of the expected product, gives a mixture of various insoluble solids, apparently, due to the quaternization of different nitrogen atoms.⁴⁸

It was also found that monomeric tetrylenes based on aminobisphenols undergo insertion into the C—Br bond upon heating with allyl bromide (Scheme 14).³²

The reaction of tetrylenes **1**, **52**, and **58** with Ph_2S_2 was another studied example of the insertion into the σ -bond (Scheme 15).

Analysis of the literature data showed that the reaction with disulfides on the example of dialkoxy(aoxy)- and diamino-tetrylenes, in contrast to the reaction with methyl iodide, is a poorly studied. Monomeric and dimeric derivatives behave differently in the reactions with diphenyl disulfide. Germanium and tin monomeric derivatives (**45**, **46**) undergo this reaction, giving the expected insertion products.^{27,29} Dimeric stannylene **14** under similar conditions gives a mixture of difficult-to-identify prod-

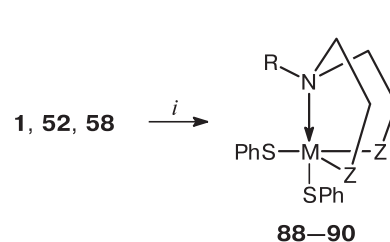
Scheme 14



M = Ge, R = Et, R' = Me (**84**); M = Sn, R = Et, R' = Me (**85**);
M = Ge, R = $\text{CH}_2(2\text{-py})$, R' = Bu^t (**86**);
M = Sn, R = $\text{CH}_2(2\text{-py})$, R' = Bu^t (**87**)

Reagents and conditions: *i.* AllylBr, toluene, $70-80^{\circ}\text{C}$.

Scheme 15



M = Ge, R = Me, Z = O (**88**); M = Ge, R = Bn, Z = NC_6F_5 (**89**);
M = Sn, R = Bn, Z = NC_6F_5 (**90**)

Reagents and conditions: *i.* Ph_2S_2 , THF (for **88**), toluene (for **89**, **90**), -40°C , then 20°C .

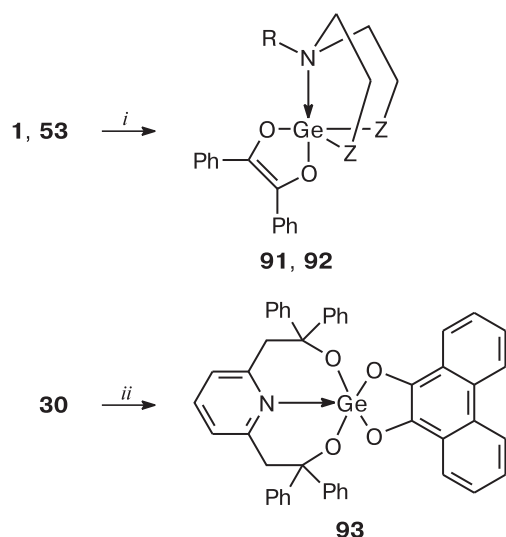
ucts.²⁴ For dimeric germylene **1**, the reaction is complicated by the formation of disproportionation products, including $\text{Ge}(\text{SPh})_4$.²⁶

We found that the structure of disulfide dramatically changes the behavior of germylens and stannylenes in the reactions with these sulfur derivatives: diethyl disulfide is inert in the reactions with germylens **6**, **52** and stannylene **58** (even under UV irradiation).^{26,27,29} This is apparently due to the stronger S—S bond in diethyl disulfide.

3.1.2. Cycloaddition reactions

The [1+4] cycloaddition processes for tetrylenes have been known for a long time, with various organic substrates having a system of two conjugated double bonds being studied in these reactions.^{6,7} We systematically investigated a series of such molecules in order to find out how the structure of the organic substrate affects the direction of the process. The main by-products in these reactions are polymers and/or oligomers. We found that monomeric germylene **53** and dimeric germylene **1** treated with benzil give the expected [1+4] cycloaddition products in satisfactory yields (Scheme 16).²⁶ Monomeric germylene **30** behaves similarly in the reaction with 9,10-phenanthrenequinone.²⁵

Scheme 16



R = Me, Z = O (**91**); R = Bn, Z = NC₆F₅ (**92**)

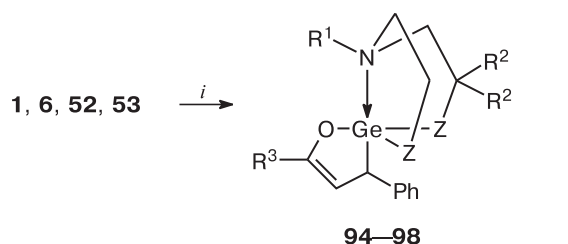
Reagents and conditions: *i.* Benzyl, toluene, 20 °C. *ii.* 9,10-Phenanthrenequinone, toluene, 20 °C.

On the contrary, stannylenes **14** (dimeric) and **59** (monomeric) in the reaction with benzil do not give the expected products.^{24,29} The results similar to those described for the reaction of tetrylenes with benzil were obtained for the reactions with chalcone and its ferrocenyl analog (Scheme 17).^{26,27}

Stannylenes **14** and **59** in the reaction with chalcone and stannylenes **16** and **59** in the reaction with ferrocenylchalcone do not give the expected products.^{24,29} There is no information on successful reactions of alkoxy(amino)stannylenes with chalcone. We believe that the formation of the tin-carbon bonds is unfavorable under the reaction conditions.

Besides, it should be noted that germylene **53** and stannylene **58** in the reaction with Bu^tN=C=C=N Bu^t, as well

Scheme 17



Compound	R ¹	R ²	R ³	Z	Compound	R ¹	R ²	R ³	Z
94	Me	H	Ph	O	97	Me	Ph	Fc	O
95	Me	H	Ph	NC ₆ F ₅	98	Bn	H	Fc	NC ₆ F ₅
96	Me	H	Fc	O					

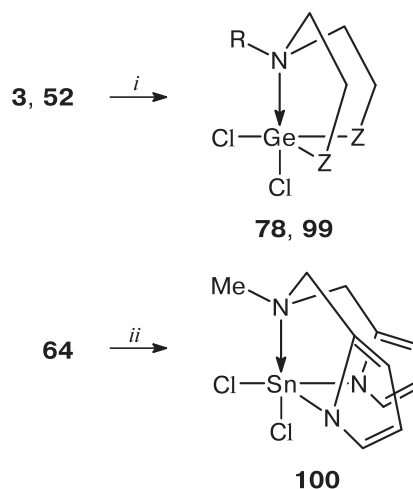
Reagents and conditions: *i.* R³C(O)CH=CHPh, toluene, 20 °C.

as germylene **53** in the reaction with CH₂=CMe—CMe=CH₂ do not give the expected cycloaddition products.^{27,29}

3.1.3. Oxidation reactions

Halogenation of tetrylenes is possible not only with halogens, but also with other halogen-containing derivatives. Examples of such reactions have been reported earlier. Thus, in the reaction of MeN(CH₂CH₂NSiMe₃)₂Sn with bismuth trichloride, the tin atom adds two chlorine atoms, giving tin(4+) dichloride MeN(CH₂CH₂NSiMe₃)₂SnCl₂.⁴⁹ We first studied the reaction of germylenes with GeCl₄. It was found that both monomeric germylene **52** and dimeric germylene **3** give in this reaction derivatives of pentacoordinated germanium in the oxidation state 4+ (Scheme 18).^{26,27} Monomeric stannylene **64** behaves similarly in the reaction with tetrachlorostannane.²⁹

Scheme 18

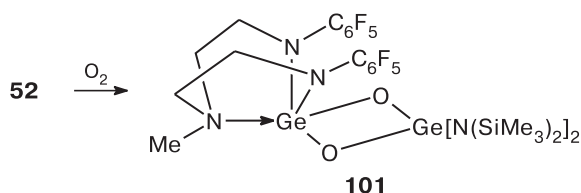


R = Bn, Z = O (**78**); R = Me, Z = NC₆F₅ (**99**)

Reagents and conditions: *i.* GeCl₄, toluene, 0 °C. *ii.* SnCl₄, toluene, 0 °C.

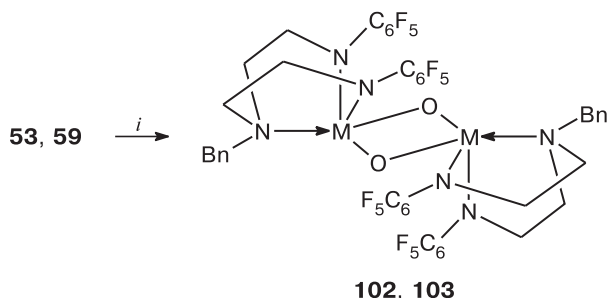
The oxidation reaction of related tetrylenes with molecular oxygen is well studied. Treatment of [(Me₃Si)₂N]₂Ge with O₂ leads to crystalline digermanoxane [{[(Me₃Si)₂N]₂Ge}(μ-O)]₂.⁵⁰ It is believed that this germanoxane is formed by the dimerization of the initially formed germanone. Under similar conditions, Lappert's stannylene gives peroxo complex [{[(Me₃Si)₂N]₂Sn}(μ-O₂)]₂.⁵¹ We were able to detect and confirm by the X-ray diffraction data the formation of compound **101** upon treatment of germylene **52** with oxygen in the presence in the solution of [(Me₃Si)₂N]₂Ge (Scheme 19).²⁷ This experimental fact can serve as evidence of the initial formation of germanones in the oxidation of germylenes with oxygen.

Scheme 19



Recently, trimethylamine oxide is often used as a reactant for the synthesis of reaction products with oxygen. The reaction of monomeric germylene **53** and stannylene **59** with $Me_3N \rightarrow O$ in both cases leads to the expected oxidation products in satisfactory yields, namely, 1,3-cyclo-dimetallloxanes **102** and **103** (Scheme 20),^{27,29} while dimeric germylene **1** and stannylene **14** do not give the expected products. Apparently, one germanium (tin) atom is oxidized at the first stage of the reaction, and sterically close $M(2+)$ and $M=O$ are present in the molecule simultaneously, which leads to polymer products.

Scheme 20



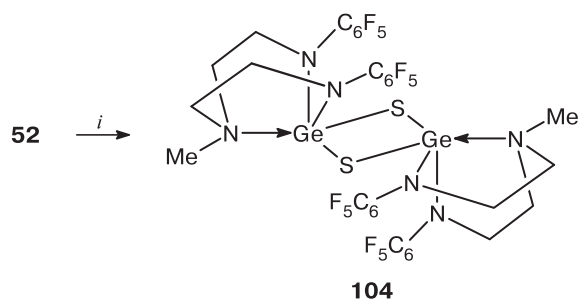
M = Ge (**102**), Sn (**103**)

Reagents and conditions: *i.* $Me_3N \rightarrow O$, toluene, 20 °C.

Among the three derivatives studied in the reaction with elemental sulfur (monomeric germylene **52** (see Ref. 27), dimeric germylene **1** (see Ref. 26), and stannylene **16** (see Ref. 24)), the expected cyclodimer **104** (the structure confirmed by X-ray diffraction) was obtained only from monomeric germylene **52** (Scheme 21). The other compounds do not react with sulfur.

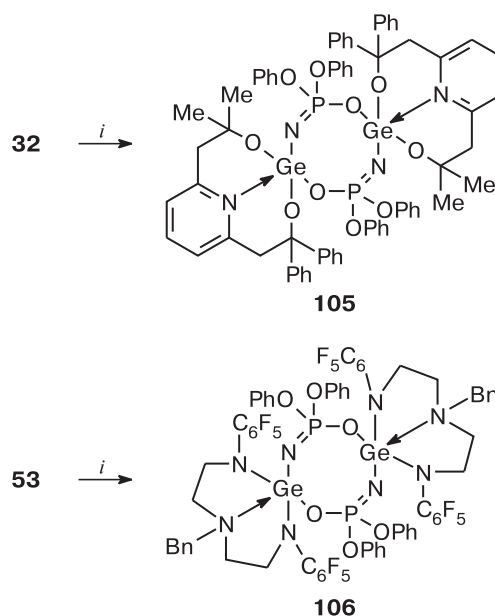
The reaction of azides with diamino- and diaoxygermylenes and stannylenes was the subject of earlier studies.⁴⁸ Monomeric germa- and stannaimines were obtained in good yields in the reaction of $(ArO)_2M$ ($Ar = 2,4,6-(Me_2NCH_2)_3C_6H_2$) with Me_3SiN_3 . We studied the reaction of diphenylphosphorylazide with monomeric germylenes **32** (see Ref. 25) and **53** (see Ref. 27), as well as with dimeric germylene **1** (see Ref. 26) and stannylene **14** (see Ref. 24). The monomeric derivatives react quite easily to give the expected compounds **105** and **106** (Scheme 22). The structure of compound **105** was confirmed by X-ray diffraction.

Scheme 21



Reagents and conditions: *i.* S_8 , THF, 20 °C.

Scheme 22



Reagents and conditions: *i.* $(PhO)_2P(O)N_3$, toluene, 20 °C.

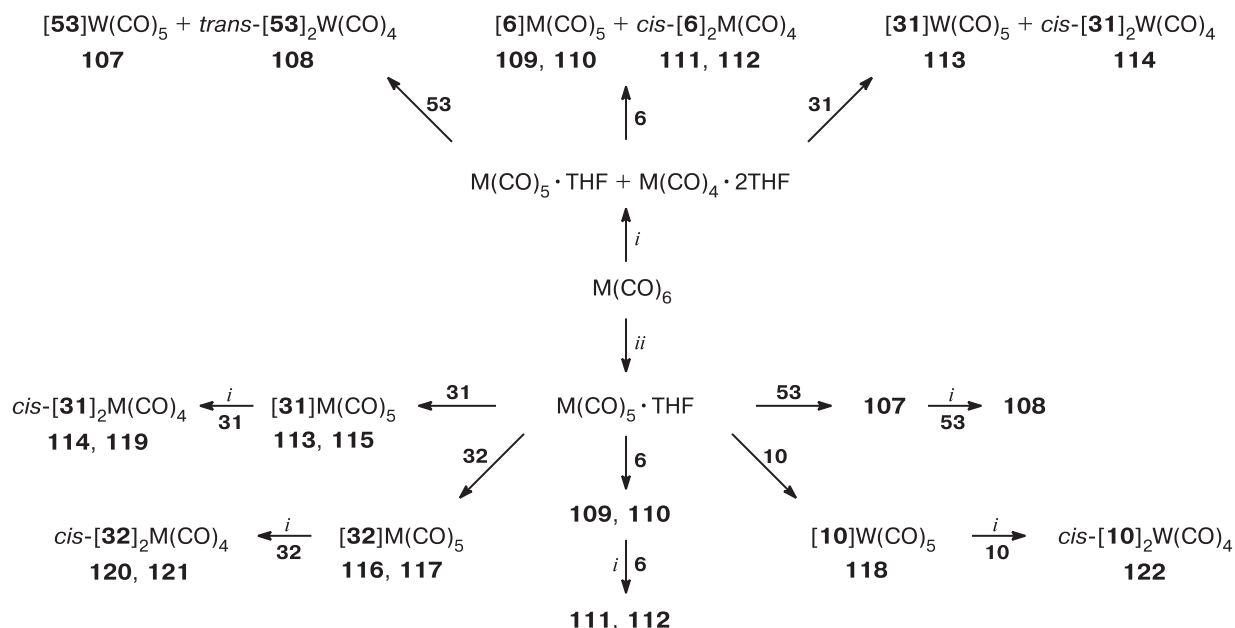
Dimeric germylene **1** and stannylene **14** do not form the expected products in the reaction with $N_3P(O)(OPh)_2$.

3.2. Tetrylenes as ligands in transition metal complexes

Germylenes and stannylenes, having a singlet structure (the presence of a lone electron pair), can be convenient ligands (σ -donors) in transition metal complexes, essentially acting as analogs of such commonly used ligands as phosphines. The studies of complexes containing germylenes and stannylenes as such ligands seemed very promising in cross-coupling reactions, in particular, because it is possible to change the Lewis acidity of germanium and tin atoms in these compounds by varying substituents in the ligand.

We used $M(CO)_5 \cdot THF$ ($M = Mo, W$) (obtained as a solution in THF immediately before use in the reaction) as the starting Mo and W compounds for the synthesis of

Scheme 23



M = W (**109**, **111**, **116**, **120**), Mo (**110**, **112**, **115**, **117**, **119**, **121**)

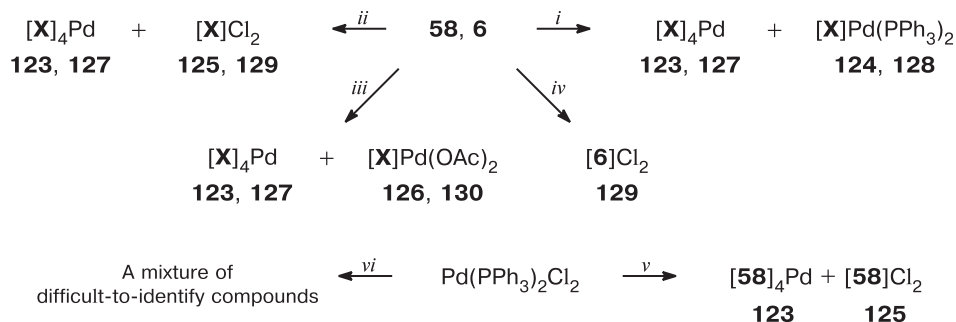
Reagents and conditions: *i*. THF, *hν*, 5 h. *ii*. THF, *hν*, 3 h.

complexes of germynes with group 6 metals. After irradiation of a solution of molybdenum or tungsten hexacarbonyls in THF for 5 h, gerylene was added to the resulting reaction mixture and it was stirred at room temperature (Scheme 23).²⁸ After the reaction completion, both the expected products of monosubstitution of the carbonyl group and the complexes containing two germynes as a ligand were detected in the reaction mixtures. The reason for the formation of digermylene complexes is the presence in the reaction mixture after the irradiation of not only the complexes $\text{M(CO)}_5 \cdot \text{THF}$, but also the unstable complexes $\text{M(CO)}_4 \cdot 2\text{THF}$. It was shown that the synthesized monogermylene complexes can be con-

verted to the digermylene ones by treatment with free germanium ligands under UV irradiation.

The structures of the three complexes, Mo (**119**) and W (**108**, **122**), were studied by X-ray diffraction. It was established that the formation of the complex is accompanied by the shortening of the Ge—O, Ge—N, and Ge←N bonds as compared to free germynes, which is caused by an increase in the Lewis acidity of the germanium atom in the complexes due to the donation of an electron pair to the vacant orbital of the metal atom. Gerylene acts as a base with respect to the transition metal (Mo, W) (σ -donor, stronger than the CO ligand), while the π -accepting ability of the germanium atom is very low.

Scheme 24



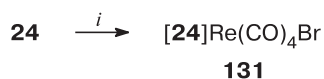
X = **58** (**123**–**126**), **6** (**127**–**130**)

Reagents and conditions: *i*. $\text{Pd}[(\text{PPh}_3)_4]$. *ii*. $\text{trans-PdX}_2\text{Cl}_2$ (X = MeCN, PPh_3). *iii*. Pd(OAc)_2 . *iv*. GeCl_4 , reflux, 10 h. *v*. 5 equiv. of compound **58**. *vi*. 2 equiv. of compound **58**.

By the beginning of our research, there were known three Pd(0) complexes containing stannylene as the ligands (Sn[CH(SiMe₃)₂]₂, Sn[N(SiMe₃)₂]₂) and two complexes containing germylene (Ge[N(SiMe₃)₂]₂).³⁰ In the present work, we investigated the reaction of monomeric stannylene **58** with Pd(PPh₃)₄ (the oxidation state of Pd is 0). The ligand exchange in the coordination sphere of palladium resulted in two compounds: palladium complex **123** with four molecules of stannylene ligands and palladium complex **124** containing one stannylene molecule as a ligand (Scheme 24). The structure **123** was confirmed by X-ray diffraction. Palladium(2+) compounds can also serve as starting agents for the synthesis of stannylene complex **123**. In this case, stannylene **58** acts simultaneously as a ligand in the formation of the palladium(0) complex and as a reducing agent. Similar results were obtained in the reaction of dimeric germylene **6** with palladium derivatives; the structure **127** was confirmed by X-ray diffraction (see Scheme 24).³⁰

The reaction of germylene **24** with Re(CO)₅Br gives complex **131** in moderate yield (Scheme 25), in which, according to the ¹³C NMR spectroscopy and X-ray diffraction data, the germylene ligand and the bromine atom are in the coordination sphere of the rhenium atom (octahedron) in *cis* positions relative to each other.³¹

Scheme 25



Reagents and conditions: *i*. Re(CO)₅Br, toluene, 70 °C, 30 h.

Having in hands palladium complexes containing tetrylenes as ligands, we tested their catalytic activity in the fundamental reactions of modern organic synthesis, the cross-coupling reactions. It is well known that varying the structure and, therefore, the steric and electronic properties of the ligand at the palladium atom directly affects

the catalytic properties of the complex. Palladium(0) tetrastannylene (**123**) and tetragermylene (**127**) complexes were tested by us as catalysts for the cross-coupling of aryl bromides and phenylboronic acid (Suzuki reaction), as well as in the Heck reaction (between styrene and phenyl bromide (iodide)). The yields of the target products were comparable with those obtained using other catalyst systems, for example, based on palladium carbene complexes.³⁰

3.3. Tetrylenes as initiators in the synthesis of biodegradable polymers

Lately, one of the fastest growing branches of modern chemistry has been the synthesis of so-called biodegradable polymers (in particular, polylactide, polyglycolide, poly-ε-caprolactone and their copolymers) and new materials on their basis.⁵² The main method for industrial production of these compounds is the ring opening polymerization (ROP) of cyclic esters, in which tin bis(octanoate) is used as the initiator.⁵² Currently, the search for both new organic initiators and new initiators based on electron-deficient metal complexes is continued. In this respect, tetrylenes continue to attract particular attention as derivatives potentially useful from the point of view of initiation of polymerization. In the course of our studies, a number of stannylenes and germlyenes were tested as the initiators of polymerization of ε-caprolactone (Table 3).

The reaction was carried out in the presence of an external nucleophile (benzyl alcohol) at a high temperature in bulk (most commonly used in industry conditions). All the tested stannylenes are active in this reaction (see Table 3), while the activity of germlyenes is low. The most active is stannylene **60** containing acceptor groups bonded to the tin atom (*N*-tosyl groups). A relatively low values of polydispersity indicate that the polymerization in these cases is of a controlled nature.

Thus, this review presented the data on the synthesis, structure, and reactivity of tetrylenes based on tri- and

Table 3. The data on polymerization of ε-caprolactone in the presence of some stannylenes and germlyenes as initiators

Initiator	M ^a	t/h	Conversion (%)	M _n ^b /g mol ⁻¹	M _w /M _n	Ref.
60	Sn	1	100	7500	1.65	37
51	Sn	7	92	7019	1.57	36
50	Sn	10	>99	5969	1.41	36
48	Sn	12	>99	10457	1.70	35
42	Ge	12	98	6546	1.77	35
47	Sn	16	93	6788	1.38	36
61	Sn	24	78	6170	1.16	37
40	Ge	16	2	—	—	36
43	Ge	16	3	—	—	36
45	Ge	16	4	—	—	36

^a Polymerization in bulk: 100 °C, [caprolactone]/[Cat]/[BnOH] = 300 : 1 : 1.

^b According to gel permeation chromatography with a correction factor of 0.56.

tetradentate ONO-, NNO-, NNN-, and ONNO-type ligands, as well as showed the relationship of the structure of the synthesized tetrylenes with their reactivity.

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