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Divalent silicon, germanium, and tin compounds with element—heteroatom bonds*,**

N. N. Zemlyanskii,[a] I. V. Borisova,[a] M. S. Nechaev,[b] V. N. Khrustalev,[c]
V. V. Lunin,[b] M. Yu. Antipin,[c] and Yu. A. Ustynyuk[b]★

[a]A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 230 2224. E-mail: zemlyan@mail.cnt.ru
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 2677. E-mail: ustynyuk@nmr.chem.msu.su
[c]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: vkh@xray.ineos.ac.ru

Principal results and trends in chemistry of organic derivatives of divalent silicon, germanium, and tin containing bonds between these elements and the halogen, nitrogen, oxygen, and sulfur atoms are briefly surveyed. Selected characteristics of compounds with the element—phosphorus and element—arsenic bonds are discussed for comparison. Data on the synthesis and structures of new types of these compounds, *viz*., germanium(II) diacylates, the alkoxy derivatives $E^{14}(OR)_2$ and $E^{14}(OR)Y$ (E^{14} = Ge, Sn; R = $Me_2NCH_2CH_2$; Y = Cl, AcO, $(Me_3Si)_2N$), and the *ate*-complexes $Li^{(+)}[E^{14}(OCH_2CH_2NMe_2)_3]^{(-)}$ and $[Li(thf)_2]^{(+)}[TsiE^{14}(SBu)_2]^{(-)}$ (E^{14} = Ge, Sn; Tsi = $(Me_3Si)_3C$), are presented. It was established for the first time that germanium(II) and tin(II) derivatives can be stabilized in the monomeric form only through the intramolecular $N_{sp3}{\rightarrow}E^{14}$ coordination bonds and the σ-acceptor effect of the oxygen atoms without introduction of bulky substituents.

Key words: silicon compounds, germanium compounds, tin compounds, X-ray diffraction analysis, molecular structure.

Introduction

Chemistry of carbene analogs, *viz*., silylenes, germylenes, and stannylenes R_2E^{14} (E^{14} = Si, Ge, Sn) containing hydrocarbon substituents R, and related monomeric organic derivatives of divalent silicon, germanium, and tin with the element—heteroatom covalent bonds $(R_nX)_2E^{14}$, $RE^{14}(XR_n)$, $RE^{14}Y$, and $(R_nX)E^{14}Y$ (R = Alk, Ar; n = 1, 2; X = O, S, N, P, As; Y = Hal, OH, AcO, *etc*.) has been extensively investigated over the last two decades.[1—10] Researchers are giving particular attention to compounds in which the coordination sphere of the E^{14} atom is expanded due to intramolecular $Z{\rightarrow}E^{14}$ donor-acceptor interactions with heteroatoms bearing a lone electron pair (LEP), which are located in the side chain of the substituents R or RX (Z = N, O, S, *etc*.). These compounds differ substantially from true carbene analogs, *viz*., silylenes, germylenes, and stannylenes R_2E^{14} (R = Alk, Ar), in thermodynamic and kinetic stability, structure, and properties. The use of compounds containing the $Z{\rightarrow}E^{14}$ bond as ligands in transitions metal complexes offers attractive prospects for the construction of new catalytic systems. The present paper briefly surveys the principal data and new trends in chemistry of organic derivatives of divalent silicon, germanium, and tin containing covalent and/or coordination bonds between these elements and the halogen, nitrogen, oxygen, or sulfur atoms. Selected characteristics of analogous compounds with the element—phosphorus and element—arsenic bonds are given for comparison. Data on new divalent germanium and tin compounds and *ate*-complexes are considered.[11—14]

Divalent silicon, germanium, and tin compounds with element—heteroatom bonds

Compounds of $E^{14}(XR_n)_2$ and $YE^{14}(XR_n)$ types. Of the acyclic compounds $Si(XR_n)_2$, only the corresponding

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* Dedicated to the blessed memory of Professor Colin Eaborn, an outstanding scientist and good friend.

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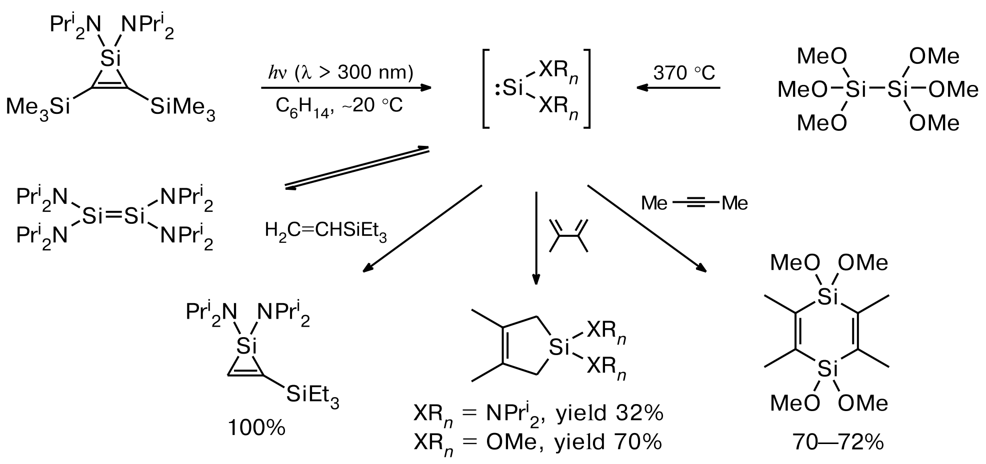
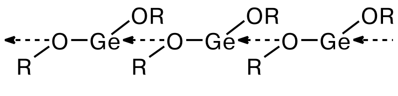
Scheme 1



dialkoxy[15—20] and bis(dialkylamino) derivatives[21] were experimentally studied. These compounds were detected as intermediates of different reactions in the gas phase and solutions using trapping agents (Scheme 1) and by physicochemical methods.[5—21]

Kinetic stability of the germanium and tin derivatives $E^{14}X_2$ (E^{14} = Ge, Sn; X = OR, NR_2) is substantially higher than that of their organosilicon analogs. The sterically unhindered $E^{14}(OR)_2$ [8,22] and $E^{14}(NR_2)_2$ [23—25] compounds (E^{14} = Ge, Sn) exist as coordination polymers with the intermolecular E^{14}—X→E^{14} coordination bonds (X = OR or NR_2).



Diacyloxy derivatives of tin are structurally similar to the above compounds. Some of these compounds, for example, tin dioleate $(C_{17}H_{33}COO)_2Sn$ and tin di(2-ethylhexanoate) $(C_7H_{15}COO)_2Sn$, are produced on the industrial scale and are used as components of catalytic systems. Prior to our study,[26] data on acyloxy derivatives of germanium(II) have been limited to the synthesis of germanium(II) oxyisobutyrate, oxysalicylate, and thiosalicylate.[27—29] The structures of these compounds have not been unambiguously established.

According to the results of the only study,[30] the bis(alkylthio) derivatives of germanium(II) $[(RS)_2Ge]_n$ (R = Bu, $PhCH_2$, Ph) exist in solutions as associates (n = 1.5—3). We studied the structure of bis(n-butylthio)tin(II) (**1**).[31] In the crystal, compound **1** exists as a coordination polymer (Fig. 1) consisting of three types of independent four-membered rings Sn_2S_2. Two of these rings adopt a butterfly conformation with the *anti*-periplanar arrangement of the substituents at the Sn and S atoms analogous to the conformation of the four-membered ring Pb_2S_2 in the $[Pb(STol\text{-}p)_2]_n$ polymer[32] (Fig. 2, *a*, *c*). The third ring has the previously unknown planar conformation with the *syn*-periplanar arrangement of the substituents (Fig. 2, *b*).

As in the case of the alkyl(aryl)-substituted compounds $E^{14}R_2$ (E^{14} = Si, Ge, or Sn), bulky substituents increase stability of the monomeric forms of $E^{14}(XR_n)_2$ under standard conditions. The synthesis of alkoxy or amino derivatives of germanium(II) and tin(II) containing bulky substituents at the metal atom was documented,[33,34] but no

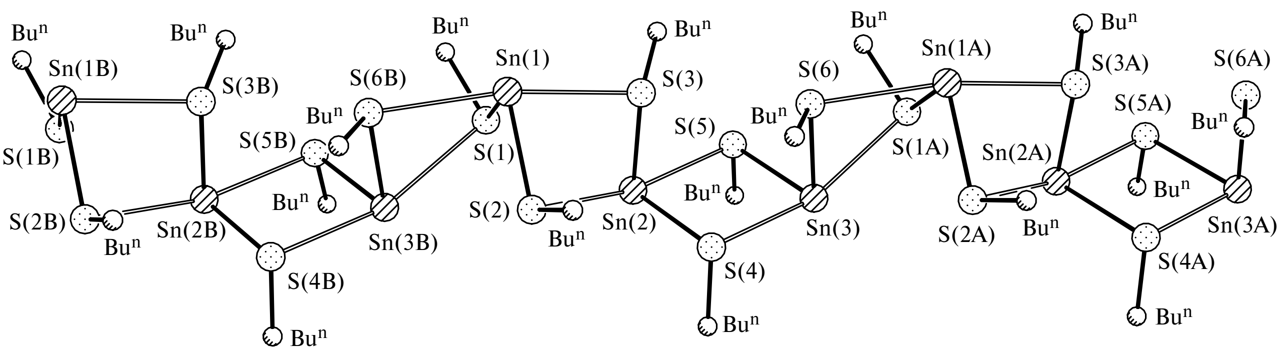


Fig. 1. Structure of polymer **1**;[31] hereinafter, the coordination bonds are shown as open lines.

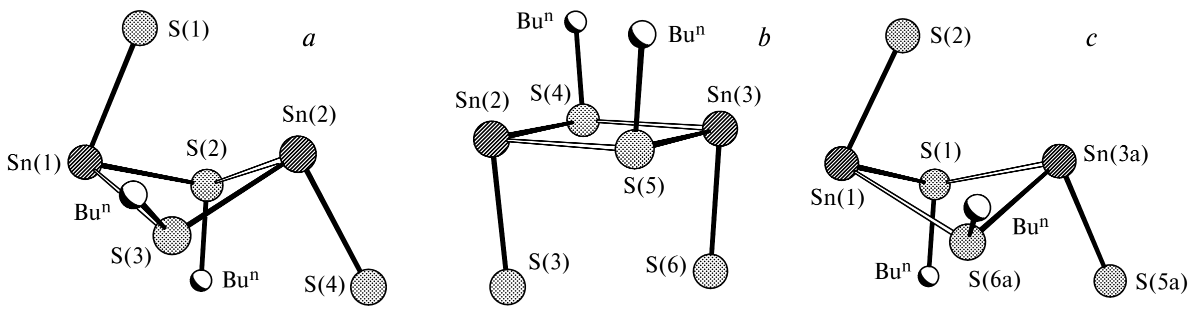
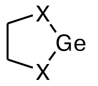


Fig. 2. Conformations of three independent four-membered rings Sn_2S_2 in polymer **1**.[31]

convincing evidence that these compounds have a monomeric structure was presented. Later on, the monomeric diamino, aminochloro, and diaryloxy derivatives of germanium(II) and tin(II) $E^{14}[N(SiMe_3)_2]_2$,[35—38] $ClE^{14}N(SiMe_3)_2$,[35—37] and $E^{14}(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_2$ [39] and the divalent tin compounds $Sn(OBu^t)_2$,[40] $(Me_3Si)_2NSn(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)$,[41] and $Sn(SC_6H_2Bu^t{}_3\text{-}2,4,6)_2$ [42] were synthesized and structurally characterized in the gas and condensed phases. The monomeric compounds $M[P(SiPr^i{}_3)R]_2$ (M = Ge, Sn, R = $Si(2,4,6\text{-}Pr^i{}_3C_6H_2)_2F$; M = Sn, R = $Si(Bu^t)(2,4,6\text{-}Bu^t{}_3C_6H_2)F$) and $Sn[As(SiPr^i{}_3)R]_2$ (R = $Si(Bu^t)(2,4,6\text{-}Pr^i{}_3C_6H_2)_2$) were synthesized and studied by NMR spectroscopy and X-ray diffraction analysis.[43]

The synthesis of cyclic structures containing oxygen, sulfur, nitrogen, or other heteroatoms opened interesting prospect for studying germanium(II) and tin(II) compounds. Heterocycles **2** and **3** were the first compounds of this type, whose synthesis was documented.[44—46]



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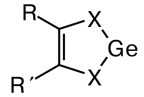
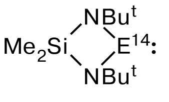


3

2: X = O, S, PPh; **3:** X = O, S; R = Me, Et, Ph; R′ = H, CN, Ph

However, like sterically unhindered dialkoxy derivatives of germanium(II), these compounds, as a rule, occur in solutions as associates.

Unlike these compounds, amino derivatives containing the E^{14} atom in the four- (**4**) or five-membered rings (**5**) are monomeric both in crystals and solutions.[47—54] Relative stability of compounds **4** and **5** decreases in going from the tin and germanium derivatives to the corresponding silicon compounds as well as with decreasing volume of substituents at the N atoms.



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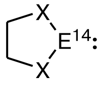


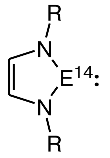
5

E^{14} = Si, Ge, Sn; X = O, S, NR

For example, germanium and tin derivatives **4** [48] are stable under standard conditions and distilled *in vacuo* without decomposition. Their silicon analog was detected spectrometrically in an Ar matrix and exists only at a temperature lower than 77 K.[47] The replacement of the Bu^tN groups with Pr^iN leads to dimerization of germylene **5**.[53] According to the results of *ab initio* quantum-chemical calculations and photoelectron spectroscopy,[38,54] stability of compounds containing the $N—E^{14}—N$ fragment is determined by both the shielding effect of bulky substituents (the kinetic factor) and orbital interactions between the N atoms and the E^{14} atom (the thermodynamic factor). The highest occupied molecular orbital (HOMO) in dialkyl(diaryl)silylenes, -germylenes, and -stannylenes, which are true analogs of singlet carbenes, is the $\sigma\text{-}E^{14}$ orbital, whereas HOMO in cyclic compounds **4** and **5** and the acyclic $Sn[N(SiMe_3)_2]_2$ compound is an antisymmetric combination of the p orbitals of LEP of two N atoms.

The reactivity of Sn derivative **4**, whose labile $E^{14}—N$ bonds are cleaved under the action of various reagents, was studied in most detail.[48]

In recent years, considerable attention has been given to the synthesis, structures, and properties of organosilicon, -germanium, and -tin analogs of the stable Arduengo carbene, *viz.*, nucleophilic bis(amino) derivatives of silicon(II),[3,4,6] germanium(II),[4,6,51,53] and tin(II) (**6**—**8**).[52,55]



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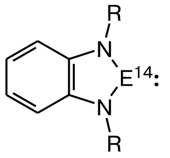

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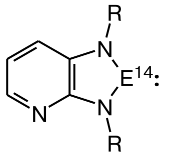

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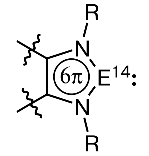


A

6: E^{14} = C, Si, Ge, Sn, R = Bu^t, Ad
7: E^{14} = Si, Ge, Sn, R = CH_2Bu^t
8: E^{14} = Si, R = CH_2Bu^t

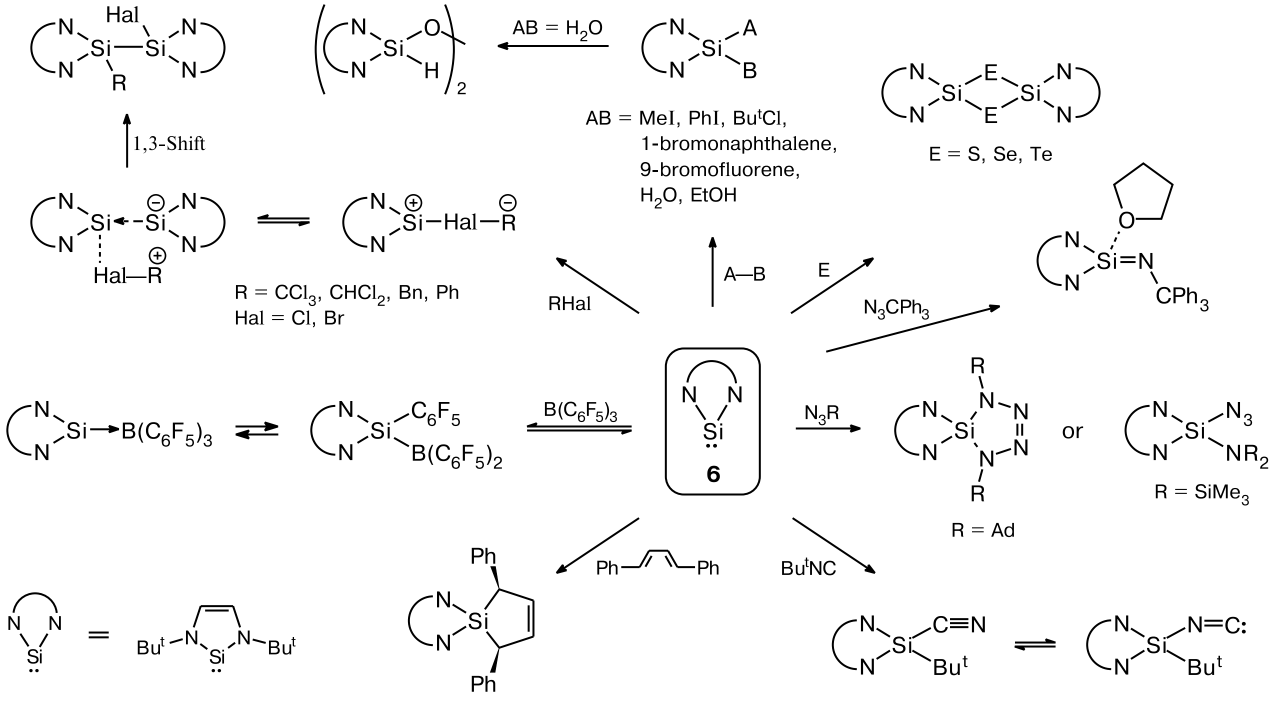
High stability of compounds **6—8** is attributable to the presence of the six-electron aromatic system **A** formed due to interactions of the π orbital of the C=C bond and the occupied p orbitals of LEP of the N atoms containing altogether six π electrons with the unoccupied $n\text{p}_z$ orbital of the divalent E^{14} atom. That is why the reactivities of compounds **6—8** differ substantially from those of true silylenes, germylenes, and stannylenes. The electrophilicity of the carbenoid center E^{14} in molecules **6—8** is essentially lower, whereas its nucleophilicity is significantly higher than those in true silylenes, germylenes, and stannylenes. The reactions of the silicon derivatives, *viz*., West's silylene **6** [3,4,6,56,57] and silylene **7**,[3,4,52] were studied in most detail. It was found that silylene **7** is more reactive than its monocyclic analog **6**. For example, West's silylene **6** does not form complexes with Lewis bases (Et_3N or Py), is not inserted at the Si—H and C—Cl bonds of triethylsilane and hexyl chloride but is introduced at the C—Hal bonds (MeI, PhI, Bu^tCl, 1-bromonaphthalene, and 9-bromofluorene) as well as at the H—OH and EtO—H bonds. The reactions of compound **6** with CH_2Cl_2, CHCl_3, CCl_4, BnCl, and, partially, PhBr afforded 2 : 1 adducts through the halophilic complex formation. Compound **6** reversibly coordinates Lewis acids and is involved in the oxidative addition to chalcogens and the [2+1]-cycloaddition at the C=X bonds (X = O, NR) of ketones and imines, the reactions being typical of silylenes. The latter reactions give rise to four-membered 1,2-disilacyclanes as a result of introduction of the second molecule **6** into intermediate silaoxiranes or silaaziridines. Examples of these reactions are presented in Scheme 2.

Most of these reactions belong to redox processes and produce polycyclic tetravalent silicon compounds. The reactions of compound **6**, unlike those of silylene **7** (E^{14} = Si), are often accompanied by the E^{14}—N bond cleavage, for example, in the case of oxidation with oxygen or elemental sulfur.

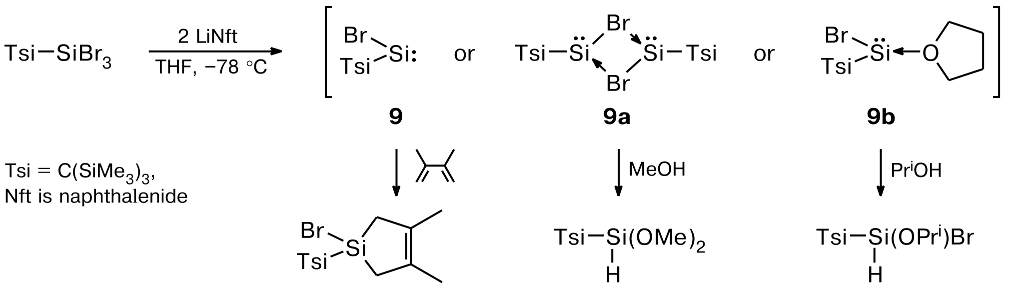
The results of the reactions of West's silylene **6** and silylene **7** with dienes, alkynes, and nitriles depend on the nature of substituents in the reagents as well as on the reaction conditions. For example, the expected adducts were synthesized by the reaction of silylene **6** with *trans*,*trans*-1,4-diphenylbutadiene and by the reaction of silylene **7** (E^{14} = Si) with 2,3-dimethylbutadiene. The reactions of silylene **7** with $\text{Me}_3\text{SiC}{\equiv}\text{CPh}$ and *tert*-butyl isocyanide gave 2 : 1 adducts as a result of insertion of the second molecule **7** into the initially formed three-membered cyclic intermediate. West's silylene **6** induces catalytic polymerization of styrene and 2,3-dimethylbutadiene but it does not react with bis(trimethylsilyl)acetylene, diphenylacetylene, and nitriles.

The reactions of silicon compounds **6** and **7** with azides afford intermediate silaimines, which are stabilized through complex formation with THF. Sterically less hindered azides (AdN_3 and Me_3SiN_3) and stable derivatives of divalent silicon are not inert with respect to silaimines and serve as their efficient trapping agents. Various cyclic

Scheme 2



Scheme 3



and spirocyclic compounds, which are generated as a result of insertion of silaimines at the N_3—$SiMe_3$ bond, 1,3-cycloaddition to AdN_3, or the addition of the second molecule of the starting silylene (in the case of compound **7**) at the Si=N bond, were isolated and characterized.

Data on the reactivities of the corresponding germanium(II) and tin(II) compounds **6** and **7** are limited to their reactions with transition metal complexes and the stable Arduengo carbene, which are beyond the scope of the present review.

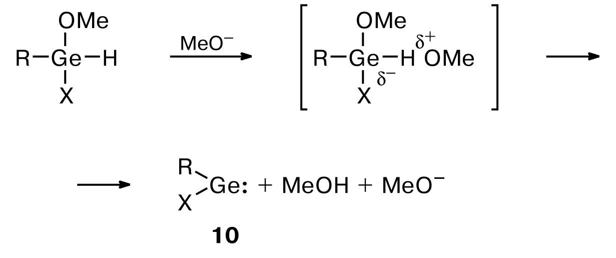
Compounds $RE^{14}Y$ and $RE^{14}(XR_m)$. The $RE^{14}Cl$ compounds are of particular interest because of their high synthetic potential.[15,58] Being the most probable intermediates for the commercially important direct synthesis of organosilicon, -germanium, and -tin compounds from alkyl halides and Group 14 elements or their alloys with metals, they are also considered as promising starting reagents for the generation of compounds with triple bonds, for example, silynes and disilynes.[59—62]

As in the case of the above-considered types of compounds, the introduction of bulky substituents stabilizes the intermediate RSiX compounds. The first supposed relatively stable intermediate of this type, *viz.*, bromo[tris(trimethylsilyl)methyl]silicon(II) (**9**), was generated only recently.[63] Compound **9** is stable in a THF solution at room temperature for 2—3 h. The reactions of compound **9** with alcohols and dienes afford products expected for silylenes in ~90% yield (Scheme 3).

However, the structure of **9** was not unambiguously established.[63,64] Bridged dimer **9a** or complex **9b** with THF could be[63] an alternative to the silylene structure. Due to the presence of the electronegative Br atom bearing a lone electron pair, the resonance signal in the ^{29}Si NMR spectrum of compound **9** is shifted upfield (δ_{Si} 106) to the region characteristic of cyclic diaminosilylenes **6—8** (δ_{Si} 78—117), whereas this signal in the spectrum of the first kinetically stabilized dialkylsilylene, 2,2,5,5-tetratrimethylsilylsilole, is observed at δ_{Si} 567. However, the theoretically calculated chemical shift $(\delta_{Si})_{calc}$ for $(Me_3Si)_3CSiBr$ (δ 446) is inconsistent with the experimentally observed position of the signal (δ 106). Apparently, this reaction gives the *ate*-complexes of silylene with LiBr and solvent molecules. The chemical shift for the $[(Me_3Si)_3CSiBr_2]^-$ anion ($(\delta_{Si})_{calc}$ 124) is in better agreement with the experimental value. The formation of tight ion pairs of this anion with the Li^+ cations, which are either solvated or nonsolvated with the solvent ($(\delta_{Si})_{calc}$ 117 and 134, respectively), is also not inconceivable.

The organogermanium compounds RGeX and RGeXR′ are more stable. An elegant procedure was developed[65—67] for their synthesis by elimination of methanol from the RGe(OMe)(H)(X) compounds (R = Et, Ph; X = F, Cl, OMe) under the catalytic action of the methoxy anion (Scheme 4).

Scheme 4

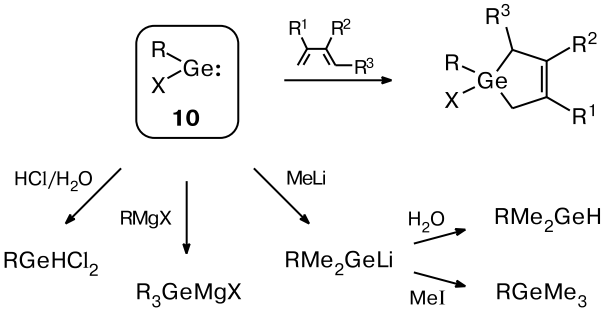


R = Et, Ph; X = Br, Cl, OMe

Compounds **10** (X = Cl) were isolated as viscous liquids associated through the Cl→Ge bridging bonds. Heating of these associates to 80 °C gave rise to polymers with Ge—Ge bonds.[65—67] Although the structures of the compounds thus formed were not unambiguously established, their high synthetic potential was exemplified by many reactions typical of germylenes: the insertion at the Ge—Ge, Ge—Hal (Hal = Cl, Br), Sn—Cl ($SnCl_4$), H—X (X = Hal, Ge), or C—X bonds (X = Cl, Br, Li, Mg) and the addition at the conjugated double bonds. Selected reactions are presented in Scheme 5.

Unlike the above-considered sterically unhindered compounds, monomeric "chlorosupermesitylgermanium(II)" Mes*GeCl (Mes* = $(2,4,6\text{-}Bu^t)_3C_6H_2$) is a yel-

Scheme 5



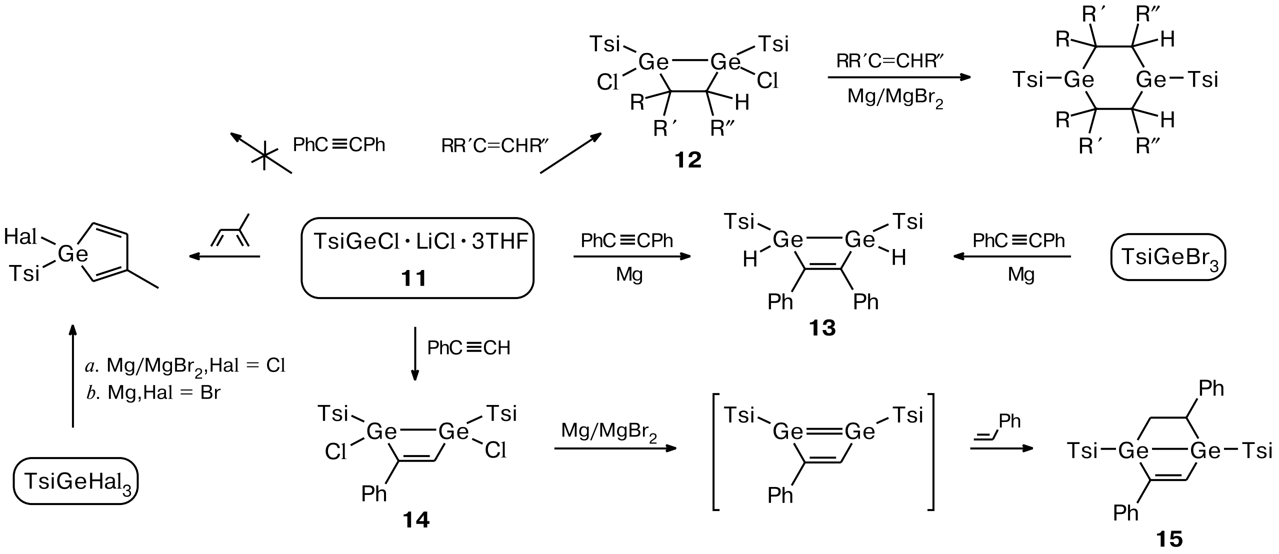
R = Et, Ph; R^1 = Me, R^2 = R^3 = H; R^1 = R^2 = Me, R^3 = H;
X = Br, Cl, OMe

low crystalline compound. Kinetic and thermodynamic stability of this germylene was accounted for by steric shielding of the Ge atom and dative interaction along the Cl→Ge bond.[68]

According to the data published in the literature,[69] the reaction of $(Me_3Si)_3CLi$ and the germanium dichloride complex with dioxane afforded the $(Me_3Si)_3CGeCl \cdot LiCl \cdot 3THF$ product (**11**), whose structure was not established. Noteworthy are the reactions of **11** with olefins and phenylacetylene, which produce digermanium derivatives (**12—15**) rather than the corresponding monogermanium derivatives. Similar adducts were prepared when generating TsiGeBr *in situ* by the reactions of $TsiGeBr_3$ with magnesium in the presence of diphenylacetylene (Scheme 6).[70]

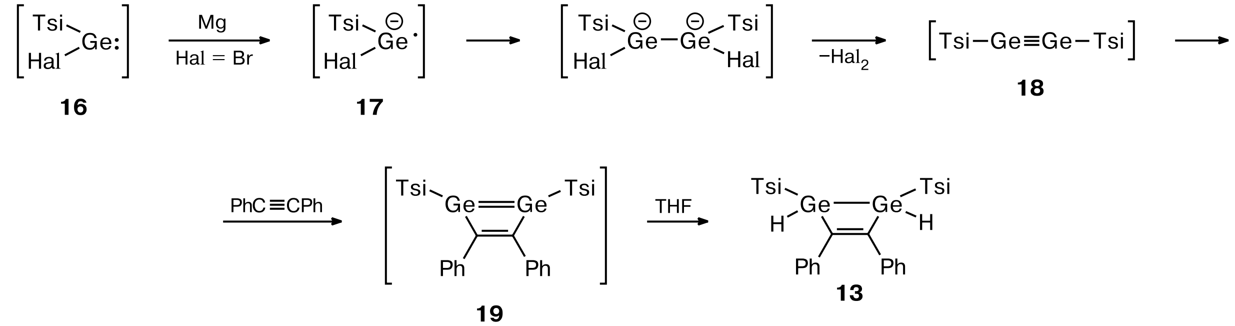
Based on the data[2,71] on the electrochemical generation of the $^{(-)\bullet}M[CH(SiMe_3)_2]_2$ radical anions (M = Ge, Sn) through one-electron transfer, the mechanism of formation of cyclic compound **13** was proposed[69,70] (Scheme 7). This mechanism involves electron transfer from magnesium to germylene **16** to form radical anion **17**, dimerization of the latter, and elimination of halogen from the intermediate dianion giving rise to digermyne **18**.

Scheme 6



Tsi = $C(SiMe_3)_3$

Scheme 7



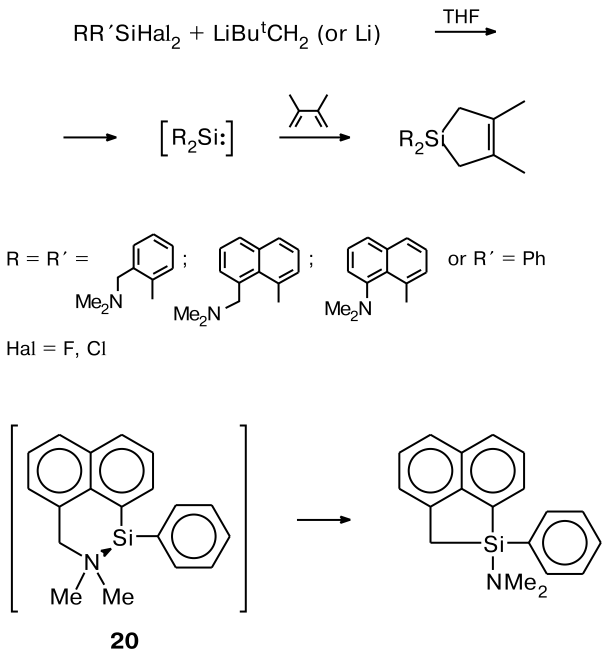
The reaction of digermyne **18** with diphenylacetylene affords intermediate 1,2-digermacyclobutadiene **19**, which abstracts H atoms from the solvent or is trapped by styrene (see Schemes 6 and 7).

Attempts to identify the products formed in various reactions, for example, in the reaction of tin vapor with butyl bromide,[72] catalytic dehydrogenation of $EtSn(H)_2Br$,[73,74] alkylation of $SnCl_4$ with diisobutyl aluminum hydride,[75] or the reaction of $SnCl_2$ with [tris(trimethylsilyl)methyl]lithium,[76] failed. However, the reaction of $SnCl_2$ with $(Me_2PhSi)_3CLi$ gave the corresponding RSnCl compound in high yield. X-ray diffraction study demnostrated that in the crystalline state this compound exists as the $\{Sn[C(SiMe_2Ph)_3]Cl\}_2$ dimer.[76]

Compounds containing coordination bonds of divalent silicon, germanium, or tin with heteroatoms. In recent years, the results of studies on the synthesis of divalent silicon compounds with the intramolecular N→Si coordination bond have been published.

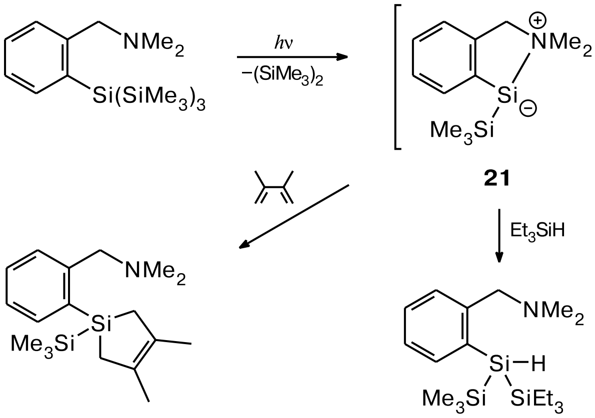
Reductive dechlorination of dichloro- or difluorodiorganosilanes containing the *o*-dimethylaminomethylphenyl, (8-dimethylamino), or (8-dimethylaminomethyl)naphthyl groups with lithium or neopentyllithium in THF was studied under various conditions.[77] The reactions with the use of 1,3-dimethylbuta-2,3-diene as a chemical trap afforded the corresponding adducts through the intermediate formation of divalent silicon compound **20**. In the absence of the trapping agent, intermediate **20** undergoes the rearrangement into the silaacenaphthene derivative (Scheme 8).

Scheme 8



The formation of the structurally similar intermediate (**21**) by photolysis of (*o*-dimethylaminobenzyl)tris(trimethylsilyl)silane (Scheme 9) was proved by the chemical trapping technique.[77]

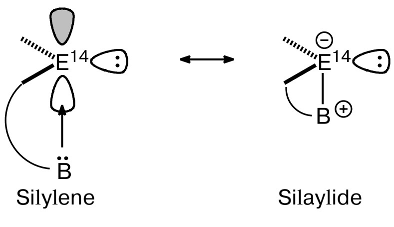
Scheme 9



Interesting results were obtained[78—82] when generating silicon(II) derivatives containing the intramolecular N→Si bonds by pyrolysis of organodisilanes. Heating of ethoxydisilane **22** with 2,3-dimethylbuta-1,3-diene or tolan gave rise to adducts **25** and **26** typical of silylenes.[78] In the absence of trapping agents, the reaction produced[79] linear trisilane **24** (Scheme 10). The proposed pathway of its formation involves two-step electrophilic-nucleophilic trimerization (**23a** + **23b** + **23b**) of intermediate compound **23** accompanied by successive migrations of the Me and Me_2N groups. The authors hypothesized[78—82] that such an ambiphilic reactivity of silicon(II) intermediates is consistent with a substantial contribution of the silaylide nucleophilic canonical form **23a** to their structures.

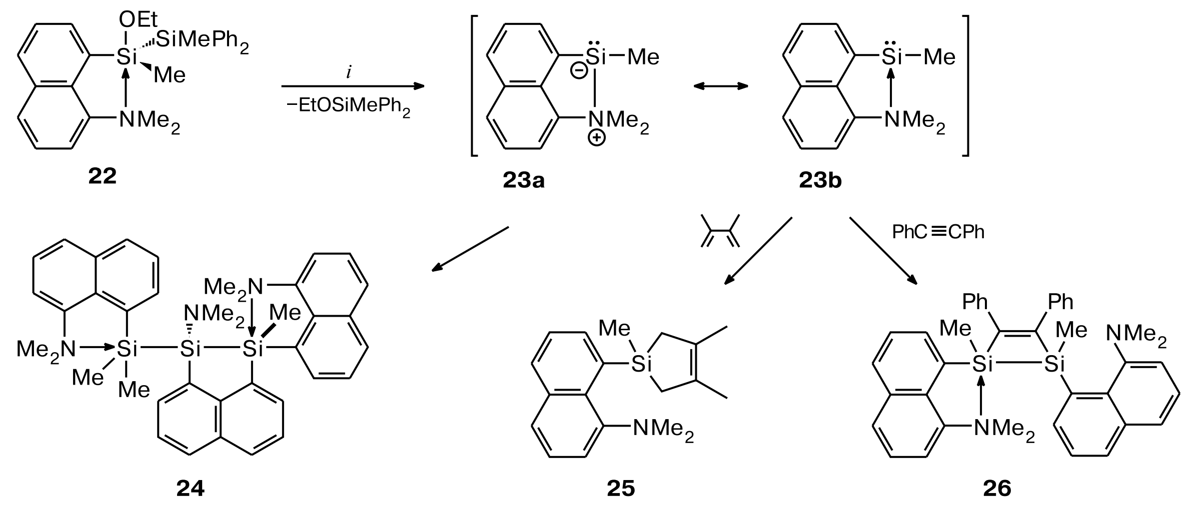
In continuation of these investigations, pyrolysis of fluorodisilanes **27** and **28** was carried out in the presence of tolan,[80,81] and the scheme of the reaction through the intermediate formation of the alkenyl anion (**29**) was proposed (Scheme 11). The formation of this anion was confirmed by the chemical trapping technique, including the use of isotope-labeled CH(D)-acids.

Based on the results of the investigation, it was hypothesized[78—82] that intermediates **23** containing the in-



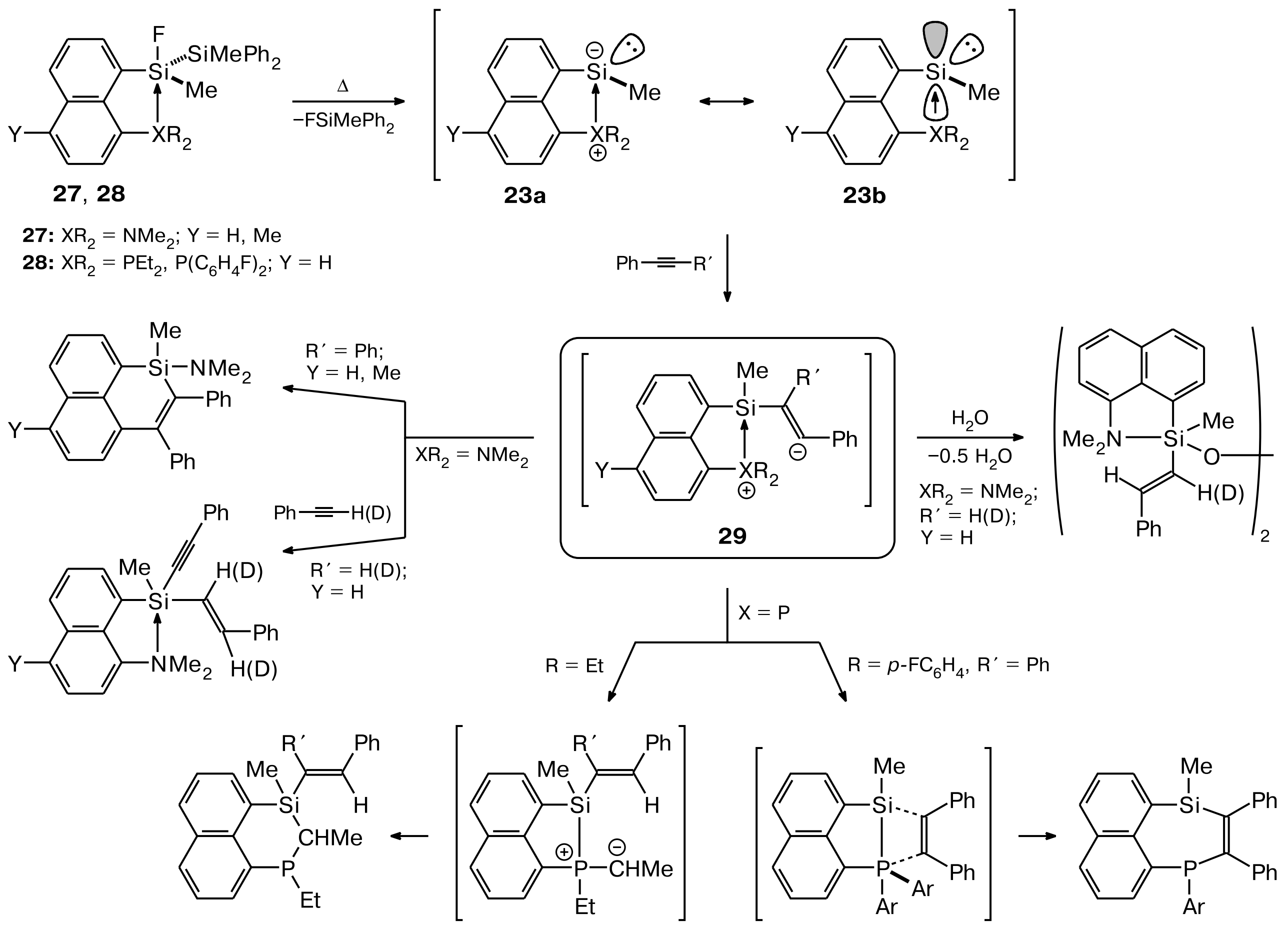
B = NR_2 or PR_2

Scheme 10

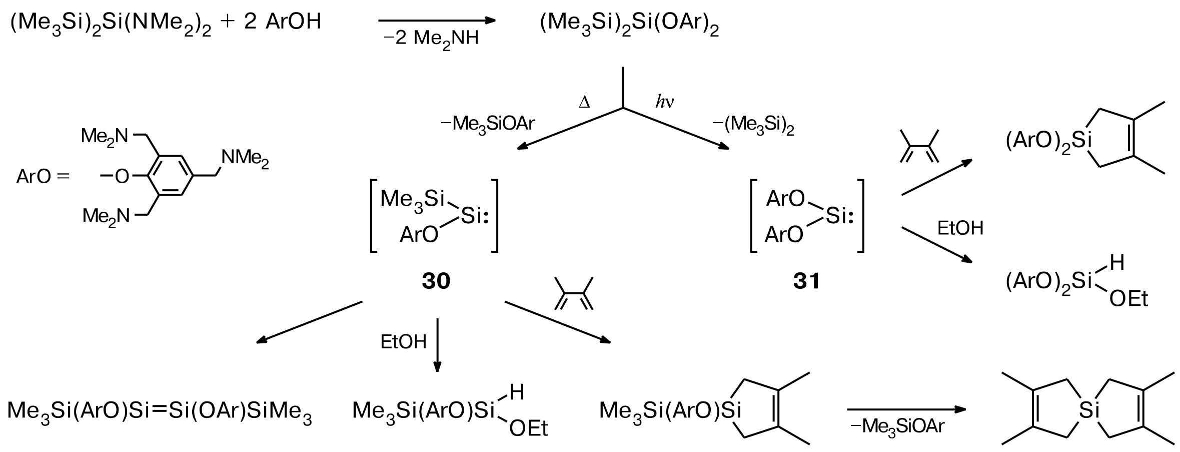


i. Toluene, 110 °C, 16 h; or DMF, 90 °C, 20 h.

Scheme 11



Scheme 12



tramolecular N→Si or P→Si coordination bond should be considered as amino-silaylides and phospha-silaylides. However, the validity of this hypothesis calls for comprehensive quantum-chemical investigation.

UV irradiation or thermal decomposition of silicon(IV) derivatives gave (trimethylsilyl)[2,4,6-tris(dimethylaminomethyl)phenoxy]silicon(II) (**30**) (the major product) and bis[2,4,6-tris(dimethylaminomethyl)phenoxy]silicon(II) (**31**) as intermediates (Scheme 12).[83]

The X→E^{14} coordination bonds (E^{14} = Ge, Sn) involving the lone electron pair of the heteroatom located in a bulky substituent more efficiently stabilize monomeric germanium(II) and tin(II) compounds compared to silicon(II) compounds. In 1980, a large series of stable aryl-substituted tin(II) compounds bearing nitrogen- or oxygen-containing substituents in different positions of the aromatic ring were synthesized and their Mössbauer and IR spectra were measured.[84] However, the structures of these compounds were not supported by rigorous evidence, and these results did not attract attention of researchers over many years. More recently, a number of the tri- and tetracoordinate germanium(II) and tin(II) compounds R_2E^{14}, $RR'E^{14}$, and $RE^{14}X$ were synthesized with the use of ligands containing the sp^2- or sp^3-hybridized N atoms. Among them are the *o*,*o*-dimethylaminophenyl $C_6H_3(NMe_2)_2$-2,6,[85] 8-dimethylaminonaphthyl $C_{10}H_7(NMe_2$-8),[86] *o*-dimethylaminobenzyl $C_6H_4(CH_2NMe_2)$-2,[87,88] and $C_6H_2(Bu^t_2$-2,4-CH_2NMe_2-6) ligands[89,90] as well as the (pyridin-2-yl)trimethylsilylmethyl ligands $CR(SiMe_3)(C_5H_4N$-2) (R = H, Ph,[91] $SiMe_3$ [92—96]) and $C(SiMe_3)_2(SiMe_2C_5H_4N$-2).[97] Examples of such compounds, which were structurally characterized, are presented on the next page.

In all these compounds with the N→E^{14} coordination bond, the E^{14} atom has a distorted trigonal-bipyramidal coordination in the presence of two N→E^{14} coordination bonds in the molecule or a distorted trigonal-pyramidal coordination in the presence of one N→E^{14} coordination bond, in accordance with the Gillespie rules[98] for the A_4BE and A_3BE compounds, respectively. It should be noted that the N→E^{14} coordination bond lengths increase in going from the sp^2- to sp^3-hybridized N atoms as well as from monocoordinated compounds to derivatives with two N→E^{14} coordination bonds (2.055—2.140 and 2.272—2.313 Å for compounds with one and two N_{sp^2}→Ge^{II} coordination bonds, respectively; 2.092—2.164 and 2.334—2.570 Å for compounds with one and two N_{sp^3}→Ge^{II} coordination bonds, respectively; 2.260—2.388 and 2.384—2.524 Å for compounds with one and two N_{sp^2}→Sn^{II} coordination bonds, respectively; 2.264—2.516 and 2.516—2.660 Å for compounds with one and two N_{sp^3}→Sn^{II} coordination bonds, respectively).

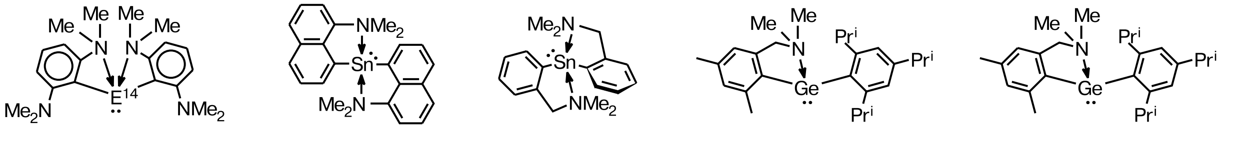
Shortening of the N→E^{14} bonds is observed in going from six- or five-membered coordination rings to four-membered rings. Simultaneously, one would expect an elongation of the element(II)—carbon (or heteroatom) bonds. However, it is difficult to follow this tendency because data on such compounds are scarce.

The interesting $(Me_3Si)_3Sn—Sn(C_5H_4N$-2)$C(SiMe_3)_2$ compound was synthesized and structurally characterized.[95,99] This compound is stabilized through N→Sn coordination and contains the Sn^{II} and Sn^{IV} atoms directly bound to each other.

In addition to the coordination bonds with the N atom, germanium(II) and tin(II) compounds could be stabilized through coordination of the metal atom by other heteroatoms.

Recently,[100] the RGeCl (**32**) and R_2Ge (**33**) compounds containing the intramolecular O→Ge bond (Scheme 13) were prepared for the first time. Aryltin(II) halides stabilized by two intramolecular O→Sn coordination bonds were synthesized[101] (Scheme 14). Their chemical transformations were also studied (Scheme 15).

R_2E^{14}



E^{14} = Ge, Sn [85]

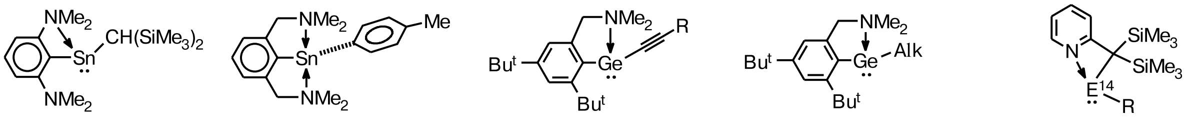
See Ref. 86

See Ref. 88

See Ref. 90

E^{14} = Sn, R = H,[91] Ph,[91] $SiMe_3$;[94] E^{14} = Ge, R = H, Ph,[91] $SiMe_3$ [91]

$RR'E^{14}$



See Ref. 85

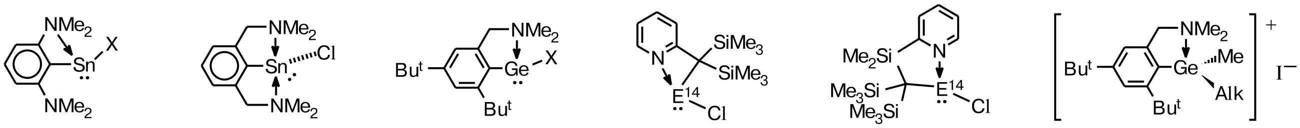
See Ref. 87

R = H, Ph [89,90]

Alk = Bu^t, Bu^n, Me [88–90]

E^{14} = Sn, R = $C_6H_2Pr^i_3$-2,4,6, $CH(PPh_2)_3$, $Sn(SiMe_3)_3$ [94]
E^{14} = Ge, R = $CH(PPh_2)_3$ [95]

$RE^{14}X$



X = Cl, $N(SiMe_3)_2$ [85]

See Refs 85 and 87

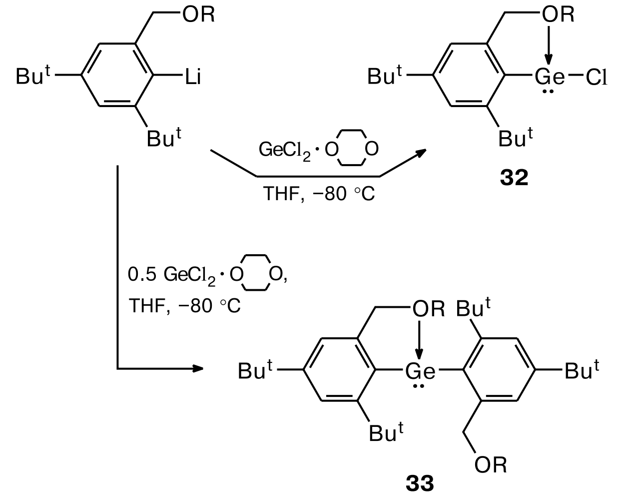
X = Cl, N_3, $N(SiMe_3)_2$
R = Bu^t, Pr^i, Et, Me [89,90]

E^{14} = Ge [95]
E^{14} = Sn [93,96]

E^{14} = Ge, Sn [97]

Alk = Bu^t, Bu^n, Me [90]

Scheme 13



32

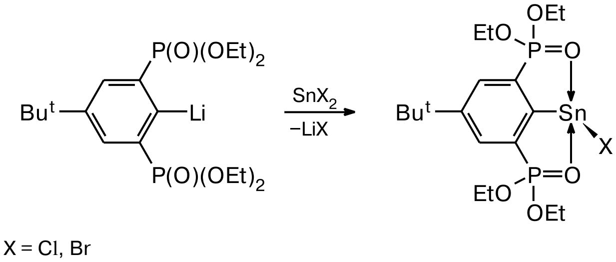
33

R = Me, Pr^i, Bu^t

The $E^{14}(OR)_2$ compounds with the intramolecular N→Ge^{II} coordination bond, in particular, dialkoxygermylene (**34**) (Scheme 16), were synthesized for the first time and their NMR, IR, and Mössbauer spectroscopic characteristics were reported in 1980.[102]

The $(ArO)_2E^{14}$ compounds (E^{14} = Ge (**35**), Sn (**36**)) were synthesized[103] by the reactions of germanium(II) and tin(II) bis(trimethylsilyl)amides with substituted phenol (Scheme 17).

Scheme 14



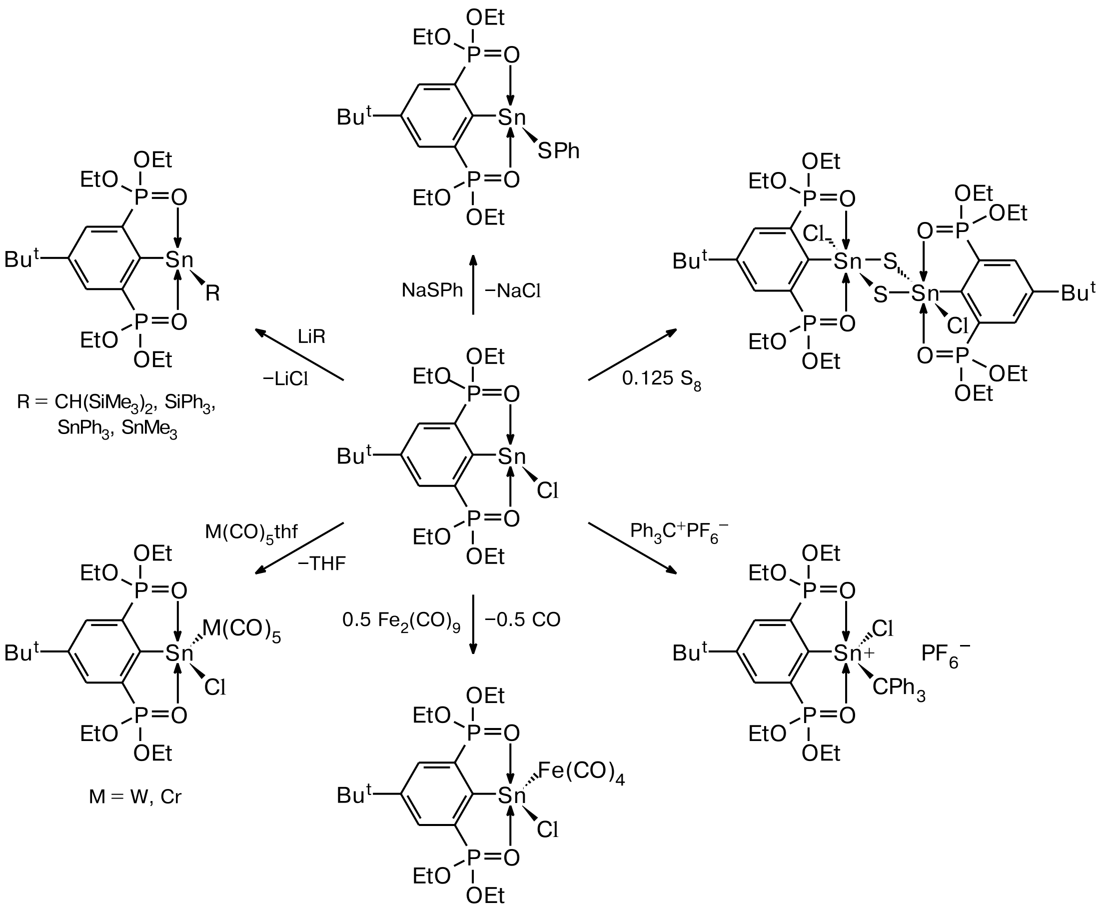
X = Cl, Br

Based on the results of ^1H and ^{13}C NMR spectroscopy, it was concluded[103] that the E^{14} atom in these compounds is either three- or tetracoordinated. In collaborative studies with J. Barrau and G. Rima, we unambiguously established that bis[2,4,6-tris(dimethylaminomethyl)phenoxy]tin(II) (**36**) is stabilized by two intramolecular N→Sn coordination bonds (see below).

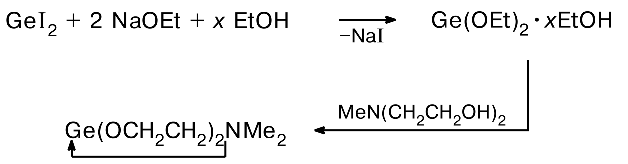
Heterocyclic germylene [η^3-{(μ-$Bu^tN)_2(SiMeNBu^t)_2$}]Ge (**37**)[104] and diaryloxystannylenes containing the 2-alkyl-8-quinolate,[105,106] (2-*tert*-butyl-4-methylsalicylaldehyde)ethylenediiminate,[107] salicylideneiminate,[108] and some other nitrogen-containing heterocyclic ligands[105] were synthesized and structurally characterized.

The monomeric $E^{14}(XR_n)_2$ and $E^{14}(XR_n)Y$ molecules stabilized by chelating monoanionic bidentate ligands be-

Scheme 15

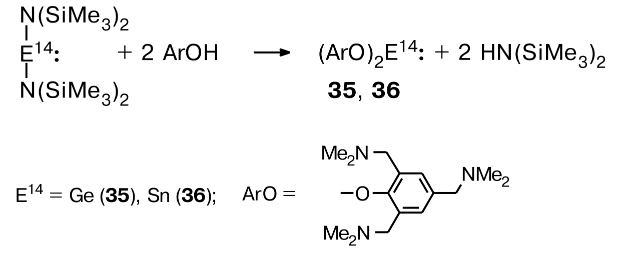


Scheme 16



34

Scheme 17



long to an interesting type of tri- or tetracoordinate germanium(II) and tin(II) compounds. The synthesis, structures, and selected properties of the corresponding compounds containing the four-electron *N*-alkylamidinate,[109—113] six-electron β-diketiminate,[114—116] ten-electron *N*-alkyl-2-(alkylamino)troponiminate,[117] or hydrotris(3,5-dimethylpyrazol-1-yl)borate ligands[118—120] were described.

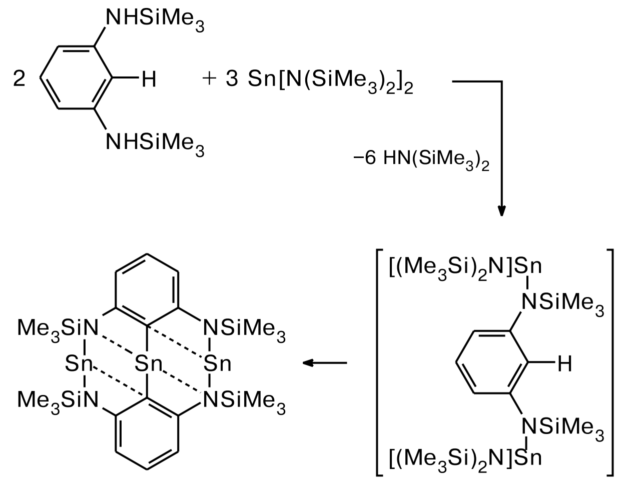
The $RE^{14}Cl$ compounds (E^{14} = Ge, Sn) containing electron-donating atoms in the hydrocarbon substituent R are commonly synthesized by the reactions of the corresponding organolithium derivatives with $GeCl_2 \cdot$diox (diox is 1,4-dioxane) or $SnCl_2$.

The reactions of $GeCl_2 \cdot$diox or $SnCl_2$ with alkoxides, mercaptides, and other alkali metal derivatives are rarely used for the synthesis of the $E^{14}(XR_n)_2$, $E^{14}R(XR_n)$, and $E^{14}(XR_n)Y$ compounds (R = Alk, Ar; n =1, 2; X = O, S, N, P, As; Y = Hal, OH, AcO, *etc.*), because these reactions are often complicated by side processes. For example, the reactions of $GeCl_2 \cdot$diox or $SnCl_2$ with ArOLi (Ar = $C_6H_2(CH_2NMe_2)_3$-2,4,6) afforded mixtures of $(ArO)_2Ge$ (**35**), ArOGeCl, and $Li_5(ArO)_2Cl_3$ or, correspondingly, $(ArO)_2Sn$ (**36**), ArOSnCl, $(ArO)_2SnLiCl$, and $Li_5(ArO)_2Cl_3$, whose separation presented considerable difficulties.[103]

The $E^{14}(XR_n)_2$ and $E^{14}(XR_n)Y$ compounds containing intramolecular coordination bonds are generally prepared by the reactions of $E^{14}[N(SiMe_3)_2]_2$ (E^{14} = Ge, Sn) with alcohols, phenols, or other analogous compounds or by redistribution of the functional groups of germanium(II) and tin(II) compounds with the corresponding di- or tetravalent germanium or tin derivatives. In some cases, alternative procedures are used for the synthesis of such compounds.

The interesting metallation reaction of 1,3-bis(trimethylsilylamino)benzene with tin(II) amide was carried our for the first time in the study[121] (Scheme 18).

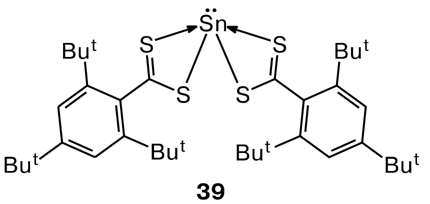
Scheme 18



38

Compound **38** contains the central tetracoordinate and two terminal tricoordinate tin(II) atoms.

The insertion of carbon disulfide at the Sn—C bond of the Ar_2Sn molecule (Ar = 2,4,6-$Bu^t{}_3C_6H_2$) accompanied by subsequent migration of the Ar group from the Sn atom to the C atom afforded the thio derivative of tin(II) (**39**) with the sulfur-containing chelating ligand.[122] Interesting silicon(II), germanium(II), and tin(II) compounds (**40**) containing the P atoms in chelate bidentate ligands were synthesized and studied.[123,124] The structures and properties of this type of compounds with the element—phosphorus and element—arsenic bonds are beyond the scope of the present review. Interested readers can find the corresponding data in the monograph[1] and reviews.[2—8]



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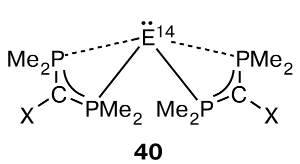


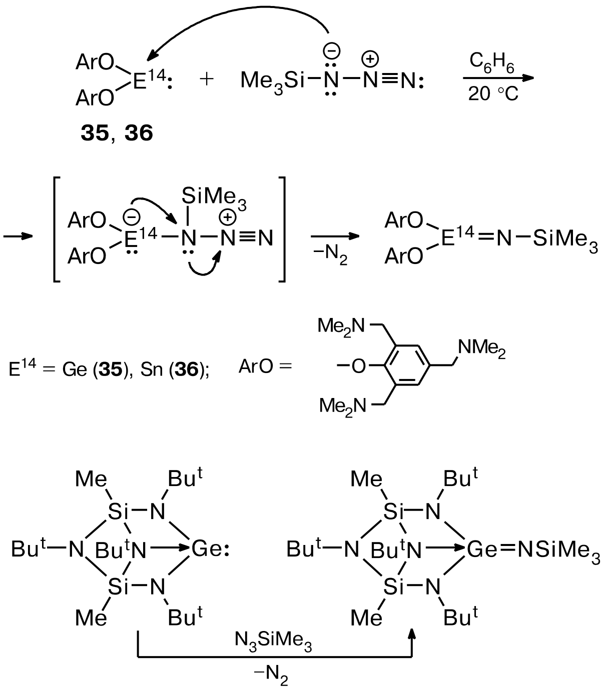
40

E = Si, Ge, Sn; X = $SiMe_3$, PMe_2

The reactivities of germanium(II) and tin(II) compounds containing intramolecular coordination bonds are poorly known. The reactions giving rise to derivatives with the $>E^{14}=X$ bond (E^{14} = Ge, Sn; X = NR, PR, S, Se, Te, transition metal carbonyls, *etc.*) are of particular interest. As an illustration we refer to the synthesis of imines and thiones.

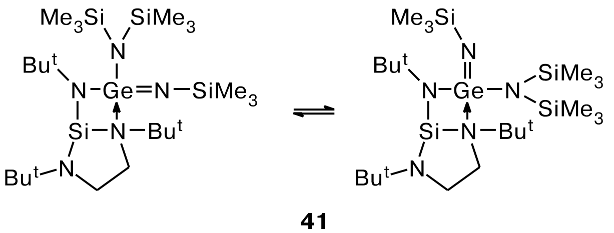
Stable germa-[125] and stannaimines[126] were synthesized by the reactions of stable divalent germanium and tin compounds with trimethylsilyl azide (Scheme 19).

Scheme 19



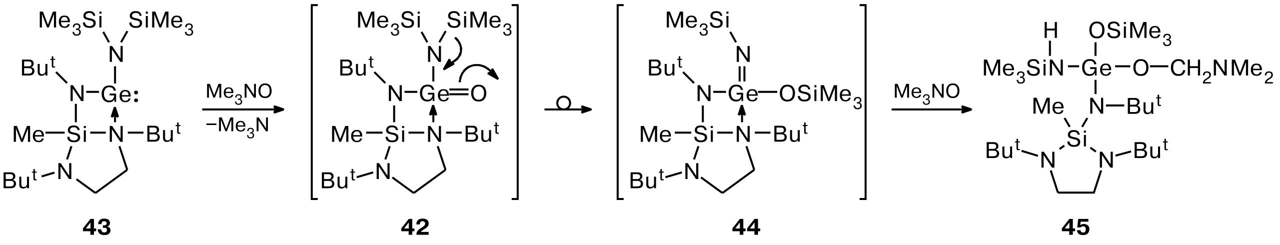
Germaimine **41**, which was prepared according to the same procedure, is the first compound in which the rapid reversible migration of the trimethylsilyl group accompa-

Scheme 20



41

Scheme 21



nied by migration of the Ge=N bond was observed (Scheme 20).[127]

The analogous [1,3]-sigmatropic migration of the trimethylsilyl group from the N atom to the O atom giving rise to intermediate germanone (**42**) was postulated for the reaction of germylene **43** with trimethylamine *N*-oxide. Intermediate germaimine **44** reacts with the second molecule of the oxidizer to form the final product **45**[127] (Scheme 21).

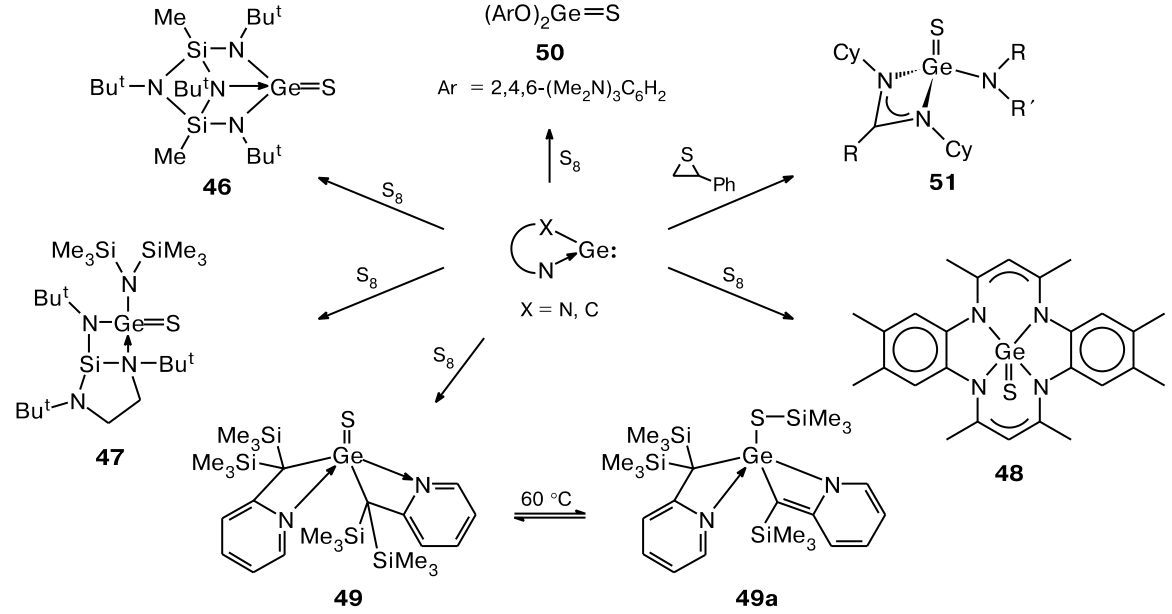
Apparently, the reactions of germanium(II) derivatives with sulfur[92,128–132] provide a general procedure for the synthesis of germathiones **46**—**51** (Scheme 22). Desulfation of thiirane[92] also afforded the corresponding derivative **51**. It should be noted that slight heating of germathione **49** leads to its isomerization, and the 1,3-migration of the Me_3Si group from the C atom to the S atom is accompanied by disruption of aromaticity of the pyridine ring.[92]

The problem of the synthesis of the corresponding stannathiones remains to be solved and calls for additional study. According to the published data,[130] the tin derivative $[(Me_2NCH_2)_3C_6H_2O]_2Sn$ (**36**) does not give stannathione upon heating with sulfur in benzene.

Some other reactions of germanium(II) and tin(II) compounds containing intramolecular coordination bonds were also carried out. For example, the reaction of iodomethane with germanium(II) compound **52** produced the salt **53** with the germanium-centered cation (Scheme 23), which was structurally characterized.[89,90]

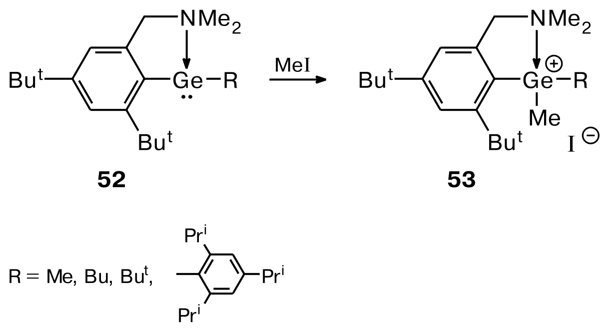
The introduction of RSnCl ($R = C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$) into iodomethane gave rise to the tetravalent tin derivative R(Me)Sn(Cl)I,[97] whereas the reaction of MeI with $Ge[OC_6H_2(CH_2NMe_2)_3]_2$ (**35**) afforded unidentifiable products.[103] The reactions of coordinatively stabilized compounds of divalent Group 14 elements with alkyl halides have not been adequately stud-

Scheme 22



Cy is cyclohexyl

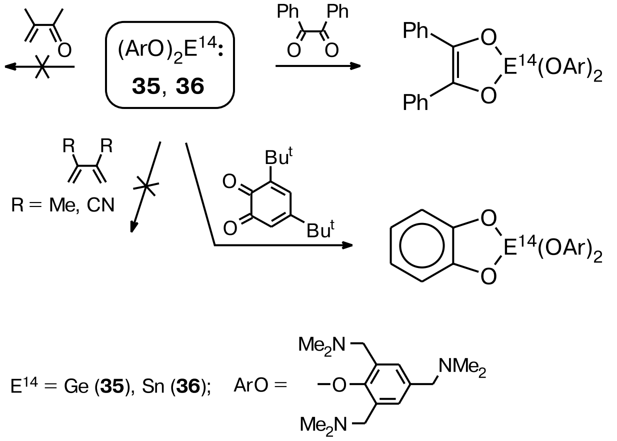
Scheme 23



ied and, consequently, it is impossible to perform comparative analysis of the influence of various factors on these processes.

Data on other reactions of this class of germanium(II) and tin(II) compounds are also scarce. According to the results of the study,[103] $Ge[OC_6H_2(CH_2NMe_2)_3]_2$ (**35**) readily reacts with diketones and 1,2-quinones (Scheme 24) but, unlike diphenoxygermanium(II), does not form an adduct with 2,3-dimethylbuta-1,3-diene.

Scheme 24

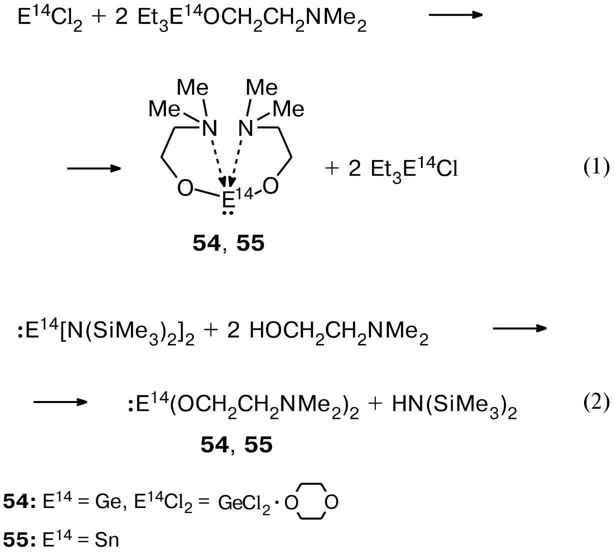


Investigations of the structures and reactivities of germanium(II) and tin(II) compounds containing intramolecular coordination bonds are still in their infancy, and many interesting properties of these compounds are poorly known, if at all.

We demonstrated that the introduction of the β-dimethylaminoethoxy groups at the Ge^{II} or Sn^{II} atom stabilizes the monomeric forms of the corresponding compounds through intramolecular coordination of the metal(II) atom by the peripheral N atom.

Treatment of $SnCl_2$ or the dioxane complex of $GeCl_2$ with two equivalents of (β-dimethylaminoethoxy)triethylgermane or -stannane under mild conditions in ethereal-type solvents afforded bis(2-dimethylaminoethoxy)germanium(II) (**54**) and -tin(II) (**55**) (Scheme 25, Eq. (1)) in 47—69% yields.[133]

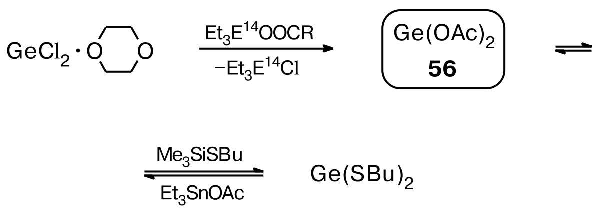
Scheme 25



An even more convenient procedure for the synthesis of these compounds involves alcoholysis of amides $E^{14}[N(SiMe_3)_2]_2$ (E^{14} = Ge, Sn) with 2-dimethylaminoethanol. The reaction proceeds exothermically and rapidly to form products in quantitative yields (see Scheme 25, Eq. (2)).

We prepared germanium(II) diacetate (**56**)[26] by the redistribution of the functional groups between the $GeCl_2 \cdot$diox complex and acetoxytriethylstannane or -germane as well as between dibutylmercaptogermanium(II) and acetoxytriethylstannane (Scheme 26).

Scheme 26



Dialkoxides **54** and **55** are white crystalline compounds, which have distinct melting points, are well soluble in all inert organic solvents, vacuum sublimed, and stable under anaerobic conditions, but are very sensitive to traces of atmospheric oxygen and moisture. Diacetoxygermanium **56** is a finely crystalline white compound soluble only in polar solvents.

The redistribution of the functional groups in a series of germanium(II) compounds affords unsymmetrical monomeric derivatives of the (RO)GeY type, *viz.*,

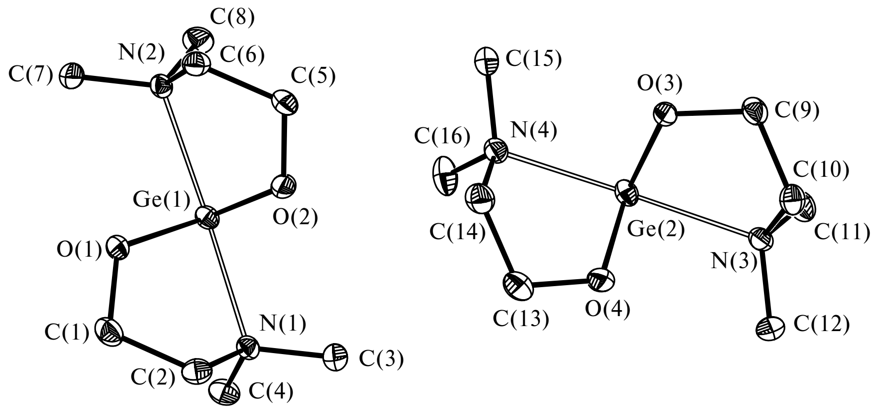
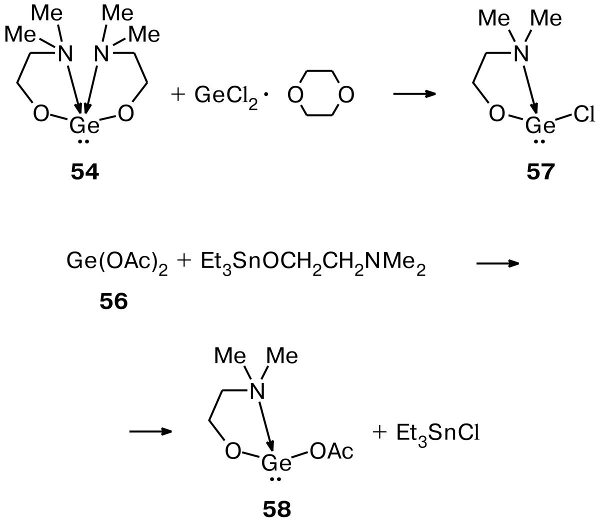


Fig. 3. Molecular structure of $Ge(OCH_2CH_2NMe_2)_2$ (**54**).[26a,133]

Scheme 27



(2-dimethylaminoethoxy)chlorogermanium(II) (**57**) and acetoxy(2-dimethylaminoethoxy)germanium(II) (**58**) (Scheme 27).[26]

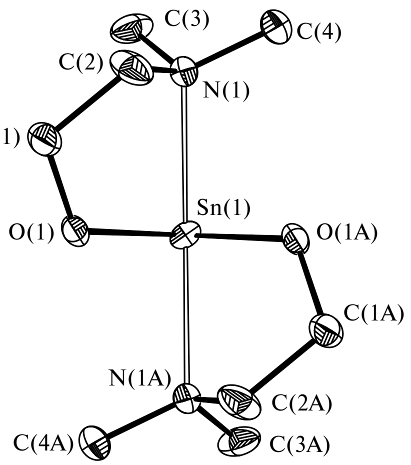


Fig. 4. Molecular structure of $Sn(OCH_2CH_2NMe_2)_2$ (**55**).[133]

Compounds **54**, **55**, **57**, and **58** are first known monomeric germanium(II) and tin(II) derivatives stabilized only by the intramolecular N→E[14] coordination bonds in the absence of steric shielding of the metal atoms. These compounds were structurally characterized by X-ray diffraction (Figs. 3—6).[26,133]

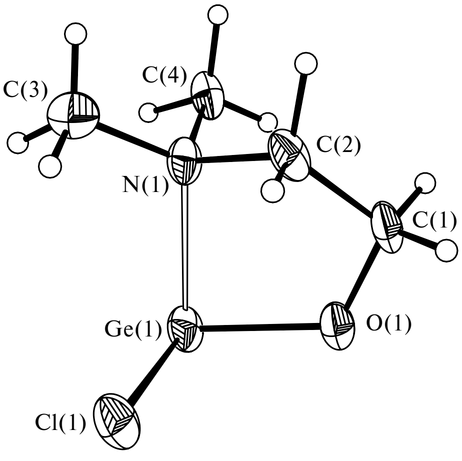


Fig. 5. Molecular structure of $ClGeOCH_2CH_2NMe_2$ (**57**).[26b]

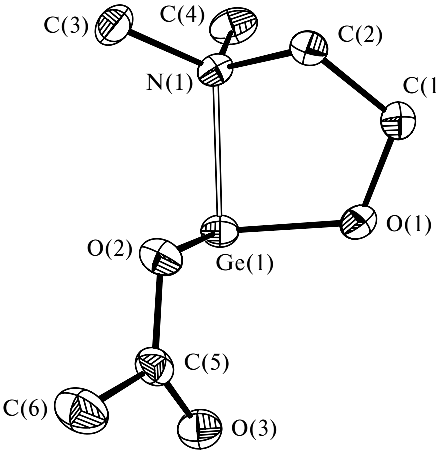


Fig. 6. Molecular structure of $AcOGeOCH_2CH_2NMe_2$ (**58**).[26b]

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compounds **36**,[26a] **54**, **55**,[133] **57**, and **58**[26b] according to the results of X-ray diffraction analysis and calculations by the PBE/TZ2P method (in brackets)

Parameter	**36**	**54***	**55****	**57**	**58**
Bond			*d*/Å		
$E^{14}—O$	2.071(2) 2.073(2)	1.868(1), 1.864(1); 1.861(1), 1.870(1) [1.896]	2.056(2) [2.082]	1.820(4) [1.850]	1.832(1) [1.846]
$E^{14}—X$	—	—	— [2.340]	2.330(2) [2.077]	1.938(1)
$E^{14}\leftarrow N$	2.427(3) 2.478(3)	2.329(2), 2.337(2); 2.324(2), 2.346(2) [2.428]	2.458(2) [2.556]	2.093(5) [2.252]	2.108(1) [2.389]
Angle			ω/deg		
$O—E^{14}—X$	91.89(9)	98.79(6); 98.91(7) [98.4]	96.52(11) [96.3]	98.0(2) [101.6]	97.09(5) [95.9]
$N\rightarrow E^{14}—X(N)$	156.56(8)	156.38(6); 156.11(6)	145.78(9)	92.9(2) [91.3]	86.90(5) [83.2]
$N\rightarrow E^{14}—O$	80.75(8), 81.18(9), 81.55(9), 84.10(8)	80.48(6), 80.78(6), 83.89(6), 84.21(6), 80.22(6), 81.00(6), 83.85(6), 84.00(6) [80.1]	76.71(6), 80.68(6) [76.0]	84.7(2) [81.4]	84.79(5) [81.2]

* For two independent molecules.

** The molecule occupies a special position on a twofold axis (C_2).

In dialkoxides **54** and **55**, the $N\rightarrow E^{14}$ bond lengths are equalized (Table 1). Compound **54** is the first known monomeric germanium(II) dialkoxide containing two $N_{sp^3}\rightarrow Ge^{II}$ coordination bonds. Their lengths are noticeably larger than the average lengths of the $N\rightarrow Ge^{II}$ coordination bonds (see above). In molecule **55**, the $N_{sp^3}\rightarrow Sn^{II}$ bond lengths are, on the contrary, substantially smaller than the average values found in the known compounds (2.521 Å),[134] whereas the $E^{14}—O$ bond lengths are virtually equal to the average lengths of the analogous bonds in the $E^{14}(OR)_2$ compounds studied earlier.[134] However, the $O—E^{14}—O$ bond angles in compounds **54** and **55** are larger than those in other structurally similar compounds, which is indicative of the absence of steric hindrance in molecules **54** and **55**. The spiro atoms E^{14} have a trigonal-bipyramidal configuration with the lone electron pair in the equatorial position and link two five-membered heterocycles adopting an envelope conformation.

The structure of monomeric diaryloxytin(II) **36** was also established[133] (Fig. 7, see Table 1). The results of X-ray diffraction analysis unambiguously demonstrated that the stabilizing effect of the aroxy ligand is associated with the formation of two stable intramolecular $N_{sp^3}\rightarrow Sn$ coordination bonds. Their lengths, like those in dialkoxytin(II) **55**, are substantially smaller than the average length of the corresponding bonds (2.521 Å).[134]

It should be noted that the lengths of two coordination bonds in diaryloxy derivative **36**, unlike those in dialkoxy derivative of tin(II) **55**, are sharply different, although these bonds should be chemically equivalent from the formal point of view. Analysis of the structures of the tin(II) compounds stabilized by two intramolecular $N_{sp^3}\rightarrow Sn$ coordination bonds based on the data available in the Cambridge Structural Database[134] demonstrated that such a nonequivalence is characteristic of most compounds of this type. However, the bond lengths in these compounds are equalized if LEP of the Sn^{II} atom is involved in coordination with such acceptors as BH_3 [135] or in binding with transition metals.[86,88,136,137] Additional interactions of these types have no substantial effect on the $N_{sp^3}\rightarrow Sn$ coordination bond lengths (the average value is 2.543 Å).

In the ^1H NMR spectra of dialkoxy derivatives **54** and **55** (in C_6D_6 or $C_6D_5CD_3$, 293 K), the resonances of the OCH_2CH_2N groups are observed as triplets and the signals of the Me_2N group occur as singlets. Broadening of the signals in the ^1H and ^{13}C NMR spectra (20 °C) of compound **55** indicates that rapid exchange accompanied by the cleavage and formation of the $N_{sp^3}\rightarrow E^{14}$ coordination bonds occurs in solutions.

In the structures of unsymmetrically substituted compounds **57** and **58**, the Ge^{II} atom is three-coordinated through two σ bonds with the substituents and the additional N→Ge donor-acceptor interaction. These bonds, like the alkoxide Ge—O bonds, are shorter than the analogous bonds in tetracoordinate monomer **54** and are similar to those in the amino-coordinated germanium(II) compounds studied earlier.[134] The Ge—O bond length in the

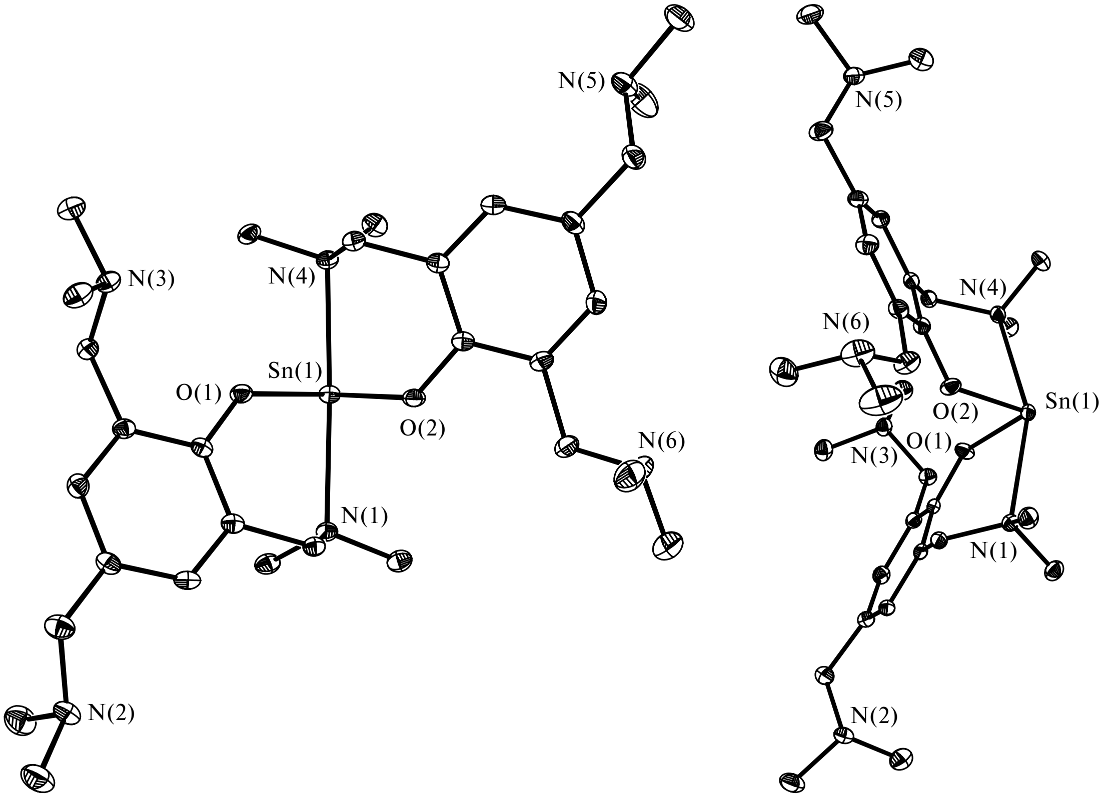


Fig. 7. Two mutually perpendicular projections of the molecular structure of $Sn[OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]_2$ (**36**).[133]

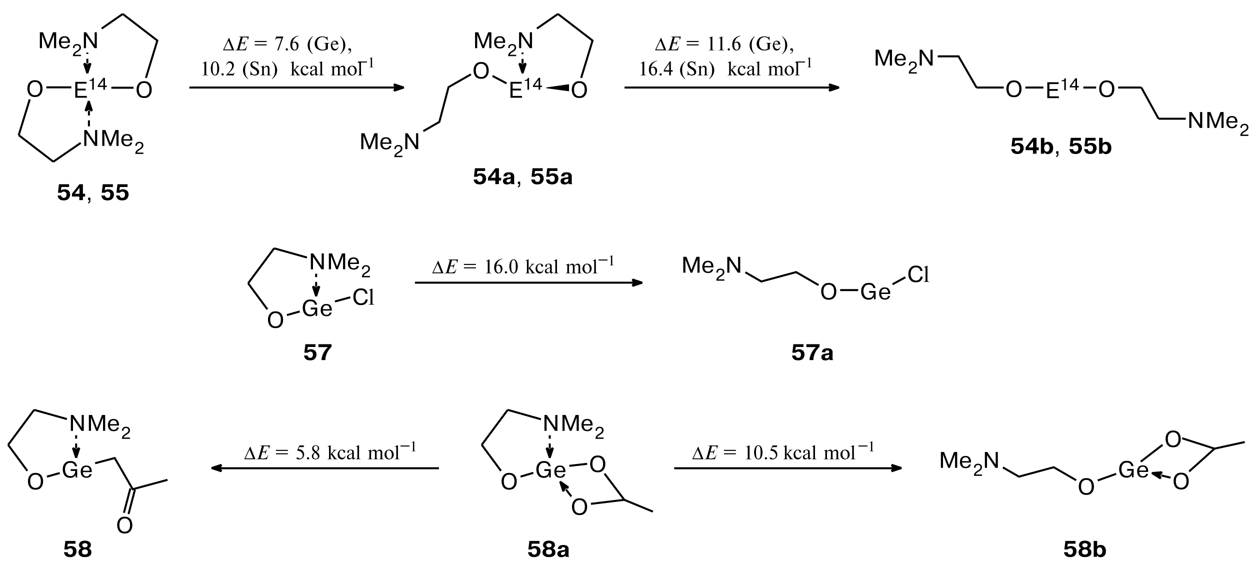
acetoxy group in molecule **58** is substantially larger than the known Ge—O bond lengths in other oxygen-containing compounds (1.765(6)—1.854(7) Å).[134] The Ge—Cl distance is similar to those found in other chloro derivatives with the N→Ge^{II} coordination bond: 2.3283(4) Å in [Mamx]GeCl [90] (Mamx is 2,4-di-*tert*-butyl-6-[(dimethylamino)methyl]phenyl) and 2.333(1) Å in [*t*-Bomx]GeCl (*t*-Bomx is 2,4-di-*tert*-butyl-6-[(*tert*-butoxymethyl)methyl]phenyl).[100]

In both compounds, the α angles (O_{ipso}—Ge—N) at the Ge atoms are smaller than 90°, the β angles (O_{ipso}—Ge—X, X = Cl, O) are close to 90°, and the γ angles (N—Ge—X, X = Cl, O) are larger than 90°. This angle distribution ($\alpha < \beta \approx 90° < \gamma$) is characteristic of all analogous germanium(II) compounds studied earlier.[89,90,100] Therefore, the Ge^{II} atoms in compounds **57** and **58** are virtually unhybridized. The lone electron pair of the Ge^{II} atom has predominantly s character, and the p orbitals are involved in the formation of σ bonds. The bond with the N atom is virtually perpendicular to the O—Ge—X plane (X = Cl, O), which is favorable for an ideal interaction of its LEP with the unoccupied p orbital of the Ge atom. The five-membered chelate rings adopt an envelope conformation. In the crystals, the molecules are located at distances larger than the close van der Waals contacts.

The structures of compounds **54**, **55**,[133] **57**, and **58** [26b] were studied also by the density functional theory (the nonempirically constructed gradient-corrected functional PBE, the extended and split TZ2P basis set, the PRIRODA program[138,139]). The calculations adequately reproduced the structural type and geometric parameters of the molecules (see Table 1). The differences are, apparently, associated with the crystal packing effects. Local minima on the potential energy surfaces (PES) were also found for isomeric structures **54a**, **54b**, **55a**, **55b**, **57a**, **58a**, and **58b** (Scheme 28), in which one (structures **a**) or both N→M or O→Ge coordination bonds (structures **b**) are broken.

The coordination bonds retained in isomers **54a** and **55a** are stronger than those in **54** and **55**. For example, the energy required for the cleavage of the first $N_{sp^3}\rightarrow E^{14}$ bond (transformations of structures **54** and **55** into isomers **a**; 7.6 and 10.2 kcal mol^{-1} for **54** and **55**, respectively) is smaller than that required for the cleavage of the second bond (transformations of isomers **a** into isomers **b**; 11.6 and 16.4 kcal mol^{-1}, respectively), the cleavage of the first $N_{sp^3}\rightarrow E^{14}$ bond being accompanied by shortening of the $N_{sp^3}\rightarrow E^{14}$ bond that remained intact (by 0.148 Å in **54a** and by 0.121 Å in **55a**) and of both E^{14}—O bonds. The cleavage of the N→Ge coordination bond in chloro derivative **57** (transformation **57** → **57a**) requires 16.0 kcal mol^{-1} and is also accompanied by shortening of the σ bonds at the Ge atom and a decrease in the O—Ge—Cl bond angle.

Scheme 28



According to the results of calculations, the carbonyl O atom in the isolated molecule of acetoxy derivative **58a** is η^2-coordinated to the Ge atom, as opposed to the structure in the crystal determined by X-ray diffraction analysis. However, the difference in the energy of the local minina on the potential energy surfaces for isomer **58a** and structure **58** (calculations for the latter were carried out with the use of the Ge—N and Ge—O(3) (the carbonyl group) bond lengths determined from the X-ray diffraction data) is as small as +2.9 kcal mol^{-1}. For chloro derivative **57**, this difference is also small (+1.7 kcal mol^{-1}). The cleavage of the N→Ge coordination bond in molecule **58a**, which requires 10.5 kcal mol^{-1}, leads to strengthening of the η^2-coordination interaction between the Ge atom and the acetoxy group, both Ge—O bonds being equalized. The cleavage of the coordination bond between the Ge atom and the carbonyl O atom (transformation **58a** → **58**) leads to strengthening of the N→Ge coordination interaction.

Analysis of the frontier orbital populations demonstrates that the highest occupied molecular orbitals in molecules **54**, **55**, **57**, **58**, and **58a** are localized on the E^{14} atoms, and LEPs are occupied. In isomers **54a,b**, **55a,b**, **57a**, and **58b**, HOMOs are localized on the uncoordinated N atoms of the Me$_2$N groups. The lowest unoccupied molecular orbitals (LUMO) in isomers **54**, **55**, **57**, and **58** are localized on the E^{14} atoms. In isomers **54b** and **55b**, LUMOs are the 4p$_z$- or 5p$_z$-atomic orbitals of the Ge and Sn atoms with insignificant contributions of the lone electron pairs of the O atoms. In compounds **54**, **54a**, **55**, **55a**, **57**, **57a**, **58**, and **58b** containing the N→E^{14} coordination bond, LUMOs involve additional contributions of the molecular orbitals of the O and N atoms. As an example, the frontier orbitals of molecule **54** are presented in Fig. 8. In isomer **58a**, LUMO is localized on the acetate ligand.

Upon the cleavage of the N→E^{14} coordination bonds, the energies of HOMO and LUMO decrease in the series **54** (**55**) > **54a** (**55a**) > **54b** (**55b**) and **57a** > **57** > **58** > > **58b** > **57a**. The positive charges on the E^{14} atoms slightly increase (particularly, in Sn derivative **55**) and the negative charge on the N atom also increases. The changes in the charges on the O atoms are insignificant. The transformation **58a** → **58** leads to an increase in the negative charge on the carbonyl O atom. One would expect that in the above-mentioned series of compounds, the reactivity with respect to electrophilic reagents will decrease, whereas the reactivity with respect to nucleophilic reagents will increase. According to the results of calculations, acyloxy derivative **58** is more nucleophilic than chloro derivative **57**.

These results demonstrate that two powerful stabilizing electronic factors, such as the formation of the N$_{sp^3}$→E^{14} coordination bonds and the σ-acceptor effect of the O atoms in the alkoxy and aryloxy derivatives of germanium(II) and tin(II) or the presence of electronegative groups and one coordination bond, provide the existence of monomeric germanium(II) and tin(II) compounds **54**, **55**, **57**, and **58** at usual temperatures under anaerobic conditions without substantial steric shielding of the metal atoms.

New germanium(II) and tin(II) *ate*-complexes

The reactions of derivatives of Group 14 elements with Lewis bases are of interest. Neutral electrophiles

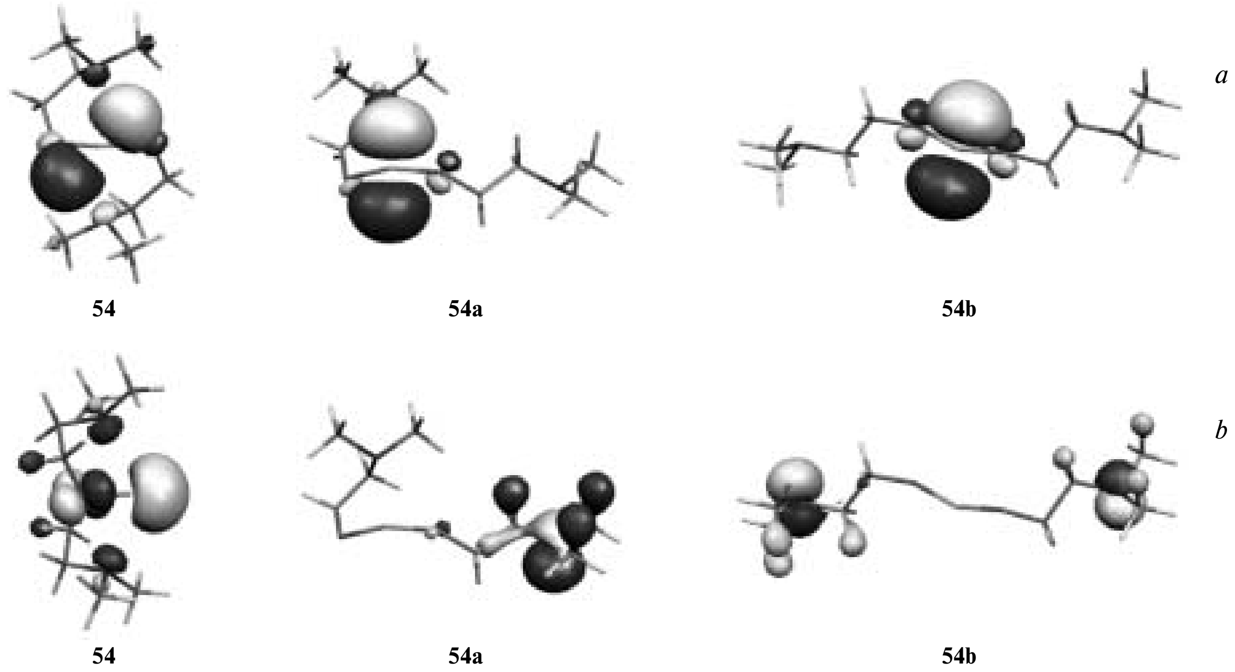
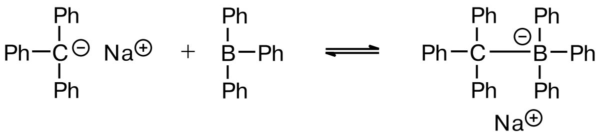


Fig. 8. View of HOMO (*a*) and LUMO (*b*) of molecules **54**, **54a**, and **54b**.[133]

(Lewis acids) form complexes with carbanions with the charge distribution opposite to that observed in onium salts, as exemplified for the first time by the reaction of triphenylboron with triphenylmethylsodium (Scheme 29).[140] The term "*ate*-complexes" was proposed for this new class of compounds.[141—145]

Scheme 29



It was demonstrated that the *ate*-complexes serve as true catalysts for triphenylmethylsodium-initiated and triphenylboron-assisted processes.[141—143,145] Rapid polymerization of THF taking place upon mixing of stable solutions of triphenylmethylsodium and Ph_3B in THF serves as a bright example. Later on, studies devoted to reactions of organometallic compounds catalyzed by Lewis acids[146,147] provided considerable supporting evidence for the conclusion about the intermediate formation of *ate*-complexes.

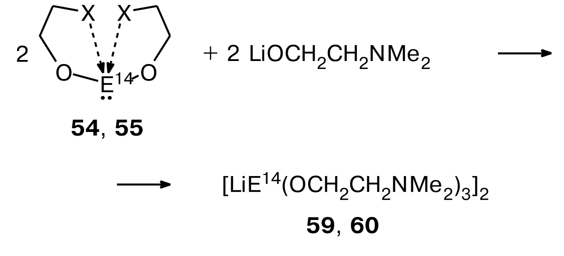
Nowadays, the chemistry of *ate*-complexes is a broad area of chemistry of organometallic compounds. These complexes attract considerable interest because of their structural features and reactivity as well as because they hold promise not only as catalysts but also as the starting compounds in the production of metal ceramics and materials for electronic industry.[148]

In the series of Group 14 elements, germanium(II) and tin(II) *ate*-complexes with oxygen- or nitrogen-containing ligands at the metal atoms have received the most study. The chemistry of these complexes was covered in reviews.[149—152] Interesting results were obtained in the study of the sulfur- and selenium-containing germanium(II) and tin(II) *ate*-complexes $[Ph_4As]^{(+)}[Sn(XPh)_3]^{(-)}$ (X = S, Se), $[Et_4N]^{(+)}[Ge(SPh)_3]^{(-)}$ and $[Ph_4P]^{(+)}[Ge(SePh)_3]^{(-)}$.[153]

The mass spectrum of the product prepared by the reaction of $SnCl_2$ with lithium alkoxide LiOAr shows the $[(ArO)_2SnLiCl]^+$ molecular ion (Ar = 2,4,6-$(Me_2NCH_2)_3C_6H_2$).[103]

We found that sterically unhindered bis(β-dimethylaminoethoxy)germanium(II) (**54**) and -tin(II) (**55**) readily react with an equimolar amount of $LiOCH_2CH_2NMe_2$ in diethyl ether to form *ate*-complexes **59** and **60**, respectively (Scheme 30).[154]

Scheme 30



E^{14} = Ge (**54**, **59**), Sn (**55**, **60**)

X = NMe_2

These compounds were prepared as white crystals, which are readily soluble in THF and pyridine and are very sensitive to traces of atmospheric oxygen and moisture.

The question about the mode of binding of the lithium cations in complexes **59** and **60** is of considerable interest. In principle, the following three modes of binding are possible: the Li—E^{14} covalent binding, the formation of the solvent-separated ion pair [Li(Solv)]$^{(+)}$...[E^{14}X$_3$]$^{(-)}$ (Solv is the solvent molecule), and intramolecular solvation of the Li atom upon its interaction with the O and/or N atoms of the ligands. We studied compounds **59** and **60** by X-ray diffraction analysis and demonstrated that there is the coordination binding in their crystals through the O→Li and N→Li bridging bonds, the N→E^{14} coordination being absent (Figs. 9 and 10).

Both complexes exist as centrosymmetrical dimers and have similar structures analogous to those of the $Sn_2Li_2(OBu^t)_6$ [155] and $Pb_2Li_2[OCH(CF_3)_2]_6$ complexes.[156] They are characterized by the presence of the $E^{14}{}_2O_6Li_2$ framework consisting of two seconorcubanes $E^{14}{}_2O_3Li_2$ sharing the Li_2O_2 face. The inversion center of the molecule is located in the center of the four-membered ring Li_2O_2.

The alkoxy groups are bound to the E^{14} atoms in a bridging mode (μ^3 and μ^2). According to the Gillespie rules,[98] the E^{14} atoms in the $E^{14}O_3$ fragments have a distorted tetrahedral coordination with the lone electron pair occupying one of the coordination sites (AB_3X coordination mode). The Ge—μ^2-O bond length (1.876(2) Å) differs substantially from the Ge—μ^3-O bond length (1.954(2) Å), whereas the analogous bonds in tin(II) compound **60** are equalized (Sn—μ^2-O, 2.055(2) and 2.095(2) Å; Sn—μ^3-O, 2.087(2) Å) (Table 2). However, these bond lengths in both compounds vary in the range typical of alkoxygermanates or -stannates.[155,157] The bond angles at the E^{14} atoms in the trioxy fragments $E^{14}O_3$ tend to increase in going from the μ^2-O—E^{14}—μ^3-O angles to the μ^2-O—E^{14}—μ^2-O angles, but the differences in these angles in germanium compound **59** (83.18(9), 88.09(10), and 92.88(10)°) are smaller than those in tin derivative **60** (75.87(8), 80.86(14), and 91.66(11)°). The coordination polyhedra of the Li atoms are distorted trigonal bipyramids (TBP) with one coordinated amino group in the equatorial position. The Li—N bond in molecule **59** (2.180(6) Å) is shorter than that in molecule **60** (2.258(6) Å), but both these bonds are substantially longer that those observed in most of lithium amides studied structurally.[137] Distortions of TBP for the Li atoms in Sn complex **60** are more pronounced than those observed in **59**, which is manifested in the differences in the Li—O bond lengths in the

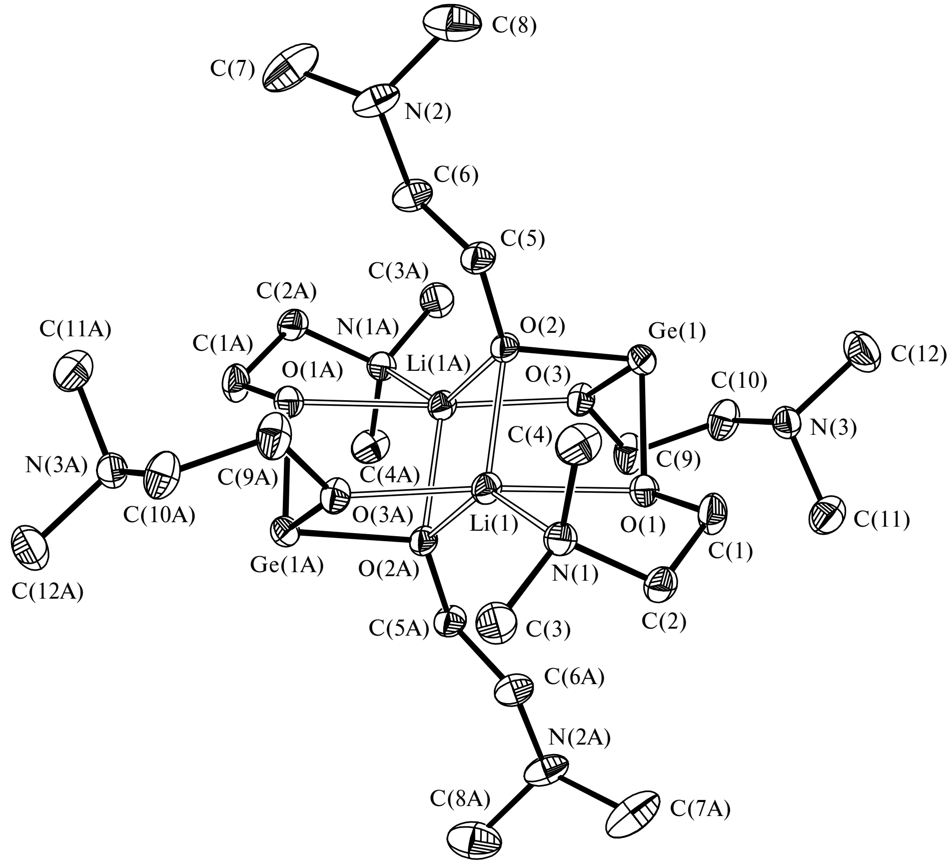


Fig. 9. Molecular structure of the *ate*-complex $[LiGe(OCH_2CH_2NMe_2)_3]_2$ (**59**).[154]

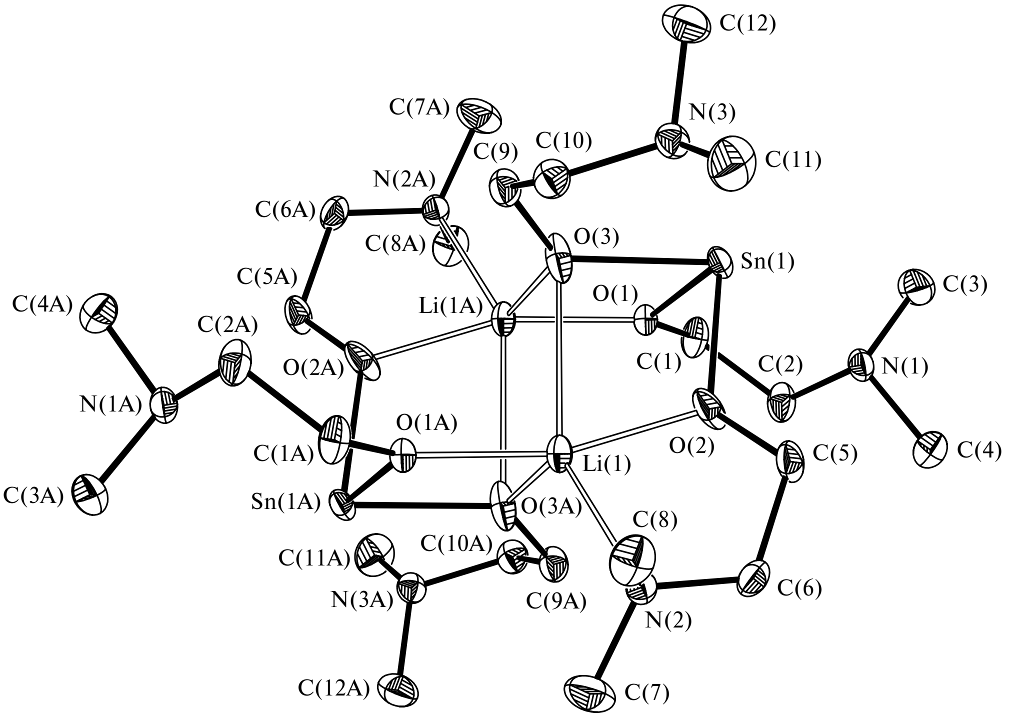


Fig. 10. Molecular structure of the *ate*-complex $[LiSn(OCH_2CH_2NMe_2)_3]_2$ (**60**).[154]

four-membered rings Li_2O_2 (2.019(6) and 2.034(6) Å in **59**; 1.926(5) and 2.511(7) Å in **60**) as well as in the axial O—Li—O angles (176.2(3) and 160.2(3)° in molecules **59** and **60**, respectively). Hence, the $E^{14}{}_2O_6Li_2$ framework in the Ge compound is closer to the ideal geometry with the highest symmetry C_{2h} $(2/m)$ compared to that in the Sn complex.

In the studies devoted to the "trisilyl" derivatives (Tsi = $C(SiMe_3)_3$) of Group 14 elements, the reactions of "trisilyllithium" with the *n*-butylthio derivatives of germanium and tin were carried out.[31,158] It is known that the chemical behavior of TsiLi differs from that of organolithium compounds of the aliphatic and aromatic series. This difference is manifested, in particular, in the fact

Table 2. Selected interatomic distances (*d*) and bond angles (ω) in *ate*-complexes **59** and **60** according to the X-ray diffraction data[154]

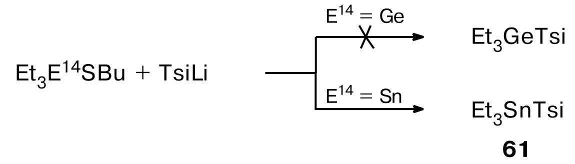
Parameter	**59** (Ge)	**60** (Sn)
Bond	*d*/Å	
$E^{14}(1)—O(1)$	1.888(2)	2.095(2)
$E^{14}(1)—O(2)$	1.954(2)	2.055(2)
$E^{14}(1)—O(3)$	1.876(2)	2.087(2)
O(1)—Li(1A)	2.193(6)	1.968(5)
O(2)—Li(1)	2.019(6)	1.935(6)
O(3)—Li(1)	2.034(6)	2.511(7)
O(3)—Li(1A)	2.033(6)	1.926(5)
N(2)—Li(1)	2.180(6)	2.258(6)
$E^{14}(1)...Li(1)$	3.010(6)	3.313(6)
$E^{14}(1)...Li(1A)$	3.012(5)	3.110(5)
Li(1)...Li(1A)	2.713(11)	2.929(11)

Parameter	**59** (Ge)	**60** (Sn)
Angle	ω/deg	
$O(1)—E^{14}(1)—O(2)$	88.09(10)	91.66(11)
$O(1)—E^{14}(1)—O(3)$	92.88(10)	75.87(8)
$O(2)—E^{14}(1)—O(3)$	83.18(9)	80.86(14)
$E^{14}(1)—O(1)—Li(1A)$	94.8(2)	99.9(2)
$E^{14}(1)—O(2)—Li(1)$	98.5(2)	112.2(2)
$E^{14}(1)—O(3)—Li(1)$	98.1(2)	91.7(2)
$E^{14}(1)—O(3)—Li(1A)$	100.7(2)	101.5(2)
O(1A)—Li(1)—O(2)	78.6(2)	160.2(3)
O(1A)—Li(1)—O(3)	100.0(2)	93.9(2)
O(1A)—Li(1)—O(3A)	176.2(3)	82.6(2)
O(2)—Li(1)—O(3)	96.0(2)	73.0(2)
O(2)—Li(1)—O(3A)	104.4(2)	113.5(3)
O(3)—Li(1)—O(3A)	77.4(2)	98.5(2)
O(1A)—Li(1)—N(2)	80.3(2)	103.9(3)
O(2)—Li(1)—N(2)	120.5(3)	80.5(2)
O(3)—Li(1)—N(2)	142.4(3)	143.9(2)
O(3A)—Li(1)—N(2)	100.0(2)	114.5(3)
Li(1)—O(3)—Li(1A)	84.0(2)	81.5(2)

that TsiLi does not react with alkoxysilanes at the Si—OR bond,[159] whereas other organolithium compounds readily alkylate (arylate) alkoxysilanes.[160] Data on the reactions of TsiLi with alkylthio derivatives of Group 14 elements have been lacking in the literature. It appeared that TsiLi reacts with Et_3SnSBu virtually at a titration rate to form Et_3SnTsi (**61**) in a good yield. We established the structure of this compound by X-ray diffraction analysis. Compound **61** belongs to one of a few "trisilyl" derivatives of tin, which were structurally characterized.

Unlike Et_3SnSBu, *n*-butylthiotriethylgermane does not react with TsiLi even upon prolonged stirring of the reagents at room temperature in a Et_2O—THF mixture (Scheme 31).

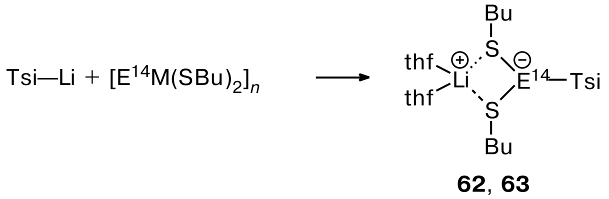
Scheme 31



Tsi = $C(SiMe_3)_3$

However, both thiolates $[E^{14}(SBu)_2]_n$ (E^{14} = Ge, Sn) easily react with TsiLi in a Et_2O—THF mixture to give *ate*-complexes **62** and **63** in good yields (Scheme 32) as slightly yellowish crystalline compounds, which are very sensitive to traces of atmospheric oxygen and moisture.

Scheme 32



E^{14} = Ge (**62**), Sn (**63**); Tsi = $C(SiMe_3)_3$

The structures of *ate*-complexes **62** and **63** were established by X-ray diffraction analysis. Molecules **62** and **63** contain four-membered rings (Figs. 11 and 12, respectively), in which the Li atoms are symmetrically bound to two S atoms. The rings adopt a butterfly conformation. The folding angles along the S...S diagonal are 22.3 and 45.8° in the structures of **62** and **63**, respectively. The Li atoms are in a distorted tetrahedral environment formed by two S atoms and two O atoms of the coordinated THF molecules, whose five-membered rings adopt an envelope conformation. The coordination polyhedra of the

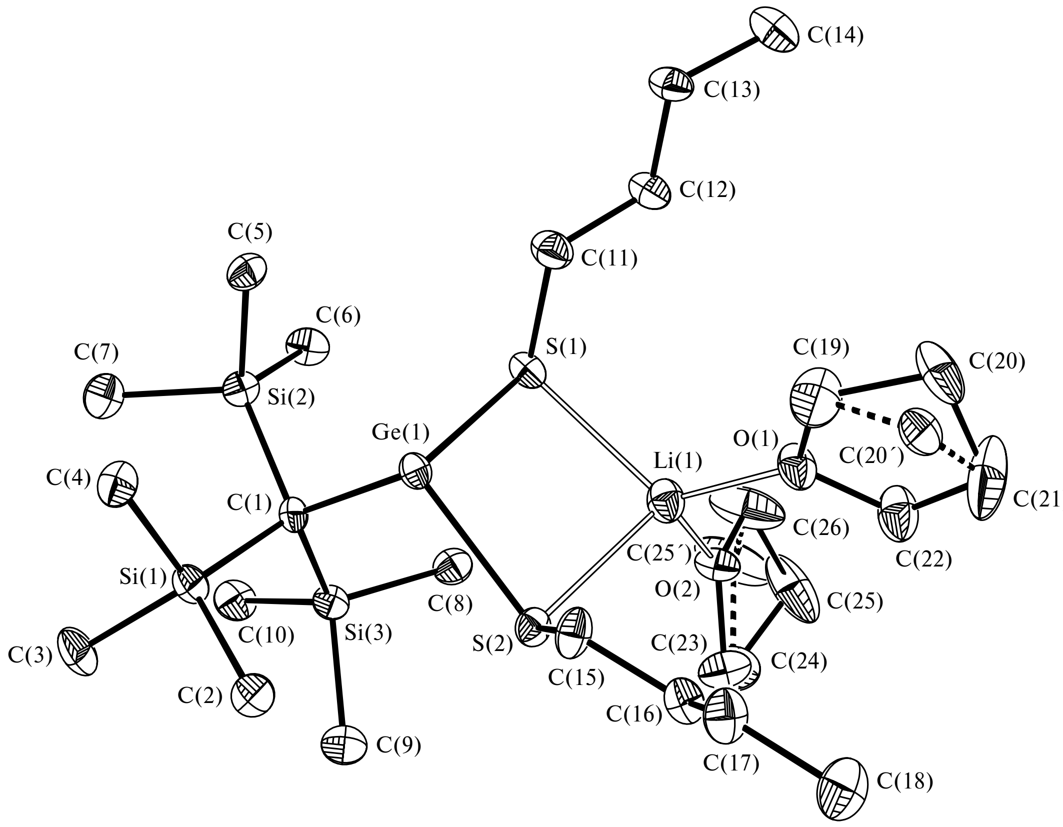


Fig. 11. Structure of *ate*-Ge-complex **62**.[158]

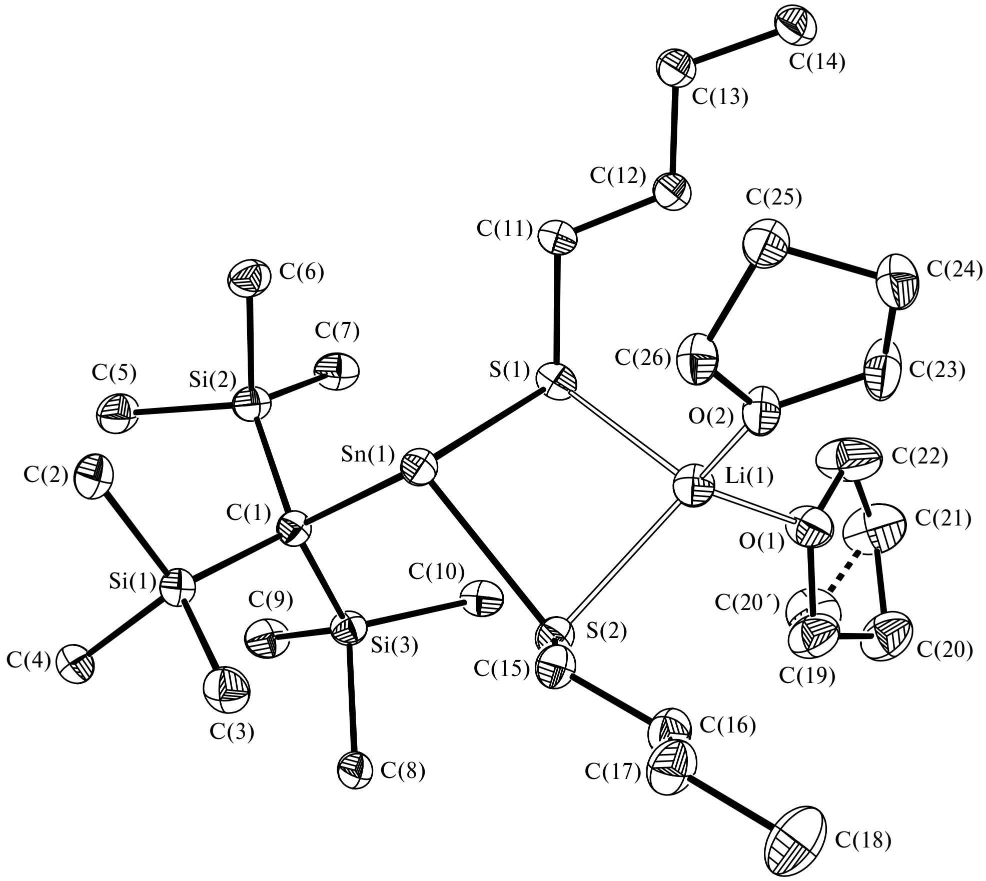


Fig. 12. Structure of *ate*-Sn-complex **63**.[158]

Ge and Sn atoms can be considered as distorted AB_3X tetrahedra, in which one of the coordination sites is occupied by LEP, in accordance with the Gillespie rules.[98] The tetrahedral configuration of the central C atom in the "trisilyl" fragments is also distorted. The Si(1)—C(1)—E^{14} and Si(2)—C(1)—E^{14} bond angles are, respectively, 100.4(3) and 105.7(2)° in **62** and 102.2(1) and 104.2(1)° in **63**, which is attributable to the *trans* effect.[161] The Sn—S bond lengths in *ate*-complex **63** (Table 3) are larger than those in the anion of the $[Ph_4As]^{(+)}[Sn(SPh)_3]^{(-)}$ salt (2.532(1), 2.552(1), and 2.532(1) Å)[32] but are comparable to the bridging Sn—S bond lengths in both four-membered rings of the $[Sn(SAr')_2]_3$ trimer (2.583, 2.588, 2.643, and 2.838 Å) (Ar´ = 2,6-diisopropylphenyl).[42]

The E^{14}—C(Tsi) bond lengths (2.096(5) and 2.295(3) Å in complexes **62** and **63**, respectively) are similar to those observed in other germylenes and stannylenes[76] containing the "trisilyl" groups. However, these bond lengths are substantially larger than the typical $E^{14(II)}$—C_{sp^3} and $E^{14(IV)}$—C_{sp^3} interatomic distances.[134] The Li—S distances (2.447(11) and 2.456(11) Å in **62**, 2.483(6) and 2.484(6) Å in **63**; see Table 3) agree well with those expected for the S→Li^+ bond lengths. The E^{14}...Li distances in *ate*-complexes **62** (3.290(9) Å) and **63** (3.300(6) Å) are determined by the geometric param-

Table 3. Selected bond lengths (*d*) and bond angles (ω) in compounds **62** and **63** according to the X-ray diffraction data[154]

Parameter	**62** (Ge)	**63** (Sn)
Bond	*d*/Å	
E^{14}—C	2.096(5)	2.295(3)
E^{14}—S(1)	2.393(2)	2.568(1)
E^{14}—S(2)	2.386(2)	2.574(1)
Li—S(1)	2.447(9)	2.484(6)
Li—S(2)	2.456(9)	2.483(6)
Li—O(1)	1.914(11)	1.925(7)
Li—O(2)	1.930(10)	1.918(6)
Angle	ω/deg	
C—E^{14}—S(1)	101.8(2)	100.2(1)
C—E^{14}—S(2)	103.3(2)	102.6(1)
S(1)—E^{14}—S(2)	93.84(5)	87.79(3)
E^{14}—S(1)—Li	85.7(2)	81.6(1)
E^{14}—S(2)—Li	85.6(2)	81.4(2)
S(1)—Li—O(2)	114.8(5)	115.6(3)
S(2)—Li—O(1)	118.6(5)	114.4(3)
E^{14}—S(1)—C(11)	99.1(2)	109.1(1)
E^{14}—S(2)—C(15)	96.6(2)	99.0(1)
Li—S(1)—C(11)	108.2(3)	109.0(2)
Li—S(2)—C(15)	101.3(3)	106.0(2)
O(1)—Li—O(2)	102.7(5)	108.4(3)
S—Li—S	90.8(3)	91.7(2)

eters of the four-membered rings and are substantially larger than the known Ge—Li or Sn—Li bond lengths.[134] For comparison, the Sn...Li distance in $LiSn(OR)_3$ is 2.784(4) Å.[162] The main geometric parameters of compounds **62** and **63** are given in Table 3.

The cyclic structure of Ge derivative **62** observed in the crystals is retained in solution. In the ^{1}H NMR spectrum of compound **62** in C_6D_6 (360 MHz, 24 °C), the SCH_2 groups are observed as a set of narrow signals (an AB part of an ABX_2 system) with $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = $^3J_{BX}$ = 7.4 Hz, and $\Delta\nu_{AB}$ = 54.4 Hz.

Tin complex **63** has a more complicated structure in solutions. Under the same conditions, the signals of the SCH_2 groups are manifested as a strongly broadened singlet ($\Delta\nu \approx 50$ Hz). The ^{1}H NMR spectrum (300 MHz) in toluene-d$_8$ at 24 °C has a multiplet with $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = $^3J_{BX}$ = 7.5 Hz, and $\Delta\nu_{AB}$ = 21.5 Hz. At −40 °C, the spectrum shows a set of narrow signals of an AB part of an ABX_2 system with $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = $^3J_{BX}$ = 7.5 Hz, and $\Delta\nu_{AB}$ = 32.3 Hz. In the ^{1}H NMR spectrum of compound **63**, the difference in the chemical shifts of the diastereotopic protons gradually decreases as the temperature increases from −40 °C to +50 °C (Table 4). The observed changes in the spectra are reversible.

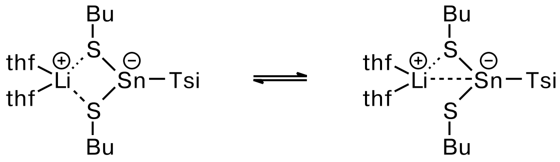
Since the resonance lines remain narrow throughout the temperature range under study, the observed changes in $\Delta\nu_{AB}$ indicate that an equilibrium nondegenerate dynamic process (rapid within the NMR time scale) occurs in solutions of **63**. The protons of the SCH_2 group exchange positions or, presumably, change chemical shifts in such a way that their difference decreases. Besides, it is evident that isomeric structures, which differ moderately in stability ($\Delta G°$ is small), coexist in equilibrium.

Reversible dissociation of complex **63** into the starting $(BuS)_2Sn$ and TsiLi components could lead to this type of the temperature dependence. However, the above-mentioned equilibrium is, apparently, absent in a deuteriotoluene solution, at least as a rapid process, because the signals of a small impurity (~2—3%) of $(BuS)_2Sn$ are not broadened, and their positions, shapes, and intensities remain constant with temperature. Apparently, the observed dependence can be most reasonably explained in the context of the equilibrium (Scheme 33) between two cyclic forms **63a** and **63b**, which should be considered as two structurally different tight ion pairs. One of the S→Li coordination bonds in complex **63** is cleaved, after which rotation about the S—C bond in this group becomes free and the diastereotopic protons in this group exchange positions. The energy expended for cleaving the S→Li coordination bond is, apparently, partially compensated by a decrease in the distance between the Li^+ ion and the Sn atom bearing LEP.

Table 4. Chemical shifts of the diastereotopic protons of the SCH_2 groups in the ^{1}H NMR spectra ($\Delta\nu_{AB}$) and the chemical shifts (δ_{Sn}) and line widths ^{119}Sn ($\omega_{1/2}$) in the ^{119}Sn NMR spectrum of *ate*-complex **63** at different temperatures[31,158]

T/°C	$\Delta\nu_{AB}$/Hz (300 MHz)	δ_{Sn}	$\omega_{1/2}$/Hz
50	—	280.5	140.0
40	11.8	278.6	119.3
24	21.5	275.2	137.7
10	23.5	273.2	117.0
0	—	272.3	121.6
−10	25.5	271.0	94.1
−20	28.1	269.9	68.8
−30	—	268.7	62.0
−40	32.3	267.5	55.1

Scheme 33



63a **63b**

To verify this hypothesis, we measured the ^{1}H NMR spectra of complex **63** in a THF-d$_8$ solution. In this strongly coordinating solvent, the ABX_2 subspectrum, as expected, collapses into the A_2X_2 spectrum, and the signals for the protons of the SCH_2 groups occur as narrow triplets ($^3J_{H,H}$ = 7.3 Hz), which is indicative of sharp acceleration of the exchange process.

The ^{119}Sn NMR spectrum of complex **63** has only one signal at δ 275.24. This signal is slightly shifted upfield and the line width substantially decreases as the temperature is decreased (see Table 4). This behavior is also indicative of the ion-pair equilibrium (see Scheme 33). The above data provide strong evidence that the structures of complexes **62** and **63** in the crystals are identical to those in solutions.[31]

Conclusions

All the aforesaid convincingly demonstrate the enormous synthetic potential of organic derivatives of divalent silicon, germanium, and tin, which are stabilized by the intramolecular $Z \to E^{14}$ coordination bonds (Z = N, O, S, *etc.*) with electron-donating atoms and groups located in the side chains of substituents at the E^{14} atom. We synthesized a series of new monomeric organic derivatives of germanium(II) and tin(II) $E^{14}(OR)_2$ and $E^{14}(OR)Y$ (E^{14} = Ge, Sn; R = $Me_2NCH_2CH_2$; Y = Cl, AcO), which are stable at normal temperatures under anaerobic conditions, and demonstrated for the first time that such compounds can be stabilized only through the intramolecular $N_{sp^3} \to E^{14}$ coordination bonds and the σ-acceptor effect of the O atoms without the introduction of bulky substituents. The exceptionally rapid progress in this area of organometallic chemistry gives promise that new important and interesting results will be obtained in the nearest future.

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